

Application of gas chromatographic retention properties to the identification of environmental contaminants

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ABSTRACT

Gas chromatographic retention indices (I) were measured for congeners of commonly encountered classes of environmental contaminants, which are often reported as tentatively identified compounds. Several commonly encountered polycyclic aromatic hydrocarbons were employed as I reference standards. These indices were related to boiling points with reasonable accuracy, allowing the estimation of I for additional members of those classes.

INTRODUCTION

Gas chromatography (GC) has long been applied to environmental analysis for both separation and identification of target analytes. High-resolution capillary columns have greatly increased the separation power, while selective detectors have improved the identification power of GC. In addition to selective detectors such as electron-capture, nitrogen-phosphorus and Hall's electrolytic conductivity detectors, both mass spectrometers and Fourier-transform infrared spectrometers have been widely employed for identification of compounds separated by GC.

The US Environmental Protection Agency (EPA) has monitored pesticides in the environment for many years using GC with selective detectors [1]. Confirmation may be performed by a second analysis using a GC column having different polarity from that of the first. The relative retention times of

analytes on the two columns are then compared against a data base for identification. As another example of the multiple-column confirmation technique, Albro *et al.* [2] analyzed polychlorinated biphenyl commercial mixtures on 13 GC column liquid phases and calculated retention index (I) values to assist in compound identification.

It is often easier to apply the power of gas chromatographic relative retention times for the identification of large numbers of compounds when multiple reference compounds are used; I values are calculated against those reference standards. Temperature programming is generally the technique of choice due to the wide variety of structures and retention properties of target environmental contaminants.

Van den Dool and Kratz [3] described a temperature-programmed I scheme using the normal hydrocarbons. This approach permitted successful I modelling of the 1700 brominated, chlorinated, and bromochlorinated dioxins [4], and of the chlorinated dibenzofurans [5]. In these studies, the mass spectra of different isomers with the same level of chlorina-

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tion/bromination were indistinguishable. Hence, mass spectrometry provided insufficient data for isomer-specific identifications. The gas chromatographic *I* data were essential to obtain isomer specificity.

Vassilaros *et al.* [6] have reported a similar scheme using several polynuclear aromatic hydrocarbons (PAHs). Their *I* scheme possesses advantages for many types of environmental analyses, because the reference compounds may be indigenous to the samples. Archived data may be studied, and tentative compound identification can be made. Furthermore, the chromatographic behavior against temperature and temperature programming rates of the PAH reference compounds may more closely parallel the behavior of other compounds of interest. The Lee and Kováts indices have been employed for certain members of other compound classes having environmental significance, including phenols, alcohols, ketones, nitriles and esters [7].

GC–MS has emerged as an extremely important routine technology for environmental analysis and confirmation. The EPA conducts thousands of analyses each year by GC–MS for compounds of environmental interest, generally using a combination of user-generated mass spectral libraries and a commercial data base of mass spectra. Many of these analyses are performed under the Contract Laboratory Program (CLP), under rigorous, prescribed conditions [8]. Components of environmental extracts that are not identified by the computerized mass spectral library search are labeled “tentatively identified compounds” (TICs). When subjected to manual mass spectral interpretation, many of these TICs turn out to be aliphatic hydrocarbons or other compounds of minor toxicological or ecological interest. Some retention time windows, however, are believed to include the retention times of compounds having more serious implications for the environment.

It was decided to tabulate the *I* of several classes of compounds having environmental significance, against the PAH reference compounds indigenous to many environmental samples. These tabulated *I* values could then be used along with the mass spectral libraries for identification of TICs found while analyzing samples, and while reviewing data packages from previous analyses.

EXPERIMENTAL

Retention indices were determined on a Hewlett-Packard 5988 gas chromatograph–mass spectrometer, with 200°C injector temperature, and auto-sampler-controlled 2- μ l injections. The mass spectrometer was operated in full-scan, electron ionization mode (70 eV). A J&W Scientific DB-5 30 m \times 0.32 mm fused-silica capillary column with 0.25- μ m film thickness was temperature programmed as follows: 3 min at 40°C, 8°C/min to 285°C, hold for 29.5 min. Helium carrier gas was used at 2.5 ml/min. Data presented in Table VIII were obtained with a 30 m \times 0.25 mm DB-5 column with 0.25- μ m film thickness, under the above conditions. Retention indices were calculated according to the method reported by Rostad and Pereira [7]. Solutions of commercially available standards were prepared in methylene chloride at 100 ng/ μ l. Retention index values were determined using high-purity analytical standards purchased from commercial suppliers. The following classes of target analytes were studied: carboxylic acids, 1-*n*-alkenes, esters, alkyl phenols, aldehydes, *n*-alkylbenzenes and cyclic alkenes. Duplicate determinations were made on three separate days.

RESULTS AND DISCUSSION

From the experimental retention time measurements, the average *I* were calculated for each analyte (see Tables I–VIII). In most cases, the R.S.D. for individual measurements of *I* did not exceed 0.1%. Indices were determined relative to naphthalene, phenanthrene, chrysene, and benzo[ghi]perylene.

The calculations of *I* were performed according to the procedure described by Rostad and Pereira [7] which was based on the equation suggested by Van den Dool and Kratz [3]. For index (I_x) of a compound X:

$$I_x = 100 \left[\frac{T_x - T_n}{T_{n+1} - T_n} \right] + 100n$$

where T_x is the retention time of compound X; T_n and T_{n+1} are the retention times of the PAHs used as reference compounds; *n* is the largest ring number of the reference compounds eluting before compound X; and *n* + 1 is the smallest number of fused

TABLE I
ALKYL-SUBSTITUTED PHENOLS

Compound	B.p. [9]	Calc. b.p.	Calc. <i>I</i>	Exptl. <i>I</i>	%Diff.
2-Methylphenol ^a	191		164.42	170.89	3.79
4-Methylphenol ^a	201.9		177.79	175.32	-1.41
3-Methylphenol ^a	202.2		178.16	175.41	0.56
2,6-Dimethylphenol ^a	212		190.18	182.78	-4.05
2-Ethylphenol ^a	207		184.04	188.28	2.25
2,4-Dimethylphenol ^a	210		187.72	190.86	1.65
2,5-Dimethylphenol ^a	211.5		189.56	190.94	0.72
4-Ethylphenol ^a	219		198.76	194.51	-2.19
3-Ethylphenol ^a	214		192.63	194.63	1.03
2,3-Dimethylphenol ^a	218		197.53	196.83	-0.46
3,4-Dimethylphenol ^a	225		206.12	199.63	-3.25
2,4,6-Trimethylphenol ^a	221		201.21	202.51	0.64
2- <i>n</i> -Propylphenol ^a	220		199.99	204.88	2.39
3-Propylphenol	228		209.80		
2,3,5-Trimethylphenol ^a	230		212.25	214.69	1.14
2,4,5-Trimethylphenol	232		214.70		
4-Propylphenol	232.6		215.44		
2- <i>n</i> -Butylphenol	236		219.61		
2,3,5,6-Tetramethylphenol ^a	247		233.10	231.28	-0.79
3- <i>n</i> -Butylphenol	248		234.32		
4- <i>n</i> -Butylphenol	248		234.32		

^a Data used for derivation of the *I* relationship yields the following equation: $\text{b.p.} = 0.815I + 56.93$; $R^2 = 0.935$.

TABLE II
n-ALKYLCARBOXYLIC ACIDS

Compound	B.p. ^b	Calc. b.p.	Calc. <i>I</i>	Exptl. <i>I</i>	%Diff.
Acetic acid	117		57.68		
Propionic acid	141		84.70		
Butanoic acid	165.5		112.28		
Pentanoic acid ^a	186		135.37	137.02	1.20
Hexanoic acid ^a	205		156.76	158.12	0.86
Heptanoic acid ^a	223		177.03	177.85	0.46
Octanoic acid ^a	239.3		195.38	196.58	0.61
Nonanoic acid ^a	268 [10]		227.69	214.27	-6.26
Decanoic acid ^a	270		229.94	231.58	0.71
Undecanoic acid ^a	280		241.20	247.95	2.72
Dodecanoic acid	131 ¹	299.58		263.25	
Tridecanoic acid	236 ¹⁰⁰	312.30		277.57	
Tetradecanoic acid	250.5 ¹⁰⁰	324.89		291.75	
Pentadecanoic acid	257 ¹⁰⁰	337.82		306.30	
Hexadecanoic acid	350, 227 ¹⁰⁰	351.89	320.02	322.15	0.66
Heptadecanoic acid	227 ¹⁰⁰	365.03		336.97	
Octadecanoic acid	360d	377.45		350.93	
Eicosanoic acid	328d	401.36		377.85	

^a Data used for derivation of the *I* relationship yields the following equation: $\text{b.p.} = 0.888I + 65.78$; $R^2 = 0.976$.

^b Ref. 9, except as noted in brackets. Superscripted numbers indicate reduced pressure boiling points, mmHg (1 mmHg = 133.322 Pa). Decomposition upon boiling is noted with d.

TABLE III
n-ALKYL ESTERS

Compound	B.p. ^b	Calc. b.p.	Calc. <i>I</i>	Exptl. <i>I</i>	%Diff.
Ethyl acetate	77.06		78.71		
Methyl butyrate	102.3		101.58		
Ethyl butyrate	124		121.23		
Propyl butyrate ^a	143		138.44	135.60	-2.09
Methyl hexanoate ^a	151 [10]		145.69	141.95	-2.64
Butyl butyrate	166.6		159.82		
Ethyl hexanoate ^a	168 [10]		161.09	159.04	-1.29
Methyl heptanoate ^a	172		164.71	164.64	-0.04
Butyl acetate	186		177.39		
Ethyl heptanoate	188 [10]		179.20		
Methyl octanoate ^a	194 [10]		184.64	185.69	0.57
Ethyl octanoate ^a	207 [10]		196.41	200.00	1.80
Methyl nonanoate ^a	213 [10]		201.85	205.26	1.66
Hexyl acetate	223		210.91		
Butyl heptanoate	226.2		213.80		
Octyl butyrate	244.1		230.02		
Ethyl decanoate ^a	245 [10]		230.83	235.83	2.12
Methyl dodecanoate ^a	262 ⁷⁶⁶ [10]	273.8	246.23	256.91	4.16
Decyl acetate	270		253.48		
Ethyl dodecanoate		285.6		267.59	
Octyl heptanoate	290		271.59		
Methyl tetradecanoate ^a	323 [10]		301.49	286.83	-5.11

^a Data used for derivation of the *I* relationship yields the following equation: b.p. = 1.104*I* - 9.838; *R*² = 0.982.

^b Ref. 9, except as noted in brackets. Superscripted numbers indicate reduced pressure boiling points, mmHg.

TABLE IV
n-ALKYL-SUBSTITUTED BENZENES

Compound	B.p. ^b	Calc. b.p.	Calc. <i>I</i>	Exptl. <i>I</i>	%Diff.
Benzene	80.1		73.25		
Toluene	110.6		102.53		
Ethylbenzene	136		126.92		
Propylbenzene ^a	159.2	159.3	149.20	149.31	0.07
Butylbenzene	183		172.06		
Pentylbenzene	205.4		193.57		
Hexylbenzene	226 [11]	225.7	213.43	213.07	-0.17
Heptylbenzene ^a	245.5	245.0	232.07	231.69	-0.16
Octylbenzene	262 [11]	263.3	248.01	249.13	0.45
Nonylbenzene ^a	280.1	280.3	265.30	265.56	0.10
Decylbenzene	298 [11]	296.4	282.59	280.92	-0.60

^a Data used for derivation of the *I* relationship yields the following equation: b.p. = 1.041*I* + 3.821; *R*² = 1.00.

^b Ref. 9, except as noted in brackets.

TABLE V
CYCLIC ALKENES

Compound	B.p. ^b	Calc. b.p.	Calc. <i>I</i>	Exptl. <i>I</i>	%Diff.
Cyclohexene	83		77.06		
4-Methylcyclohexene ^a	102.7		95.91	95.57	-0.36
3-Methylcyclohexene	104		97.16		
1-Methylcyclohexene	110		102.90		
1,3,5-Cycloheptatriene ^a	116 [10]		108.64	108.93	0.27
4-Vinylcyclohexene ^a	128.9		120.98	120.10	-0.73
1,5-Cyclooctadiene ^a	150.8 ⁷⁵⁷	153.37	141.94	144.40	1.70
<i>d</i> -Limonene ^a	178		167.97	166.62	-0.81

^a Data used for derivation of the *I* relationship yields the following equation: $\text{b.p.} = 1.045I + 2.472$; $R^2 = 0.957$.

^b Ref. 9, except as noted in brackets. Superscripted numbers indicate reduced pressure boiling points, mmHg.

TABLE VI
PRIMARY ALKENES

Compound	B.p. [9]	Calc. b.p.	Calc. <i>I</i>	Exptl. <i>I</i>	%Diff.
Hexene	63.3		53.98		
Heptene	93.6		83.28		
Octene	121.3		110.08		
Nonene	146		133.97		
Decene ^a	170.5		157.66	157.55	-0.07
Dodecene ^a	213.4		199.16	199.34	0.09
Pentadecene	268		251.87		
Hexadecene ^a	284.4		267.83	267.76	-0.03

^a Data used for derivation of the *I* relationship yields the following equation: $\text{b.p.} = 0.951I + 17.18$; $R^2 = 0.998$.

TABLE VII
ALDEHYDES

Compound	B.p. ^b	Calc. b.p.	Calc. <i>I</i>	Exptl. <i>I</i>	%Diff.
Butanal	76 [12]		35.78		
Pentanal	103 [12]		72.21		
Hexanal ^a	128	133.0	105.97	112.67	5.95
Heptanal ^a	152.8	151.0	139.44	137.01	-1.77
Octanal ^a	171	168.6	164.01	160.75	-2.03
Nonanal ^a	191	184.8	191.00	182.61	-4.59
Decanal ^a	208	213.5	213.95	221.34	3.34
Undecanal	117 ¹⁸	226.6		239.08	
Tridecanal	156 ¹³	254.7		277.01	
Tetradecanal	166 ²⁴	255.8		278.43	

^a Data used for derivation of the *I* relationship yields the following equation: $\text{b.p.} = 0.741I + 49.49$; $R^2 = 0.974$.

^b Ref. 9, except as noted in brackets. Superscripted numbers indicate reduced pressure boiling points, mmHg.

TABLE VIII

RETENTION INDICES FOR SOME ENVIRONMENTAL MONITORING TARGET ANALYTES

Compound	Average <i>I</i>	Compound	Average <i>I</i>
[² H ₄]1,4-Dichlorobenzene	161.50	2,6-Dinitrotoluene	250.02
2-Fluorophenol	128.01	3-Nitroaniline	254.17
[² H ₆]Phenol	154.35	Acenaphthene	254.81
Phenol	154.73	2,4-Dinitrophenol	257.01
Bis(2-chloroethyl)ether	156.16	4-Nitrophenol	260.36
2-Chlorophenol	156.75	Dibenzofuran	259.69
1,3-Dichlorobenzene	160.41	2,4-Dinitrotoluene	261.83
1,4-Dichlorobenzene	162.02	Diethylphthalate	269.94
Benzyl alcohol	167.16	4-Chlorophenyl phenyl ether	270.89
1,2-Dichlorobenzene	167.36	Fluorene	270.45
2-Methylphenol	171.29	4-Nitroaniline	273.55
Bis(2-chloroisopropyl)ether	171.64	[² H ₁₀]Phenanthrene	299.25
4-Methylphenol	175.76	4,6-Dinitro-2-methylphenol	274.09
N-Nitroso-di- <i>n</i> -propylamine	176.04	N-Nitrosodiphenylamine	274.93
Hexachloroethane	176.00	2,4,6-Tribromophenol	278.46
[² H ₈]Naphthalene	199.33	4-Bromophenyl phenyl ether	285.82
[² H ₅]Nitrobenzene	178.88	Hexachlorobenzene	289.85
Nitrobenzene	179.46	Pentachlorophenol	295.77
Isophorone	186.60	Phenanthrene	300.00
2-Nitrophenol	188.87	Anthracene	301.64
2,4-Dimethylphenol	191.20	Di- <i>n</i> -butylphthalate	324.02
Benzoic acid	196.52	Fluoranthene	344.75
Bis(2-chloroethoxy)methane	193.99	[² H ₁₂]Chrysene	398.90
2,4-Dichlorophenol	196.26	Pyrene	351.40
1,2,4-Trichlorobenzene	198.23	[² H ₁₄]Terphenyl	358.16
Naphthalene	200.00	Butylbenzylphthalate	378.40
4-Chloroaniline	202.75	3,3'-Dichlorobenzidine	395.28
Hexachlorobutadiene	205.81	Benz[<i>a</i>]anthracene	398.07
4-Chloro-3-methylphenol	218.50	Chrysene	400.00
2-Methylnaphthalene	221.13	Bis(2-ethylhexyl)phthalate	402.21
[² H ₁₀]Acenaphthene	253.79	[² H ₁₂]Perylene	442.31
Hexachlorocyclopentadiene	228.14	Di- <i>n</i> -octylphthalate	420.38
2,4,6-Trichlorophenol	231.04	Benzo[<i>b</i>]fluoranthene	430.03
2,4,5-Trichlorophenol	231.91	Benzo[<i>k</i>]fluoranthene	430.83
2-Chloronaphthalene	236.02	Benzo[<i>a</i>]pyrene	440.32
2-Fluorobiphenyl	233.54	Indeno[1,2,3- <i>cd</i>]pyrene	488.94
2-Nitroaniline	241.07	Dibenz[<i>a,h</i>]anthracene	488.15
Dimethylphthalate	247.99	Benzo[<i>ghi</i>]perylene	500.00
Acenaphthylene	248.87		

rings in the reference compounds eluting after compound X.

The tabulated *I* values often make it possible to identify environmental contaminants that cannot be readily determined by the mass spectra alone. Since the reference PAH are present in many environmental samples, it is possible to calculate *I* values for the TICs reported in those analytical data packages. Tentative identifications of those TICs can then be

made based upon both the mass spectra and the *I*. It may also be possible to use *I* windows to identify which TICs may be compounds of particular significance because they elute in specific *I* windows.

This study demonstrated a practical application for calculation of *I* from boiling points, when non-polar or very slightly polar GC columns are used for the analysis. Using the general equation $y = mx + b$, boiling points (*y*) could be related to *I*

values (x) multiplied by a factor (m), with a constant value (b) added. This simple relationship provided satisfactory approximations (see Tables I–VIII) for the I of suspected TICs that did not have readily available standards for verification of the structural assignments. Most cases of the calculated and experimental values differed by less than 3%, demonstrating the utility of this technique for calculating I of these classes of compounds. The percent differences (%Diff.) were calculated as follows: %Diff. = $[(\text{experimental } I - \text{calculated } I) / \text{experimental } I] \times 100$.

Two potential limitations of the technique are (1) the need for a number of compounds having similar structures in order to establish values for m and b in the equation $y = mx + b$, and (2) the equation may be too simple to adequately describe some compound classes, or those with multiple functional groups.

Once the relationship between I and boiling point has been determined, it is possible to predict the I for other members of the same compound class. It is then possible to identify additional I windows that may or may not be likely to contain TICs from these classes of compounds. Investigations and data reporting could then focus on I windows occupied by compound classes of interest, or on different I windows that do not contain commonly encountered classes of little interest.

Experimental I values were determined for 71 environmental target compounds (see Table VIII). Reproducibility was good for these target compounds, with R.S.D.s less than 1.8% for the analytes (except benzoic acid, 2.4%) and for the six deuterated internal standards.

CONCLUSIONS

To assist in the identification of tentatively identified compounds found during environmental monitoring analyses, retention time characteristics were expressed as retention indices relative to commonly encountered polynuclear aromatic hydrocarbons. For a relatively non-polar GC column, these indices

could be related to boiling points with reasonable accuracy for various members of the chemical classes (or homologous series) tested. This relationship allows for predicting the I of other members of those classes, which may not be readily available as analytical standards.

NOTICE

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