A CATALOG OF RETENTION TIMES OF A NUMBER OF ORGANIC COMPOUNDS

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In earlier publications, in connection with the present study, the procedure for collecting gaseous air pollutants, a method for the estimation of the total amount of air pollutants and the principle of determining the optimum column conditions were described[1-3]. In the present study, the relative retention times of a large number of probable air pollutants are given. Some of the compounds studied do not constitute an immediate air pollution hazard but were included for the sake of completeness. The retention times have been obtained on two columns and at two widely different temperatures. Because in a routine analysis the use of a large number of columns would not be feasible, it was decided to restrict the study to the use of a general purpose column together with a second, more selective, unit. After some preliminary study, tri-*m*-tolyl phosphate and β,β'-oxydipropionitrile columns were chosen as being the most suitable for this kind of application. Originally, two hundred compounds, including the following amines, were studied: *tert.*-butylamine, diallylamine, 4-methylpiperidine, 1,2-propanediamine, pyridine. Of the amines, only pyridine could be eluted from the columns in question. A number of compounds gave indications of de composition on the column.

EXPERIMENTAL

Burell Corporation's Kromo-Tog Model K-2 was used throughout the study. An Agla micrometer syringe was used for introducing the liquid samples and a 1 ml gas pipet was used for the gaseous samples. Matheson helium was used as the carrier gas and pressure was regulated at the inlet of the column by means of a Matheson Regulator. The flow rate at the inlet was measured by means of a Burrell No. 340-70 orifice type mercury flow meter. The column was a U-shaped glass tube, 2 m long and 5 mm I. D. The column packing was prepared in the usual way by coating a 30/60 screen fraction Johns-Manville Chromosorb with the substrate. The weight ratio of the substrate to chromosorb was 20 to 80. The column temperatures were adjusted by means of Variac settings which were calibrated by means of a Sargeant Thermistor thermometer.

Carbon tetrachloride was used as the reference solute. For any given temperature

the optimum column condition was established with respect to carbon tetrachloride by varying the flow rate until maximum number of plates were obtained. Subsequently, the column condition was checked by measuring the retention time and the width of carbon tetrachloride peak.

RESULTS AND DISCUSSION

The relative retention ratios of the compounds are given in their increasing order in Tables I, II, III, and IV. The relative retention times are given at two temperatures.

TABLE I

Column condition: 20 g of β,β'-oxydipropionitrile per 80 g of 30/60 mesh chromosorb (Johns–Manville).
Total weight of packing material: 22 g (approx.).
Column temperature: 53°.
Flow rate: 52 to 56 ml/min.
Detector cell temperature: 100°.
Peak characteristics of references solute (carbon tetrachloride):
Emergence time: 3.7 min.
Peak retention time: 4.0 min.
Peak width: 0.5 min.
1 cm on the chart = 1.20 min.

Name of the compound	*B. p. °C*	*Relative retention ratio*
Propane	—42.0	0.179
Dichlorodifluoromethane (Freon 12)	—28.0	0.182
Dichlorotetrafluoroethane (Freon 114)	3.8	0.182
Propylene	—47.0	0.194
2-Methylpentane	60.0	0.208
n-Pentane	36.2	0.208
2,2-Dimethylbutane	49.7	0.209
2,3-Dimethylbutane	58.1	0.224
3-Methylbutene-1	25.0	0.224
3-Methylpentane	64.0	0.242
2,4-Dimethylpentane	80.5	0.254
n-Hexane	69.0	0.254
Pentene-2	36.4	0.254
2-Methylbutene-2	38.4	0.272
Cyclopentane	49.5	0.288
Trichlorofluoromethane (Freon 11)	24.1	0.288
3-Methylhexane	91.85	0.303
4-Methylpentene-2	58.0	0.328
2,2,4-Trimethylpentane	99.3	0.328
2,3-Dimethylpentane	89.8	0.330
Methylcyclopentane	71.8	0.330
Hexenes (mixed, 2 and 3)	64.7	0.343
Hexene-1	63.49	0.344
n-Heptane	98.4	0.360
Hexene-2	67.9	0.360
2-Methylpentene-1	61.5	0.373
Cyclohexane	81.4	0.397
Dimethylhexanes (mixed)	108–16	0.403

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TABLE I (*continued*)

Name of the compound	*B. p. °C*	*Relative retention ratio*
Ethyl ether	34.6	0.439
Heptene-3	95.8	0.463
Di-isobutylene	102.6	0.470
Isopropyl ether	67.5	0.480
2,2,5-Trimethylhexane	—	0.480
1-Chloropropene	35.0	0.484
Carbon disulfide	46.30	0.490
2,4,4-Trimethylpentene-2	101.1	0.508
n-Octane	125.8	0.510
2-Chloropropane	35.4	0.515
Methylcyclohexane	100.3	0.523
Heptene-2	98.0	0.538
tert.-Butyl ethyl ether	68.9	0.538
2,4,4-Trimethylpentene-1	101.44	0.538
tert.-Butyl chloride	51.2	0.568
Propyl isopropyl ether	51.2	0.568
tert.-Butyl methyl ether	—	0.597
Octene-1	121.3	0.688
Octene-2	121–122	0.700
2-Bromopropene	48.4	0.712
1-Chloropropane	47.2	0.716
n-Nonane	150.80	0.730
Cyclohexene	83.0	0.775
Bromoethane	38.0	0.794
Propyl ether	91.0	0.818
1-Chloro-2-methylpropane	68.9	0.853
Iodomethane	42.5	0.865
2-Bromopropane	59.6	0.882
4-Methylcyclohexene	102–3	0.925
Acetaldehyde	21.0	0.985
2-Chloro-2-methylbutane	86.0	1.01
1-Bromo-1-propene	60.2	1.02
3-Chloropropene	44.6	1.04
2-Bromo-2-methylpropane	73.03	1.06
Dimethoxymethane	44.0	1.09
1-Chlorobutane	78.0	1.17
1-Bromopropane	70.9	1.32
Cycloheptene	115.0	1.39
Iodoethane	72.2	1.41
Propionaldehyde	48.8	1.52
Isoamyl chloride	98.9	1.53
3-Chloro-2-methylpropene	72.2	1.55
2-Bromobutane	91.3	1.56
1-Bromo-2-methylpropane	91.5	1.56
Ethyl isocyanate	60.0	1.61
Dichloromethane	40.1	1.70
1,1-Dimethoxyethane	64.5	1.70
2-Iodopropane	89.5	1.70
Butyl ether	142.0	1.76
4-Vinylcyclohexene-1	130.0	1.86
Isobutyraldehyde	61.5	1.91
Diethoxymethane	89.0	1.94
3-Bromopropene	71.3	2.00
Trichloroethylene	87.0	2.045
Methyl acetate	57.1	2.10
Ethyl formate	54.3	2.18
1-Iodopropane	102.4	2.19

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TABLE I (*continued*)

Name of the compound	*B. p. °C*	*Relative retention ratio*
1,2-Dichloroethylene (*cis*)	60.1	2.20
tert.-Butyl alcohol	82.8	2.29
Methyl alcohol	64.65	2.38
Acetone	56.5	2.42
Isopropyl alcohol	82.3	2.50
Benzene	80.1	2.55
Isopropyl acetate	89.0	2.59
tert.-Butyl nitrite	63.0	2.60
Trichloromethane	61.26	2.64
Vinyl acetate	163.0	2.72
Bromotrichloromethane	104.07	2.76
2-Iodobutane	117.5	2.79
Butyraldehyde	75.7	2.80
Ethyl alcohol	78.5	2.88
Ethyl acetate	77.15	2.94
2-Fluoroethanol	103.35	3.24
Thiophene	84.12	3.70
sec.-Butyl acetate	112–13	4.03
2,3-Dichloropropene	94.0	4.15
n-Propyl acetate	101.6	4.17
sec.-Butyl alcohol	99.5	4.27
Methyl ethyl ketone	79.6	4.32
1,2-Dibromoethylene	108–10	4.44
Di-isopropyl ketone	123.7	4.60
1,2-Dichloropropane	96.8	4.67
Ethyl acrylate	99.8	4.70
Ethyl nitrate	88.7	4.88
Methyl methacrylate	100.0	5.00
Methyl isopropyl ketone	93.0	5.16
Diethyl ketone	102.7	5.17
1,2-Dichloroethane	83.5	5.50
3-Bromopropyne	88.0	5.55
1,2-Dimethoxyethane	—	5.55
Propyl alcohol	97.19	5.60
Isobutyl methyl ketone	119.0	5.73
Isopropyl nitrate	102.0	5.91
Chloropicrin	112.0	6.15
Propyl propionate	123.4	6.15
Acrylonitrile	78.0	6.29
Allyl acetate	103.4	6.45
Ethylbenzene	136.15	6.63
p-Xylene	138.35	6.63
Propyl nitrate	110.5	6.65
sec.-Isoamyl alcohol	114.0	6.65
Paraldehyde	124.4	7.83
2-Bromo-1-chloropropane	117.0	7.94
m-Xylene	139.10	7.96
Dimethyldiketone	88.0	8.60
Allyl alcohol	96–97	8.64
Cumene	152.39	8.63
Butyl alcohol	117.7	8.71
1-Bromo-2-chloroethane	107.0	10.55
o-Xylene	144.1	10.65
Ethyl carbonate	125.8	11.70
1,4-Dioxane	101.5	13.15
2-Nitropropane	120.0	14.6
1,1,2-Trichloroethane	113.5	14.8
Nitromethane	101.0	15.8
Nitroethane	114.8	18.95

TABLE II

Column condition: 20 g of β,β'-oxydipropionitrile per 80 g of 30/60 mesh chromosorb (Johns-Manville).
Total weight of packing material: 22 g (approx.).
Column temperature: 73°.
Flow rate: 48 to 54 ml/min.
Detector cell temperature: 100°.
Peak characteristics of reference solute (carbon tetrachloride):
Emergence time: 2.60 min.
Peak retention time: 2.90 min.
Peak width: 0.40 min.

Name of the compound	*B. p. °C*	*Relative retention ratio*
Propane	—42.0	0.254
3-Methylpentane	64.0	0.276
Propylene	—47.0	0.298
Dichlorodifluoromethane (Freon 12)	—28.0	0.300
2,2-Dimethylbutane	49.7	0.300
n-Pentane	36.2	0.309
2-Methylbutene-2	38.4	0.319
Dichlorotetrafluoroethane (Freon 114)	3.8	0.320
2,3-Dimethylbutane	58.1	0.340
n-Hexane	69.0	0.340
3-Methylbutene-1	25.0	0.340
2-Methylpentane	60.0	0.340
4-Methylpentene-2	58.0	0.340
Pentene-2	36.4	0.340
2,4-Dimethylpentane	80.5	0.361
3-Methylhexane	91.85	0.362
n-Heptane	98.4	0.333
Methylcyclopentane	71.8	0.383
Cyclopentene	49.5	0.404
2,2,4-Trimethylpentane	99.3	0.404
2,3-Dimethylpentane	89.8	0.425
Dimethylhexanes (mixed)	108–16	0.446
2-Methylpentene-1	61.5	0.448
Hexenes (mixed, 2 and 3)	64.67	0.448
Hexene-1	63.49	0.470
Hexene-2	67.9	0.470
Trichlorofluoromethane (Freon 11)	24.1	0.470
Ethyl ether	34.6	0.480
Isopropyl ether	67.5	0.500
Cyclohexane	81.4	0.510
Di-isobutylene	102.6	0.510
Heptene-3	95.8	0.510
2,2,5-Trimethylhexane	—	0.510
1-Chloropropane	47.2	0.522
tert.-Butyl ethyl ether	68.9	0.553
1-Chloropropene	35.0	0.553
Methylcyclohexane	100.3	0.553
n-Octane	125.8	0.553
2,4,4-Trimethylpentene-2	101.1	0.553
Heptene-2	98.0	0.574
Carbon disulfide	46.3	0.575
2,4,4-Trimethylpentene-1	101.44	0.595
2-Chloropropane	35.4	0.605
tert.-Butyl methyl ether	—	0.660
tert.-Butyl nitrite	63.0	0.723
2-Bromopropene	48.4	0.760

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TABLE II (*continued*)

Name of the compound	*B. p. °C*	*Relative retention ratio*
Propyl ether	91.0	0.760
Octene-1	121.3	0.805
n-Nonane	150.8	0.810
Cyclohexene	83.0	0.850
Octene-2	121–22	0.850
Bromoethane	38.0	0.865
1-Chloro-2-methylpropane	68.9	0.915
Methylthiomethane	37.5–38	0.915
Iodomethane	42.5	0.930
4-Methylcyclohexene	102–3	0.950
2-Bromopropane	59.6	1.000
1-Bromo-1-propene	60.2	1.02
2-Bromo-2-methylpropane	73.03	1.04
Dimethoxymethane	44.0	1.06
3-Chloropropene	44.6	1.08
2-Chloro-2-methylbutane	86.0	1.12
1-Chlorobutane	78.0	1.16
Cycloheptene	115.0	1.21
1-Bromopropane	70.9	1.30
Iodoethane	72.2	1.40
1-Chloro-3-methylbutane	98.9	1.49
1,1-Dimethoxyethane	64.5	1.49
3-Chloro-2-methylpropene	72.2	1.49
1-Bromo-2-methylpropane	91.5	1.52
2-Bromobutane	91.3	1.57
Butyl ether	142.0	1.62
Dichloromethane	40.1	1.62
2-Iodopropane	89.5	1.63
Propionaldehyde	48.8	1.70
Ethyl isocyanate	60.0	1.74
Diethoxymethane	89.0	1.78
Ethyl formate	54.3	1.78
1-Chloropentane	108.2	1.88
Isobutyraldehyde	61.5	1.89
1,2-Dichloroethylene (*cis*)	60.1	1.91
Trichloroethylene	87.0	1.92
Methyl acetate	57.1	1.95
1-Bromobutane	101.6	2.00
tert.-Butyl alcohol	82.8	2.04
4-Vinylcyclohexene-1	130.0	2.06
3-Bromopropene	71.3	2.10
Vinyl acetate	163.0	2.19
1-Iodopropane	102.4	2.20
Trichloromethane	61.26	2.28
Methyl alcohol	64.65	2.30
Benzene	80.1	2.34
Isopropyl acetate	89.0	2.35
Isopropyl alcohol	82.3	2.40
Ethyl acetate	77.15	2.48
Ethyl alcohol	78.5	2.54
2-Iodobutane	117.5	2.65
Acetone	65.5	2.68
Butyraldehyde	75.7	2.76
Bromotrichloromethane	104.07	2.78
Ethyl acrylate	99.8	3.24
Methyl methacrylate	100.0	3.34
Thiophene	84.12	3.39

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TABLE II (*continued*)

Name of the compound	*B. p.* °C	*Relative retention ratio*
Isopropyl nitrate	102.0	3.53
sec.-Butyl acetate	112–13	3.82
sec.-Butyl alcohol	99.5–100	3.83
sec.-Isoamyl alcohol	114.0	3.94
Methyl ethyl ketone	79.6	4.00
n-Propyl acetate	101.6	4.00
1,2-Dibromoethylene	108–10	4.05
Trichloroacetaldehyde	98.0	4.20
2,3-Dichloropropene	94.0	4.21
Ethyl nitrate	88.7	4.39
Di-isopropyl ketone	123.7	4.49
1,2-Dichloropropane	96.8	4.55
Methyl isopropyl ketone	93.0	4.60
Allyl alcohol	96–7	4.85
1,2-Dichloroethane	83.5	4.85
1,2-Dimethoxyethane	—	4.85
2-Fluoroethanol	103.35	4.87
Propyl propionate	123.4	4.90
Allyl acetate	103.4	5.05
Acrylonitrile	78.0	5.23
Ethylbenzene	136.15	5.28
Butyl alcohol	117.7	5.33
3-Bromopropyne	88.0	5.40
Propyl nitrate	110.5	5.60
Chloropicrin	112.0	5.64
Dimethyldiketone	88.0	5.75
Paraldehyde	124.4	6.23
Butyl acetate	126.5	6.27
p-Xylene	138.35	6.55
2-Bromo-1-chloropropane	117.0	6.64
Isobutyl methyl ketone	119.0	6.65
Cumene	152.39	7.28
Ethane nitrile	82.00	7.35
Butyl nitrite	75.0	7.50
Isobutyronitrile	107.0	7.53
1-Bromo-2-chloroethane	107.0	7.65
1,4-Dioxane	101.5	7.78
o-Xylene	144.41	8.23
Propane nitrile	97.10	9.10
Amyl nitrite	—	9.20
Ethyl carbonate	125.8	9.63
Isoamyl alcohol	130.5	9.75
1,1,2-Trichloroethane	113.5	11.6
Pyridine	115.3	13.0
Nitromethane	101.0	14.25
2-Nitropropane	120.0	15.1
Nitroethane	114.8	18.0

TABLE III

Column condition: 20 g of tri-*m*-tolyl phosphate per 80 g of 30/60 mesh chromosorb.
Total weight of packing material: 22 g (approx.).
Column temperature: 93°.
Flow rate: 49–54 ml/min.
Detector cell temperature: 150°.
Peak characteristics of reference solute (carbon tetrachloride):
Emergence time: 4.0 min.
Peak retention time: 4.3 min.
Peak width: 0.60 min.

Name of the compound	*B. p.* °C	*Relative retention ratio*
n-Pentane	36.2	0.219
2,2-Dimethylbutane	49.7	0.219
Isopentane	28.0	0.220
Propane	—42.17	0.232
Trichlorofluoromethane (Freon 11)	24.1	0.233
Propylene	—47.0	0.246
Pentene-2	36.4	0.247
2-Methylbutene-2	38.4	0.267
Dichlorodifluoromethane (Freon 12)	—28.0	0.274
Dichlorotetrafluoroethane (Freon 114)	3.8	0.274
2,3-Dimethylbutane	58.1	0.274
2-Methylpentane	60.0	0.301
Ethyl ether	34.6	0.310
3-Methylbutene-1	25.0	0.328
n-Hexane	69.0	0.329
Cyclopentane	49.5	0.356
3-Methylpentane	64.0	0.360
Hexene-1	63.48	0.363
2,4-Dimethylpentane	80.5	0.370
4-Methylpentene-2	58.0	0.373
1-Chloropropene	35.0	0.384
2-Chloropropane	35.4	0.390
Hexenes (mixed, 2 and 3)	64.67	0.410
2-Methylpentene-1	61.5	0.410
tert.-Butyl methyl ether	—	0.425
Dimethoxymethane	44.0	0.425
Hexene-2	67.9	0.438
Isopropyl ether	67.5	0.460
Methylcyclopentane	71.8	0.467
Methylthiomethane	37.5–38	0.485
Methyl alcohol	64.65	0.500
2,3-Dimethylpentane	89.7	0.507
Bromoethane	38.0	0.508
tert.-Butyl ethyl ether	68.9	0.520
Carbon disulfide	46.3	0.520
1-Chloropropane	47.2	0.520
2,2,4-Trimethylpentane	99.3	0.520
3-Methylhexane	91.85	0.530
Isopropenyl bromide	48.4	0.548
3-Chloropropene	45.6	0.550
Iodomethane	42.5	0.550
Ethyl formate	84.3	0.585
n-Heptane	98.4	0.589
Propyl isopropyl ether	82.0–83	0.590
Methyl acetate	57.1	0.600
1,2-Dichloroethylene (*trans*)	48.4	0.615
Propionaldehyde	48.8	0.618

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TABLE III (*continued*)

Name of the compound	*B. p. °C*	*Relative retention ratio*
Acetone	56.5	0.630
Cyclohexane	81.4	0.630
1,1-Dimethoxyethane	64.5	0.657
2-Bromopropane	59.6	0.660
Dichloromethane	40.1	0.660
Cyclohexane epimethylene oxide	—	0.671
Isobutyraldehyde	61.5	0.685
Dimethylhexanes (mixed)	108–16	0.696
Heptene-3	95.8	0.699
Ethyl isocyanate	60.0	0.712
1-Bromo-1-propene	60.2	0.720
Ethyl alcohol	78.5	0.720
Butyl nitrite	75.0	0.726
1-Chloro-2-methylpropane	68.9	0.730
Di-isobutylene	102.6	0.740
2,4,4-Trimethylpentene-1	101.44	0.740
tert.-Butyl alcohol	82.8	0.760
Isopropyl alcohol	82.3	0.765
tert.-Butyl nitrite	63.0	0.767
Vinyl acetate	72.3	0.770
Propyl ether	91.0	0.775
2-Bromo-2-methylpropane	73.3	0.800
Heptene-2	98.0	0.808
2,4,4-Trimethylpentene-2	101.1	0.810
2,2,5-Trimethylhexane	—	0.850
Cyclohexene	83.0	0.876
Ethyl acetate	77.15	0.880
Iodoethane	72.2	0.905
1-Bromopropane	70.9	0.920
2-Chloro-2-methylbutane	86.0	0.930
1-Chlorobutane	78.0	0.955
2-Iodopropane	89.5	0.985
Butyraldehyde	75.7	1.01
Diethoxymethane	89.0	1.04
Ethane nitrile	82.0	1.04
n-Octane	125.8	1.04
3-Chloro-2-methylpropene	72.2	1.04
Isopropyl acetate	89.0	1.06
Acrylonitrile	78–9	1.09
Methylcylohexane	100.3	1.12
Methyl ethyl ketone	79.6	1.12
1,2-Dichloroethylene (*cis*)	60.1	1.15
4-Methylcyclohexane	102–3	1.17
Octene-1	121.3	1.23
Benzene	80.1	1.24
1-Bromo-2-methylpropane	91.5	1.28
3-Bromopropene	71.3	1.28
Trichloromethane	61.26	1.28
Propyl alcohol	97.19	1.29
Dimethyldiketone	88.00	1.31
2-Bromobutane	91.3	1.33
1-Chloro-3-methylbutane	98.9	1.34
Ethyl nitrate	88.7	1.37
Octene-2	121–2	1.39
sec.-Butyl alcohol	99.5–100	1.43
Allyl alcohol	96–7	1.45
1,2-Dimethoxyethane	—	1.46

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TABLE III (*continued*)

Name of the compound	*B. p. °C*	*Relative retention ratio*
Methyl isopropyl ketone	93.0	1.50
Trichloroethylene	87.0	1.52
n-Propylacetate	101.6	1.56
Propane nitrile	97.1	1.62
Thiophene	84.12	1.62
1,2-Dichloroethane	83.5	1.63
1-Bromobutane	101.6	1.65
Allyl acetate	103–4	1.76
Ethyl acrylate	99.8	1.78
Methyl methacrylate	100.0	1.78
1-Iodopropane	102.4	1.82
Isopropyl nitrate	102.0	1.83
Nitromethane	101.0	1.84
Cycloheptene	115.0	1.84
Diethyl ketone	102.7	1.85
1-Chloropentane	108.2	1.86
Isobutyronitrile	107–8	1.86
3-Bromopropyne	88–90	1.89
2-Fluoroethanol	103.35	1.89
n-Nonane	150.8	1.93
sec.-Butyl acetate	112–13	1.94
Butyl formate	106.8	2.17
1,2-Dichloropropane	96.8	2.04
1,4-Dioxane	101.5	2.20
Crotonaldehyde	104–5	2.22
2,3-Dichloropropene	94.0	2.30
Isobutyl methyl ketone	119.0	2.32
Trichloroacetaldehyde	98.0	2.32
1,2-Dibromoethylene (*trans*)	108.0	2.52
Butyl ether	142.0	2.53
2-Iodobutane	117.5	2.55
Vinylcyclohexene-1	130.0	2.58
sec.-Isoamyl alcohol	114.0	2.60
Butyl alcohol	117.7	2.62
Propyl propionate	123.4	2.62
Propyl nitrate	110.5	2.63
Nitroethane	114.80	2.71
Di-isopropyl ketone	123.70	2.74
Butane nitrile	118.0	2.90
Tetrachloroethylene	121.02	2.90
1-Bromo-2-chloroethane	107.0	3.10
Paraldehyde	124.4	3.10
Butyl acetate	126.5	3.22
2-Nitropropane	120.0	3.25
2-Propyn-1-ol	114–5	3.31
Ethyl carbonate	125.8	3.43
Chloropicrin	112.0	3.51
3-Butane nitrile	116–9	3.53
Epichlorohydrin	117.0	3.60
n-Decane	174.0	3.70
2-Bromo-1-chloropropane	117.0	3.83
Pyridine	115.3	4.16
1,2-Dibromoethylene (*cis*)	110.0	4.35
Ethylbenzene	136.15	4.36
Isoamyl alcohol	130.5	4.40
p-Xylene	138.35	4.52
1,1,2-Trichloroethane	113.5	4.75

(Continued on p. 230)

TABLE III (*continued*)

Name of the compound	*B. p.* °C	*Relative retention ratio*
m-Xylene	139.1	4.75
Isoamyl acetate	142.5	4.86
n-Amyl alcohol	138.0	4.94
2,4-Pentanedione	139.0	5.68
o-Xylene	144.41	6.11
Amyl acetate	148.0	6.19
Cumene	152.39	6.70
Octyl alcohol	195.0	8.15
Cyclohexanone	156.7	10.77
Bromocyclohexane	163–65	11.79
Decahydronaphthalene	194.6	13.46

TABLE IV

Column condition: 20 g of tri-*m*-tolyl phosphate per 80 g of 30/60 mesh chromosorb.
Total weight of packing material: 22 g (approx.).
Column temperature: 113°.
Flow rate: 56–60 ml/min.
Detector cell temperature: 150°.
Peak characteristics of reference solute (carbon tetrachloride):
Emergence time: 1.70 min.
Peak retention time: 1.90 min.
Peak width: 0.30 min.

Name of the compound	*B. p.* °C	*Relative retention ratio*
n-Pentane	36.2	0.378
Dichlorodifluoromethane (Freon 12)	—28.0	0.387
Dichlorotetrafluoroethane (Freon 114)	3.8	0.387
2,2-Dimethylbutane	49.7	0.387
Propane	—42.17	0.387
Propylene	—47.0	0.387
2-Bromo-2-methylpropane	73.3	0.420
2,3-Dimethylbutane	58.1	0.420
Isopentane	28.0	0.420
2-Methylbutene-2	38.4	0.420
3-Methylpentane	64.0	0.450
4-Methylpentene-2	58.0	0.450
Pentene-2	36.4	0.450
Cyclopentane	49.5	0.485
2,4-Dimethylpentane	80.5	0.485
3-Methylbutene-1	25.0	0.485
tert.-Butyl methyl ether	—	0.515
1-Chloropropene	35.0	0.515
Dimethoxymethane	44.0	0.515
Ethyl ether	34.6	0.515
n-Hexane	69.0	0.515
Hexene-1	63.49	0.515
2-Methylpentane	60.0	0.515
2-Methylpentene-1	61.5	0.515

(Continued on p. 231)

TABLE IV (*continued*)

Name of the compound	*B. p. °C*	*Relative retention ratio*
2-Chloropropane	35.4	0.517
3-Bromopropene	71.3	0.548
Trichlorofluoromethane (Freon 11)	24.1	0.548
Isopropyl ether	67.5	0.550
Bromoethane	38.0	0.580
Ethyl acetate	77.15	0.580
Hexene-2	67.9	0.580
Hexenes (mixed, 2 and 3)	64–67	0.580
Methyl alcohol	64.65	0.580
Methylcyclopentane	71.80	0.580
2,2,4-Trimethylpentane	99.3	0.580
2,3-Dimethylpentane	89.7	0.610
3-Methylhexane	91.85	0.610
tert.-Butyl ethyl ether	68.9	0.615
Ethyl formate	54.3	0.64
Carbon disulfide	46.3	0.645
Cyclohexane	81.4	0.645
1,1-Dimethoxyethane	64.5	0.645
Iodomethane	42.5	0.645
Isopropenylbromide	48.4	0.645
Methyl acetate	57.1	0.645
Propyl isopropyl ether	82–83	0.645
1-Chloropropane	47.2	0.678
n-Heptane	98.4	0.680
2-Bromopropane	59.6	0.710
tert.-Butyl nitrite	63.0	0.710
3-Chloropropene	44.6	0.710
Dimethylhexanes (mixed)	108–16	0.710
2-Iodopropane	89.5	0.710
Ethyl alcohol	78.5	0.740
Propionaldehyde	48.8	0.743
Dichloromethane	40.1	0.745
Heptene-2	98.0	0.750
Acetone	56.5	0.775
tert.-Butyl alcohol	82.8	0.775
1-Chloro-2-methylpropane	68.9	0.775
Ethyl isocyanate	60.0	0.775
Isobutyraldehyde	61.5	0.775
Isopropyl alcohol	82.3	0.775
1-Bromo-1-propene	60.2	0.840
Di-isobutylene	102.6	0.840
Heptene-3	95.8	0.840
Propyl ether	91.0	0.840
2,4,4-Trimethylpentene-1	101.44	0.840
2,4,4-Trimethylpentene-2	101.1	0.840
Vinyl acetate	72.3	0.840
Methylcyclohexane	100.3	0.870
2,2,5-Trimethylhexane	—	0.903
1-Bromopropane	70.9	0.935
Cyclohexene	83.0	0.935
2-Chloro-2-methylbutane	86.0	0.960
1-Chlorobutane	78.0	0.967
Methyl ethyl ketone	79.6	1.00
Isopropyl acetate	89.0	1.00
n-Octane	125.8	1.03
Butyraldehyde	75.7	1.06
1,2-Dichloroethylene (*cis*)	60.1	1.09

(Continued on p. 232)

TABLE IV (*continued*)

Name of the compound	*B. p. °C*	*Relative retention ratio*
Trichloromethane	61.26	1.10
Diethoxymethane	89.0	1.11
Acrylonitrile	78–79	1.13
Benzene	80.1	1.16
Dimethyl diketone	88.0	1.19
Propyl alcohol	97.19	1.193
1-Bromo-2-methylpropane	91.5	1.22
Octene-1	121.3	1.22
2-Bromobutane	91.3	1.225
sec.-Butyl alcohol	99.5–100	1.25
4-Methylcyclohexene	102–103	1.255
1-Chloro-3-methylbutane	98.9	1.29
Octene-2	121–22	1.32
tert.-Amyl alcohol	101.8	1.35
Ethyl nitrate	88.7	1.35
Allyl alcohol	96–97	1.355
2-Fluoroethanol	103.35	1.42
Methyl isopropyl ketone	93.0	1.42
Trichloroethylene	87.0	1.42
n-Nonane	150.79	1.48
1-Bromobutane	101.6	1.485
1,2-Dichloroethane	83.5	1.485
Thiophene	84.12	1.485
Propane nitrile	97.1	1.515
Cycloheptene	115.0	1.55
n-Propyl acetate	101.6	1.55
1-Chloropentane	108.2	1.58
Nitromethane	101.0	1.58
Ethyl acrylate	99.8	1.59
Allyl acetate	103–104	1.61
sec.-Butyl acetate	112–113	1.61
Diethyl ketone	102.7	1.61
1-Icdopropane	102.4	1.61
Butyl formate	106.8	1.67
Isopropyl nitrate	102.0	1.67
Methyl methacrylate	100.0	1.67
3-Bromopropyne	88–90	1.71
1,2-Dichloropropane	96.8	1.74
Isobutyronitrile	107–108	1.77
3-Iodopropene	103.1	1.80
Butyl alcohol	117.7	2.00
1,4-Dioxane	101.5	2.03
Crotonaldehyde	104–105	2.06
Isobutyl methyl ketone	119.0	2.06
Butyl ether	142.0	2.10
Trichloroacetaldehyde	98.0	2.13
4-Vinylcyclohexene-1	130.6	2.13
2,3-Dichloropropene	94.0	2.14
Tetrachloroethylene	121.02	2.21
2-Iodobutane	117.5	2.22
Bromotrichloromethane	104.07	2.32
Butyl acetate	126.50	2.35
1-Bromo-2-chloroethane	107.0	2.42
Ethyl carbonate	125.8	2.45
Butane nitrile	118.0	2.45
Chloropicrin	112.0	2.52
Di-isopropyl ketone	123.7	2.54

(Continued on p. 233)

TABLE IV (*continued*)

Name of the compound	*B. p. °C*	*Relative retention ratio*
Epichlorohydrin	117.0	2.58
2-Propyn-1-ol	114–115	2.58
Nitroethane	114.8	2.605
Propyl propionate	123.4	2.71
3-Butane nitrile	116–119	2.77
Paraldehyde	124.4	2.80
Isoamyl alcohol	130.5	2.97
n-Decane	174.0	3.00
2-Nitropropane	120.0	3.03
2-Bromo-1-chloropropane	117.0	3.06
1,1,2-Trichloroethane	113.5	3.45
Ethyl benzene	136.15	3.48
Isoamyl acetate	142.5	3.48
p-Xylene	138.35	3.74
n-Amyl alcohol	138.0	3.80
Pyridine	115.3	4.05
o-Xylene	144.41	4.35
Amyl acetate	148.0	4.40
2,4-Pentanedione	139.0	4.40
m-Xylene	139.1	4.40
Cumene	152.39	4.90
Butyl nitrite	75.0	6.70
Bromocyclohexane	163–165	7.75
Cyclohexanone	156.7	9.15
1,2,3-Trichloropropane	156.0	10.25

The relative retention times have varied between 0 % and 40 % for different compounds over the temperature differential of 20°. There is no definite pattern for this deviation. Also, in the majority of cases, the relative retention time was lower at a higher temperature. This deviation is quite obvious from the relation between the retention time and the column temperature[3].

$$\ln R_t = \text{const} + \frac{\alpha T_b}{R} \cdot \frac{1}{T} \qquad (1)$$

where R_t = the retention time,

α = a constant characteristic of the solute and the substrate,

T_b = the boiling point,

R = the gas constant,

T = the column temperature.

Each solute and the standard will give rise to one such equation. A plot of the log retention times of a solute at different temperatures against the inverse temperature will be a straight line whose slope will be given by $\alpha\, T_b/R$. Unless the slopes of the $\ln R_t$ *vs.* $1/T$ plots for different compounds are the same, *i.e.*, $\alpha\, T_b/R$ is a constant irrespective of the solute, the ratio of the retention times of different compounds at different temperatures will not be the same. It is realized that log R_t *vs.* $1/T$ or log V_g *vs.* $1/T$ plots for each compound on each column would have been most ideal identification plots. LITTLEWOOD, PHILLIPS AND PRICE[4] have shown that straight lines are obtained for alcohols, esters and aromatics by plotting log V_g against $1/T$;

V_g was named as corrected retention volume per gram by these authors[4] and is expressed as[5]:

$$V_g = \frac{273\ K}{Tc \cdot Pc} = \frac{273\ V°_m}{T_m \cdot w} = \frac{F_m.f.d}{V_c}\ \frac{273}{T_m \cdot w} \qquad (2)$$

where,:

K = $\dfrac{\text{weight of solute per ml of substrate}}{\text{weight of solute per ml of gas}}$

$V°_m$ = the retention volume of the solute measured from air peak at the flow meter temperature T_m

T_m = temperature at the flow meter

w = weight of the substrate in the column

F_m = volumetric flow rate at temperature T_m

f = pressure gradient correction[5]

d = distance on the recorder chart between air peak and the solute peak

V_c = recorder chart speed

Because V_g is directly proportional to R_t, log R_t *vs.* $1/T$ plots will also be straight lines as is indicated by eqn. (1). LITTLEWOOD *et al.*[4] also observed that the slopes of log V_g *vs.* $1/T$ plots of the members of homologous series were the same, but the slopes of such curves due to the solutes belonging to different homologous series may not be the same. There are four possible cases: (1) log R_t *vs.* $1/T$ plot of the solute is parallel to that due to the standard solute, (2) log R_t *vs.* $1/T$ plots diverge with increasing temperature in the range studied, (3) log R_t *vs.* $1/T$ converge with increasing temperature in the range studied, and (4) these plots intersect. In the first case, R_t/R_{ts} = constant at all temperatures (R_{ts} = retention time of the standard). In the second and third cases, this ratio increases and decreases respectively. In the fourth case, the ratio first decreases, becomes one and then increases. Because these plots are straight lines, these deviations will be proportional to the change of temperature. So knowing the value of the R_t/R_{ts} ratio at two different temperatures on the same column, it should be possible to approximately calculate the R_t/R_{ts} ratio at intermediate column temperatures. In this connection, the statement by HIVELY[6] that "under very different conditions, the variation was only 5%" is somewhat misleading. The variation of retention time with the temperature is theoretically expected and is experimentally observed[5].

Such observations are consistent with those made in the present study of nearly two hundred compounds. However, as has been pointed out earlier, knowing the R_t/R_{ts} ratio at two temperatures, it should be possible to calculate the ratio at an intermediate temperature. The present data should be useful for those using the indicated columns operating in the temperature range shown in the tables.

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SUMMARY

The relative retention times of organic compounds on tri-*m*-tolyl phosphate and β,β'-oxydipropionitrile columns have been determined and tabulated. The method for the use of these tables has been suggested. Through the use of the two columns with subsequent reference to the data on the respective retention times, a wide variety of compounds can be tentatively identified.

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