Identification of Hydrocarbons by Gas Chromatography

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GAS-LIQUID chromatography can be used to identify hydrocarbons tentatively. On any given substrate, each compound has a characteristic retention time. Compounds with similar retention times on one substrate may be easily separated on another partitioning medium. If retention times are available on several liquid substrates, it should be possible to identify an unknown by gas chromatography alone. The chances of success are increased if a limited field is studied such as the C_1 to C_6 hydrocarbons.

Retention data are most usefully presented as relative retention times, specific retention volumes, or partition coefficients (*2*). Several very useful tables have already appeared in the literature (*1, 3, 5-10, 12, 13, 16, 18, 19*). Relative retention times of some of the less common compounds as well as the hydrocarbons of general interest are reported here. Substrates with widely differing selectivities were studied.

Table I. List of Hydrocarbons Studied

	Hydrocarbon[a]	Boiling Point, ° C.		Hydrocarbon[a]	Boiling Point, ° C.
1	Methane	−161.49	47	2,3-Dimethyl-1-butene	55.62
2	Ethene	−103.71	48	2-Pentyne	56.07
3	Ethane	−88.63	49	4-Methyl-*cis*-2-pentene	56.39
4	Acetylene	−84	50	2,3-Dimethylbutane	57.99
5	Propene	−47.70	51	4-Methyl-*trans*-2-pentene	58.61
6	Propane	−42.07	52	1,5-Hexadiene	59.46
7	Allene	−34.5	53	2-Methylpentane	60.27
8	Cyclopropane	−34	54	2-Methyl-1-pentene	62.11
9	Propyne	−23.22	55	3-Methylpentane	63.28
10	2-Methylpropane	−11.73	56	1-Hexene	63.49
11	2-Methylpropene	−6.90	57	2-Ethyl-1-butene	64.68
12	1-Butene	−6.26	58	*cis*-3-Hexene	66.44
13	1,3-Butadiene	−4.41	59	*trans*-3-Hexene	67.08
14	Butane	−0.50	60	2-Methyl-2-pentene	67.31
15	*trans*-2-Butene	0.88	61	3-Methyl-*trans*-2-pentene	67.70
16	*cis*-2-Butene	3.72	62	*trans*-2-Hexene	67.88
17	1-Butyne	8.07	63	Hexane	68.74
18	2,2-Dimethylpropane	9.50	64	2,3-Dimethyl-1,3-butadiene	68.78
19	1,2-Butadiene	10.85	65	*cis*-2-Hexene	68.89
20	3-Methyl-1-butene	20.06	66	3-Methyl-*cis*-2-pentene	70.44
21	1,4-Pentadiene	25.97	67	1-Hexyne	71.33
22	2-Butyne	26.99	68	Methyl cyclopentane	71.81
23	2-Methylbutane	27.85	69	2,3-Dimethyl-2-butene	73.21
24	1-*trans*-2-Dimethyl-cyclopropane	28.20	70	2-Ethyl-1,3-butadiene	75
25	1-Pentene	29.97	71	2-Methyl-1,3-pentadiene[b]	75.76
26	2-Methyl-1-butene	31.16	72	1-Methylcyclopentene	75.8
27	Isoprene	34.07	73	4-Methyl-1,3-pentadiene	76.3
28	2-Methyl-1-buten-3-yne	34.5	74	3,3-Dimethyl-1-pentene	77.54
29	Pentane	36.07	75	1,3-Cyclohexadiene	79–80
30	*trans*-2-Pentene	36.35	76	Benzene	80.10
31	*cis*-2-Pentene	36.94	77	2,4-Dimethylpentane	80.50
32	1-*cis*-2-Dimethyl-cyclopropane	37.03	78	Cyclohexane	80.74
			79	3-Hexyne	81.43
33	2-Methyl-2-butene	38.57	80	Cyclohexene	82.98
34	3-Methyl-1,2-butadiene	40	81	2,4-Dimethyl-2-pentene	83.44
35	1-Pentyne	40.18	82	2-Hexyne	84.52
36	1,3-Cyclopentadiene	40–42	83	3-Ethyl-1-pentene	85.13
37	3,3-Dimethyl-1-butene	41.25	84	1,4-Cyclohexadiene	86–87
38	1-*trans*-3-Pentadiene	42.03	85	4-Methyl-1-hexene	86.73
39	1-*cis*-3-Pentadiene	44.07	86	2,3-Dimethylpentane	89.78
40	Cyclopentene	44.24	87	3-Methylhexane	91.85
41	1,2-Pentadiene	44.86	88	3-Ethyl-2-pentene	96.01
42	2,3-Pentadiene	48.27	89	Heptane	98.43
43	Cyclopentane	49.26	90	Methylcyclohexane	100.93
44	2,2-Dimethylbutane	49.74	91	4-Methylcyclohexene	102.74
45	4-Methyl-1-pentene	53.87	92	1-Methylcyclohexene	110.0
46	3-Methyl-1-pentene	54.18	93	Toluene	110.63

[a] Source: Matheson 1-3, 5, 6, 8-10, 12, 14-18, 20, 28, 78; Air Reduction 4, 22; Columbia Organic Chemicals 7; Phillips 11, 23, 25-27, 29, 31, 33, 43-45, 49-51, 53-56, 63, 68, 77, 86, 87, 89; Enjay 13; A.P.I. 19, 21, 24, 30, 32, 34, 37-39, 41, 42, 46, 47, 52, 57-59, 61, 62, 65, 66, 69, 72, 85; Farchan 35, 48, 67, 75, 79, 82, 84; Goodyear Research 36, 70, 71, 73, 81, 83; Aldrich 40; Ohio State 60, 74, 92; Borden 64; Merck 76; Eastman Kodak 80, 88, 90, 91; Ohio Solvents 93.

[b] It is not known whether this compound has *cis* or *trans* structure or both.

Any gas chromatographic apparatus with the necessary supporting equipment can be used. The following apparatus was used for this work:

Kromo-Tog Model K-2, micrometer pipet, flowmeter, and unfilled glass columns, 1 and 2-1/2 meters in length from the Burrell Corp. A Regulator No. 8418 for helium cylinders from Air Reduction Sales Co. Helium, 99.8% pure, from Air Reduction Sales Co. Dimethylsulfolane from Shell Chemical Corp. Tritolyl phosphate from Harwick Standard Chemical Co. Di-*n*-decyl phthalate, 2,2′-oxydipropionitrile, and isoquinoline from Eastman Kodak. Triethylene glycol from the Matheson Co. Mineral oil, viscosity 100 to 110, from Purity Laboratories, Los Angeles, Calif. Columpak, 30 to 60 mesh, from Fisher Scientific. Silver nitrate reagent grade.

PROCEDURE

The silver nitrate-saturated triethylene glycol was prepared by triturating silver nitrate and triethylene glycol in a mortar. After standing for several days, the supernatant liquid was used as the substrate.

All packing materials were prepared by adding 40 grams of the appropriate liquid substrate directly to 100 grams of Columpak. The mixture was rolled overnight to ensure a uniform mixture. Several columns were prepared, using the different column packings. Helium was used as the carrier gas in all cases.

The following operating conditions were used with the 2-1/2-meter column: A soap bubble flowmeter at the exit of the column indicated a flow rate of 70 ml. per minute. When the flow rate was adjusted properly, isoprene was eluted at 20 minutes on the dimethylsulfolane column at 25° C. The sample size was adjusted so that no peak was higher than that produced by 2 μl. of isoprene. The flow rate on the 1-meter column was 77 ml. per minute. One to three compounds were mixed in the proper proportions with an internal standard. The helium flow was interrupted for the sample injection, and then the flow was resumed. The recorder chart speed was 1 inch per minute for all observations. Most of the relative retention times were calculated for runs of 1 hour or less; all were corrected for dead air space before the relative values were calculated.

RESULTS AND DISCUSSION

The compounds are listed in order of increasing boiling point in Table I with the source of supply and a literature value for the boiling point (*4, 11, 14, 15, 17*).

Tables II to VIII list the compounds in order of increasing retention times relative to methylal (arbitrary value 1.000) for each of the columns.

The number of theoretical plates was calculated for isoprene at 25° C. on the 2-1/2-meter columns. These values along with the elution times are given in Table IX.

Relative retention values have advantages in qualitative work because of the simplicity of the calculations. When the operating conditions were carefully controlled, the relative retention times could be reproduced to within 2%; and under very different conditions, the variation was only 5%. A closer control of the column temperature and a reduction of the sample size would undoubtedly improve the reproducibility.

The change in the order of elution from different column packings at various temperatures could best be seen when all of the retention times were reported relative to a single standard. The principal objections to this method of reporting data are twofold: The retention time of the standard might be too long or too short for accurate measurement. Or, the standard might not be miscible with

Table II. Dimethylsulfolane Columns

Compound	Column Temperature, ° C.[a] 1-Meter Column 31	1-Meter Column 25	2-1/2-Meter Column 37	2-1/2-Meter Column 29	2-1/2-Meter Column 25
Methane					0.001
Ethane					0.004
Ethene					0.006
Propane					0.013
Propene					0.023
Methylpropane					0.023
2,2-Dimethylpropane					0.036
Butane					0.038
Cyclopropane					0.047
Acetylene					0.049
1-Butene					0.061
2-Methylpropene					0.065
Allene					0.072
2-Methylbutane					0.075
trans-2-Butene					0.079
cis-2-Butene					0.093
Pentane					0.101
3-Methyl-1-butene					0.104
1-*trans*-2-Dimethylcyclopropane					0.128
2,2-Dimethylbutane					0.133
1,3-Butadiene					0.136
Propyne					0.147
1-Pentene					0.155
3,3-Dimethyl-1-butene					0.170
2-Methyl-1-butene					0.182
2,3-Dimethylbutane					0.190
2-Methylpentane					0.192
trans-2-Pentene					0.192
1,2-Butadiene					0.204
cis-2-Pentene			0.236		0.210
1-*cis*-2-Dimethylcyclopropane					0.214
3-Methyl pentane					0.228
1,4-Pentadiene					0.232
2-Methyl-2-butene					0.243
Hexane					0.264
3-Methyl-1-pentene					0.272
4-Methyl-1-pentene					0.275
Cyclopentane					0.291
4-Methyl-*cis*-2-pentene					0.298
4-Methyl-*trans*-2-pentene					0.308
1-Butyne					0.316
2,4-Dimethylpentane			0.384	0.339	0.330
2,3-Dimethyl-1-butene			0.358		0.332
Isoprene			0.433	0.410	0.396
1-Hexene			0.431		0.407
3-Methyl-1,2-butadiene					0.415
Cyclopentene					0.422
2-Methyl-1-pentene					0.424
trans-3-Hexene					0.438
cis-3-Hexene					0.458
trans-2-Hexene					0.467
Methyl cyclopentane			0.52		0.469
2-Ethyl-1-butene			0.54		0.479
1,2-Pentadiene			0.52		0.51
2-Methyl-2-pentene			0.55		0.51
2,3-Pentadiene			0.53		0.52
cis-2-Hexene			0.54		0.53
1-*trans*-3-Pentadiene			0.57		0.54
3,3-Dimethyl-1-pentene			0.57	0.56	0.55
3-Methyl-*trans*-2-pentene			0.57		0.55
3-Methylhexane					0.56
2,3-Dimethylpentane					0.56
2-Butyne			0.59		0.57
1-*cis*-3-Pentadiene			0.63		0.60
3-Methyl-*cis*-2-pentene			0.64		0.61
1,5-Hexadiene			0.63		0.63
3-Ethyl-1-pentene					0.66
Cyclohexane	0.69		0.70		0.67
Heptane		0.69	0.68	0.70	0.68
2,4-Dimethyl-2-pentene					0.69
2,3-Dimethyl-2-butene			0.75		0.75
1,3-Cyclopentadiene			0.81		0.78
4-Methyl-1-hexene			0.82		0.82
1-Pentyne			0.82		0.84
2-Methyl-1-buten-3-yne			0.91		0.94
2-Ethyl-1,3-butadiene					1.03
1-Methylcyclopentene			1.02	1.05	1.05
Methylcyclohexane			1.13	1.15	1.10
2-Pentyne			1.10		1.15
2,3-Dimethyl-1,3-butadiene			1.12		1.15
3-Ethyl-2-pentene			1.28	1.36	1.36
Cyclohexene		1.43	1.41	1.43	1.40
2-Methyl-1,3-pentadiene[b]	1.49	1.53	1.47		1.50
4-Methyl-1,3-pentadiene			1.71		
3-Hexyne		1.94	1.80		
1-Hexyne		2.17	1.99		
4-Methylcyclohexene	2.16	2.24	2.16		
1,3-Cyclohexadiene		2.39	2.36		
2-Hexyne		2.61	2.45		
1-Methylcyclohexene	3.19	3.32	3.04		
1,4-Cyclohexadiene		3.75	3.27		
Benzene	4.74				
Toluene					

[a] At 38° C. on the 1-meter column, relative retention times are: methylcyclohexane 1.13, cyclohexene 1.41, 4-methylcyclohexene 2.12, benzene 4.44, toluene 10.3. [b] See footnote[b], Table I.

Table III. 2-1/2 Meter Tritolyl Phosphate Column

Compound	Column Temperature, ° C.[a] 55	45	37	29	25
Methane					0.001
Ethene					0.008
Ethane					0.008
Propane					0.023
Acetylene					0.024
Propene					0.031
Methylpropane					0.049
Cyclopropane					0.071
Butane					0.076
2,2-Dimethylpropane					0.078
Allene					0.078
1-Butene					0.095
2-Methylpropene					0.097
Propyne					0.113
trans-2-Butene					0.130
cis-2-Butene					0.149
1,3-Butadiene					0.162
2-Methylbutane			0.193	0.177	0.168
3-Methyl-1-butene					0.182
Pentane			0.268		0.233
1-*trans*-2-Dimethylcyclopropane	0.350				0.253
1,2-Butadiene					0.275
1-Pentene			0.324		0.279
1-Butyne					0.284
2,2-Dimethylbutane					0.301
3,3-Dimethyl-1-butene			0.343		0.303
2-Methyl-1-butene					0.315
1,4-Pentadiene					0.330
trans-2-Pentene					0.364
cis-2-Pentene					0.387
1-*cis*-2-Dimethylcyclopropane			0.453		0.410
2-Methyl-2-butene					0.433
2,3-Dimethylbutane					0.451
2-Methylpentane			0.51		0.470
Isoprene	0.63		0.58	0.53	0.54
4-Methyl-1-pentene					0.54
3-Methyl-1-pentene					0.54
3-Methyl pentane					0.56
4-Methyl-*cis*-2-pentene					0.59
2,3-Dimethyl-1-butene					0.63
2-Butyne					0.63
3-Methyl-1,3-butadiene			0.68	0.67	0.64
4-Methyl-*trans*-2-pentene					0.65
Cyclopentane			0.74	0.71	0.67
Hexane					0.68
1-*trans*-3-Pentadiene					0.75
1,2-Pentadiene			0.80		0.77
Cyclopentene					0.80
2-Methyl-1-buten-3-yne					0.80
1-Pentyne			0.84		0.83
2-Methyl-1-pentene					0.83
1-Hexene					0.84
2,4-Dimethylpentane					0.85
2,3-Pentadiene					0.86
1-*cis*-3-Pentadiene					0.86
cis-3-Hexene		0.96			0.93
trans-3-Hexene					0.95
2-Ethyl-1-butene					0.97
trans-2-Hexene		1.00	1.02		0.99
1,5-Hexadiene		1.01		0.92	0.99
1,3-Cyclopentadiene					1.01
2-Methyl-2-pentene				0.96	1.05
cis-2-Hexene					1.10
3,3-Dimethyl-1-pentene					1.10
3-Methyl-*trans*-2-pentene		1.11			1.10
Methyl cyclopentane					1.17
3-Methyl-*cis*-2-pentene			1.26		1.24
2,3-Dimethylpentane					1.39
3-Ethyl-1-pentene					1.41
3-Methyl hexane					1.43
2,4-Dimethyl-2-pentene			1.40		1.43
2,3-Dimethyl-2-butene			1.48	1.34	1.48
2-Ethyl-1,3-butadiene					1.52
2-Pentyne			1.51		1.54
2,3-Dimethyl-1,3-butadiene			1.80		1.68
Cyclohexane	1.72	1.74		1.61	1.71
4-Methyl-1-hexene					1.71
Heptane	1.71		1.82	1.76	2.02
1-Methylcyclopentene			2.09	2.16	
2-Methyl-1,3-pentadiene[b]			2.34		2.20
1-Hexyne		2.14	2.40		
4-Methyl-1,3-pentadiene			2.56		
3-Ethyl-2-pentene			2.64	2.62	
Cyclohexene	2.63	2.77	2.93		
3-Hexyne		2.77	3.02		
Methylcyclohexane		2.91	3.08		
1,3-Cyclohexadiene	3.22	3.46			
2-Hexyne	2.94	3.47	3.68		
4-Methyl cyclohexene	3.97	4.40			
Benzene	4.36	4.74			
1,4-Cyclohexadiene	4.64	4.96			
1-Methylcyclohexene	5.5				

[a] At 75° C. relative retention times are: 1,4-cyclohexadiene 4.11, 1-methylcyclohexene 4.77, toluene 8.5. [b] See footnote[b], Table I.

Table IV. 2-1/2-Meter Di-*n*-decyl Phthalate Column

Compound	Column Temperature, ° C.[a] 55	45	37	29	25
Methane					0.002
Ethene					0.011
Ethane					0.014
Acetylene					0.019
Propane					0.049
Propene					0.051
Allene					0.099
Cyclopropane					0.105
Propyne					0.109
Methylpropane					0.111
Methylpropene					0.165
Butane					0.169
1-Butene					0.169
2,2-Dimethylpropane					0.187
1,3-Butadiene					0.224
trans-2-Butene					0.230
cis-2-Butene					0.255
1-Butyne					0.302
3-Methyl-1-butene					0.358
1,2-Butadiene		0.440	0.402		0.360
Methyl butane			0.435		0.399
1-*trans*-2-Dimethylcyclopropane	0.59	0.55	0.51		0.474
1,4-Pentadiene		0.59	0.55	0.54	0.51
1-Pentene					0.53
Pentane			0.57		0.54
2-Methyl-1-butene		0.65	0.62	0.61	0.58
3,3-Dimethyl-1-butene		0.71	0.70	0.68	0.66
trans-2-Pentene		0.72		0.69	0.66
cis-2-Pentene		0.77	0.73	0.72	0.70
2-Butyne			0.73		0.70
1-*cis*-2-Dimethylcyclopropane		0.81			0.75
2-Methyl-2-butene		0.84			0.80
2,2-Dimethyl butane		0.84	0.81		0.81
Isoprene		0.87	0.86	0.85	0.82
2-Methyl-1-buten-3-yne					0.83
3-Methyl-1,2-butadiene		0.96			0.92
1-Pentyne		0.98	0.97		0.98
1-*trans*-3-Pentadiene			1.10		1.10
4-Methyl-1-pentene		1.12	1.13	1.14	1.11
1,2-Pentadiene		1.13	1.11	1.14	1.12
3-Methyl-1-pentene			1.14	1.15	1.13
2,3-Dimethyl butane			1.15	1.16	1.14
2,3-Pentadiene			1.16		1.17
2-Methyl pentane			1.18	1.21	1.19
1-*cis*-3-Pentadiene			1.20		1.20
4-Methyl-*cis*-2-pentene			1.21	1.23	1.21
Cyclopentane			1.25		1.23
1,3-Cyclopentadiene			1.27		1.24
Cyclopentene			1.25	1.27	1.24
2,3-Dimethyl-1-butene		1.26	1.27	1.31	1.28
4-Methyl-*trans*-2-pentene			1.27	1.31	1.30
3-Methyl pentane	1.52		1.59	1.75	1.68
1,5-Hexadiene	1.53		1.63	1.70	1.68
Hexane	1.35	1.37	1.37		1.42
2-Methyl-1-pentene			1.57	1.62	1.67
1-Hexene	1.55	1.60	1.65	1.72	1.71
2-Pentyne	1.56	1.66	1.72	1.82	1.82
trans-3-Hexene	1.60	1.69	1.77	1.89	
cis-3-Hexene		1.75	1.81	1.92	
2-Ethyl-1-butene		1.78	1.85	1.95	1.96
trans-2-Hexene		1.81	1.89	2.00	
2-Methyl-2-pentene		1.86	1.95	2.05	
cis-2-Hexene		1.96	2.03		
3-Methyl-*trans*-2-pentene	1.87	1.99	2.08	2.20	
2,4-Dimethyl pentane		2.05	2.19		2.35
3-Methyl-*cis*-2-pentene	2.00	2.16	2.29	2.48	2.46
Methyl cyclopentane	2.17	2.27	2.32		2.46
3,3-Dimethyl-1-pentene		2.36	2.39		
2-Ethyl-1,3-butadiene		2.35	2.40		
2,3-Dimethyl-2-butene	2.28	2.51	2.64	2.89	
2,3-Dimethyl-1,3-butadiene	2.36	2.62	2.75	2.97	2.96
2,4-Dimethyl-2-pentene		2.62	2.80		
1-Hexyne	2.38	2.66	2.84		
3-Ethyl-1-pentene		2.85	3.01		
2,3-Dimethyl pentane	2.93	3.22	3.24		
Cyclohexane	2.96	3.20	3.33		3.55
1-Methyl cyclopentene	2.92	3.18	3.42		3.55
2-Methyl-1,3-pentadiene[b]	2.91	3.21			
3-Methyl hexane	3.01	3.28			
3-Hexyne	2.92	3.36	3.61		
4-Methyl-1,3-pentadiene	3.04	3.39			
2-Hexyne	3.54	4.10			
Cyclohexene	3.81	4.16			
Heptane	3.69	4.20			
1,3-Cyclohexadiene	3.97	4.31			
3-Ethyl-2-pentene	4.24	4.66			
Benzene	4.43	4.96			
Methyl cyclohexane	5.1				
1,4-Cyclohexadiene	5.4				
4-Methyl cyclohexene	6.4				
1-Methyl cyclohexene	8.3				

[a] At 75° C. relative retention times are: 4-methyl-1,3-pentadiene 2.68, benzene 3.97, methylcyclohexane 4.51, 4-methylcyclohexene 5.6, 1-methylcyclohexene 6.9, toluene 9.2. [b] See footnote[b], Table I.

Table V. 2-1/2-Meter Mineral Oil Column

Compound	Column Temperature, ° C. 55	45	37	29	25
Methane					0.003
Acetylene					0.010
Ethene					0.017
Ethane					0.029
Propene					0.084
Propyne					0.091
Propane					0.099
Allene					0.121
Cyclopropane					0.165
Methylpropane					0.223
Methylpropene					0.282
1-Butene					0.284
1-Butyne					0.289
1,3-Butadiene					0.290
Butane		0.293			0.351
trans-2-Butene					0.380
2,2-Dimethylpropane		0.327			0.396
cis-2-Butene					0.427
1,2-Butadiene		0.423	0.437	0.398	0.480
3-Methyl-1-butene		0.480			0.63
2-Methyl-1-buten-3-yne			0.60		0.69
1,4-Pentadiene		0.59	0.64	0.60	0.73
2-Butyne		0.62	0.66		0.78
2-Methylbutane		0.68	0.71		0.83
1-*trans*-2-Dimethylcyclopropane	0.84	0.71	0.77		0.89
1-Pentene		0.70	0.78	0.73	0.91
1-Pentyne	0.97	0.72	0.82		0.96
2-Methyl-1-butene		0.73	0.85		0.99
Isoprene		0.84	0.94	0.89	1.11
Pentane	1.03	0.86			1.12
trans-2-Pentene		0.88			1.16
3,3-Dimethyl-1-butene		0.90	1.02	0.96	1.19
cis-2-Pentene		0.92			1.21
3-Methyl-1,2-butadiene		0.97	1.10		1.32
1-*cis*-2-Dimethylcyclopropane		1.00	1.13		1.35
2-Methyl-2-butene		0.99	1.14		1.36
1-*trans*-3-Pentadiene		1.02	1.17		1.39
1,3-Cyclopentadiene	1.25	1.12	1.25		1.46
1-*cis*-3-Pentadiene		1.11	1.28		1.54
1,2-Pentadiene		1.14	1.29		1.58
2,2-Dimethyl butane	1.55	1.20	1.39		1.66
2,3-Pentadiene	1.61	1.17	1.36		1.69
4-Methyl-1-pentene	1.59	1.39	1.64	1.58	2.00
Cyclopentene	1.54	1.44	1.67	1.60	2.02
3-Methyl-1-pentene	1.64	1.42	1.67	1.64	
2-Pentyne	1.69	1.40	1.69	1.65	2.13
4-Methyl-*cis*-2-pentene	1.73	1.49	1.79	1.74	
2,3-Dimethyl-1-butene		1.54	1.83	1.80	
4-Methyl-*trans*-2-pentene	1.81	1.60	1.91	1.89	
Cyclopentane		1.65	1.96		2.37
2,3-Dimethylbutane	1.86	1.66	1.96		2.40
1,5-Hexadiene		1.65	1.96	1.93	
2-Methyl pentane	2.14	1.70	2.05		
2-Methyl-1-pentene		1.93	2.34		
3-Methyl pentane	2.22	1.95	2.38	2.35	
1-Hexene		1.98	2.39		
1-Hexyne		2.09	2.47		
cis-3-Hexene		2.16	2.67		
2-Ethyl-1-butene		2.20	2.68		
trans-3-Hexene		2.19	2.69		
trans-2-Hexene		2.30	2.82		
2-Ethyl-1,3-butadiene		2.30	2.83		
Hexane		2.34			3.61
2-Methyl-2-pentene		2.35			
3-Methyl-*trans*-2-pentene	2.60	2.43			
cis-2-Hexene		2.46			
2,3-Dimethyl-1,3-butadiene	2.79	2.72			
3-Methyl-*cis*-2-pentene	2.84	2.72			
3,3-Dimethyl-1-pentene		2.95			
2,4-Dimethyl pentane		3.03			
Methyl cyclopentane	3.33	3.07			
3-Hexyne	3.18	3.09			
2-Methyl-1,3-pentadiene[a]	3.27	3.14			
2,3-Dimethyl-2-butene	3.17	3.14			
4-Methyl-1,3-pentadiene	3.37	3.16			
2,4-Dimethyl-2-pentene	3.61	3.48			
2-Hexyne	3.79	3.60			
Benzene	3.80				
3-Ethyl-1-pentene	3.91	3.71			
1-Methylcyclopentene	3.86	3.97			
1,3-Cyclohexadiene	4.33				
Cyclohexane	4.43				
2,3-Dimethylpentane	4.88	4.55			
Cyclohexene	5.0				
3-Methylhexane	5.1	4.67			
1,4-Cyclohexadiene	5.8				
Heptane	6.4				
Methylcyclohexane	8.3				

[a] See footnote[b], Table I.

Table VI. Relative Retention Times on a 2-1/2 Meter 2,2′-Oxydipropionitrile Column

Compound	Column Temp., 25° C.	Compound	Column Temp., 25° C.	Compound	Column Temperature, ° C. 55	45	37	29	25
Methane	0.0006	2-Methyl-2-butene	0.090	2,3-Pentadiene					0.202
Ethane	0.003	2,3-Dimethyl-1-butene	0.098	2,3-Dimethyl-2-butene					0.217
Propane	0.006	Cyclopentane	0.099	1,5-Hexadiene					0.231
2,2-Dimethylpropane	0.012	1,2-Butadiene	0.102	1-*trans*-3-Pentadiene					0.236
2-Methylbutane	0.021	3-Methylhexane	0.106	Methylcyclohexane					0.254
Pentane	0.029	1,4-Pentadiene	0.109	1-*cis*-3-Pentadiene					0.284
1-Butene	0.029	2,3-Dimethylpentane	0.111	3-Ethyl-2-pentene					0.318
Methylpropene	0.032	*trans*-3-Hexene	0.114	1-Methylcyclopentene					0.339
2,2-Dimethylbutane	0.037	1-Hexene	0.116	1-Pentyne					0.376
3-Methyl-1-butene	0.039	*trans*-2-Hexene	0.122	2-Butyne					0.376
1-*trans*-2-Dimethylcyclopropane	0.043	Heptane	0.123	2-Ethyl-1,3-butadiene					0.378
2-Methylpentane	0.045	2-Methyl-1-pentene	0.127	2-Methyl-1-buten-3-yne					0.410
Allene	0.045	Methylcyclopentane	0.129	2,3-Dimethyl-1,3-butadiene					0.434
2,3-Dimethylbutane	0.050	*cis*-3-Hexene	0.132	1,3-Cyclopentadiene					0.462
3,3-Dimethyl-1-butene	0.050	3,3-Dimethyl-1-pentene	0.144	Cyclohexene					0.53
1-Pentene	0.055	2-Ethyl-1-butene	0.144	2-Methyl-1,3-pentadiene[a]				0.55	0.55
3-Methylpentane	0.057	2-Methyl-2-pentene	0.148	2-Pentyne					0.58
Hexane	0.058	3-Ethyl-1-pentene	0.154	4-Methyl-1,3-pentadiene				0.67	0.66
trans-2-Pentene	0.065	*cis*-2-Hexene	0.156	4-Methylcyclohexene					0.68
2,4-Dimethylpentane	0.066	3-Methyl-1,2-butadiene	0.159	3-Hexyne					0.78
2-Methyl-1-butene	0.069	2,4-Dimethyl-2-pentene	0.161	1-Hexyne				0.79	0.81
1,3-Butadiene	0.075	3-Methyl-*trans*-2-pentene	0.165	1-Methylcyclohexene					0.94
1-*cis*-2-Dimethylcyclopropane	0.077	3-Methyl-*cis*-2-pentene	0.175	2-Hexyne					1.09
3-Methyl-1-pentene	0.078	Isoprene	0.181	1,3-Cyclohexadiene				1.12	1.12
cis-2-Pentene	0.078	Cyclopentene	0.186	1,4-Cyclohexadiene		1.63	1.72	1.78	1.83
4-Methyl-1-pentene	0.079	4-Methyl-1-hexene	0.193	Benzene	2.51	2.55	2.72	2.86	
4-Methyl-*trans*-2-pentene	0.083	1,2-Pentadiene	0.196	Toluene	4.63	4.14			
4-Methyl-*cis*-2-pentene	0.088	Cyclohexane	0.197						

[a] See footnote[b], Table I.

a wide variety of compounds to be analyzed by gas chromatography. The advantages of methylal were a low boiling point and solubility in many materials. However, methylal tailed badly on the mineral oil substrate. To minimize errors due to tailing and to unfavorable retention times, secondary standards were introduced. After the column conditions were selected, a mixture of a suitable secondary standard and methylal was run. The retention time of the secondary standard was calculated relative to methylal, and the new standard was then used for further work where the same conditions were employed.

Most of the 93 compounds can be identified by a judicious selection of column substrates. Only the 3-methyl-1-pentene and 4-methyl-1-pentene pair and the 2,3-dimethyl-pentane and 3-methylhexane pair were not resolved sufficiently to permit their identification on the substrates studied using 2-1/2-meter columns. It might be possible to separate the latter pair on an isoquinoline column, but this has not been tried.

Table VII. 2-1/2 Meter Isoquinoline Column

Compound	Column Temp., 25° C.
2,2-Dimethylpropane	0.054
Butane	0.062
Methylpropene	0.081
1-Butene	0.083
2-Methyl-1-butene	0.276
2,3-Dimethylbutane	0.357
2-Methylpentane	0.403
3-Methylpentane	0.467
Isoprene	0.467
1-*trans*-3-Pentadiene	0.69
1-*cis*-3-Pentadiene	0.77
cis-3-Hexene	0.86
trans-2-Hexene	0.90
2-Methyl-2-pentene	0.95
cis-2-Hexene	0.97

Table VIII. 2-1/2-Meter Silver Nitrate–Saturated Triethylene Glycol Column

Compound	Column Temp., 25° C.
Methylpropene	0.077
1-Butene	0.116
Isoprene	0.448
1-Hexene	0.490

Table IX. Retention Time and Number of Theoretical Plates for a 2-1/2-Meter Column at 25° C. for Isoprene

Substrate	Theoretical Plates	Retention Time, Min.
Silver nitrate–saturated triethylene glycol	464	8
Tritolyl phosphate	775	18
2,2′-Oxydipropionitrile	912	8
Mineral oil	926	35
Di-*n*-decyl phthalate	1070	32
Dimethylsulfolane	1500	20
Isoquinoline	1670	20

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LITERATURE CITED

(1) Abraham, M. H., Davies, A. G., others, *Anal. Chim. Acta* **17**, 499 (1958).
(2) Ambrose, D., Keulemans, A. I. M., Purnell, J. H., *Anal. Chem.* **30**, 1582 (1958).
(3) Brooks, V. T., Collins, G. A., *Chem & Ind. (London)* **1956** 921.
(4) Camin, D. L., Rossini, F. D., *J. Phys. Chem.* **60**, 1446 (1956).
(5) Desty, D. H. ed., "Vapour Phase Chromatography," pp. 98, 154, 332, 413, Academic Press, New York, 1956.
(6) Desty, D. H., Whyman, B. H. F., *Anal. Chem.* **29**, 320 (1957).
(7) Dupire, F., Botquin, G., *Anal. Chim. Acta* **18**, 282 (1958).
(8) Gil-Av, Emanuel, Herling, J., Shabtai, J. *J. Chromatography* **1**, 508 (1958).
(9) Haslam, J. ed., Jeffs, A. R., *Analyst* **83**, 455 (1958).
(10) James, A. T., Martin, A. J. P., *J. Appl. Chem.* **6**, 105 (1956).
(11) Kelso, R. G., Greenlee, K. W., Derfer, J. M., Boord, C. E., *J. Am. Chem. Soc.* **77**, 1751 (1955).
(12) Keulemans, A. I. M., Kwantes, A., Zaal, P., *Anal Chim. Acta* **13**, 357 (1955).
(13) Podbielniak, W. J., Preston, S. T., *Petrol. Refiner* **35**, 215 (1956).
(14) Pomerantz, P., Fookson, A., others *J. Research Natl. Bur. Standards* **52**, 51 (1954).
(15) *Ibid.*, p. 59.
(16) Porter, P. E., Deal, C. H., Stross, F. H., *J. Am. Chem. Soc.* **78**, 2999 (1956).
(17) Rossini, F. D., Pitzer, K. S., others, in "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.
(18) Spencer, C. F., Baumann, Fred, Johnson, J. F., *Anal. Chem.* **30**, 1473 (1958).
(19) Sullivan, L. J., Lotz, J. R., Willingham, C. B., *Ibid.*, **28**, 495 (1956).

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