Kovats Indices for C_2-C_9 Hydrocarbons with Alumina PLOT Capillary Columns

by Randall Bramston-Cook, Lotus Consulting

Alumina Porous Layer Open Tubular (PLOT) capillary columns generate full separations of the C_2-C_5 hydrocarbons, significantly better than columns employed for the full range of hydrocarbons, especially for sorting out alkenes and alkynes from their related alkanes. However, they cannot perform the whole range of hydrocarbons found in vehicle exhaust and ambient air, as their maximum temperature of 200 ^oC limits proper elution of the heavier hydrocarbons (above Octane), and they are readily degraded by moisture from injected samples. These columns are usually configured in special arrangements with stripper columns to prevent water and heavy compounds from reaching them.[1,2]

Alumina is deactivated with either KCl or Na_2SO_4. KCl was the first reagent used when the column was introduced in the early 1990s and is commonly written into protocols established during this era. Both columns are very susceptible to dramatic changes in its chromatography as it ages and cannot be fully regenerated to its original performance, notably with the retention time shift of Ethyne. New Alumina-KCl columns can exhibit retention of Ethyne just after Butane, whereas older columns will show Ethyne shifting progressively earlier through Butane and almost to Methylpropane. The Na_2SO_4 version places Ethyne well separated from other analytes. The light olefins - notably Ethene and Ethyne - have some of the greatest variations in elution times of all of the hydrocarbons due to this degradation in column performance. The MAPD version is intended to increase column stability for analyzing reactive compounds, including Propyne and Allene (Propadiene).

Relative retention indices, commonly called Kovats Indices[3], help to assign labels to eluting peaks in samples of ambient air and vehicle exhaust samples, based on elution relative to nearby n-Alkanes. Since most chromatograms for a wide range of hydrocarbons are generated with temperature programmed conditions, the Kovats Index (*KI*) simplifies to:

$$KI_{unknown} = \left[\frac{t_{\mathrm{r(unknown)}} - t_{r(n)}}{t_{r(N)} - t_{r(n)}}\right] * [100 * (N - n)] + (100 * n)$$

where n = number of carbon atoms in the smaller n-alkane, N = number of carbon atoms in the larger n-alkane, and t_r = retention time of associated compounds.

This compilation of Kovats Indices is generated from 10 gas chromatographs, 16 different chromatograms from related columns, and dissimilar temperature programs. Remarkably, Kovats Indices remain quite consistent. Peak identifications are made from known standard gas mixtures and from mass spectral interpretations.

---

1 Air Resources Board, *California Non-Methane Organic Gas Test Procedures*, Part D, Method 1002, www.arb.ca.gov/testmeth/vol2/tp201_2h.pdf, 2002.

2 Air Resources Board SOP No. MLD 032, *Standard Operating Procedure for the Determination of Non-Methane Organic Compounds in Ambient Air by Gas Chromatography Using Dual Capillary Columns and Flame Ionization Detection*, www.arb.ca.gov/aaqm/sop/sop032.pdf, 2002.

3 Kovats, E. (1958). "Gas-chromatographische Charakterisierung organischer Verbindungen. Teil 1: Retentionsindices aliphatischer Halogenide, Alkohole, Aldehyde und Ketone". *Helv. Chim. Acta* **41**: 1915–32.; and *Nomenclature of Organic Chemistry* (3 ed.). London: Butterworths. 1971 (3rd edition combined) [1958 (A: Hydrocarbons, and B: Fundamental Heterocyclic Systems), 1965 (C: Characteristic Groups)]. And en.wikipedia.org/wiki/Kovats_retention_index.

Alumina PLOT - KCl

	Common Name	IUPAC Name	Average Kovats Index	Standard Deviation	Number of Chromatogram Sources
1		**ETHANE**	200	=0	10
2	Ethylene	Ethene	239	±8	10
3		**PROPANE**	300	=0	10
4		Cyclopropane	351	-	1
5	Propylene	Propene	360	±6	10
6	Isobutane	Methylpropane	389	±2	10
7	Acetylene	Ethyne	393	±2	4
8		**BUTANE**	400	=0	10
9	Propadiene	Allene	403	±1	4
10		trans-But-2-ene	453	±3	10
11		But-1-ene	455	±3	10
12	Isobutylene	Methylpropene	466	±2	4
13		cis-But-2-ene	472	±4	10
14	2,2-Dimethylpropane	Neopentane	473	-	1
15		Cyclopentane	487	±2	10
16	Isopentane	Methylbutane	490	±1	10
17		Buta-1,2-diene	497	-	1
18		**PENTANE**	500	=0	10
19	Methylacetylene	Propyne	504	±1	3
20		Buta-1,3-diene	519	±11	4
21		3-Methylbut-1-ene	533	±2	3
22		Cyclopentene	534	±2	3
23		trans-Pent-2-ene	540	±2	10
24		Methylbut-2-ene	549	±3	4
25		Pent-1-ene	550	±2	10
26		2-Methylbut-1-ene	555	±2	4
27		cis-Pent-2-ene	560	±3	10
28		But-1-ene-3-yne	570	-	1
29		But-1-yne	573	-	2
30		Methylcyclopentane	577	±3	9
31		2,2-Dimethylbutane	577	±2	10
32		But-2-yne	578	±3	4
33		Cyclohexane	582	±3	10
34		2,3-Dimethylbutane	586	±2	10
35		2-Methylpentane	588	±2	10
36		3-Methylpentane	590	±2	10
37		**HEXANE**	600	=0	10
38	Isoprene	Methylbuta-1,3,-diene	608	±4	7
39		Cyclopenta-1,3-diene	615	-	2
40		cis-1,3-Dimethylcyclopentane	624	-	2
41		trans-1,3-Dimethylcyclopentane	627	-	2
42		2-Methylpent-2-ene	629	-	2
43		2-Methylpent-1-ene	630	±2	8
44		4-Methylpent-1-ene	633	-	2
45		3-Methylpent-1-ene	636	-	2
46		trans-Hex-2-ene	641	-	2
47		cis-Hex-2-ene	646	-	2
48		Methylcyclopentene	647	±2	3
49		2,4-Dimethylpentane	671	±1	9

50		Methylcyclohexane	675	±3	9
51		2,2,3-Trimethylbutane	678	±0.5	3
52		2,3-Dimethylpentane	683	±1	9
53		2-Methylhexane	686	±1	9
54		3-Methylhexane	687	±1	9
55		**HEPTANE**	700	=0	9
56		1-Methylcyclohex-1-ene	713	-	2
57		Benzene	726	±6	8
58		2,2,4-Trimethylpentane	758	±2	5
59		2,2-Dimethylhexane	762	±4	7
60		4-Methylheptane	774	±2	3
61		2-Methylheptane	775	±3	9
62		3-Methylheptane	782	±2	9
63		2,3,4-Trimethylpentane	785	±2	9
64		**OCTANE**	800	=0	9
65	Methylbenzene	Toluene	851	±4	5
66		**NONANE**	900	=0	9

Notes:

1. Listed compound names follow IUPAC protocol (see: en.wikipedia.org/wiki/ IUPAC_nomenclature). For example: Isobutane or 2-Methylpropane is simply Methylpropane, as the methyl group can only be substituted in the second position with propane.
2. Suggested column conditions - Column: Varian CP-Al_2O_3/KCl, 50 meters, 0.32 mm ID, 10 micron film thickness; temperature program: 0 ^oC, hold for 0.60 minutes, 6 ^oC/minute to 50 ^oC, 3 ^oC/min to 200 ^oC, hold for 4.07 minutes; column flow: 2.0 ml/minute.

Alumina PLOT - MAPD

	Common Name	IUPAC Name	Average Kovats Index	Standard Deviation	Number of Chromatogram Sources
1		**METHANE**	100	=0	1
2		**ETHANE**	200	=0	1
3	Ethylene	Ethene	242	-	1
4		**PROPANE**	300	-	1
5	Propylene	Propene	368	-	1
6	Isobutane	Methylpropane	391	-	1
7		**BUTANE**	400	=0	1
8	Propadiene	Allene	408	-	1
9	Acetylene	Ethyne	414	-	1
10		trans-But-2-ene	457	-	1
11		But-1-ene	464	-	1
12	Isobutylene	Methylpropene	474	-	1
13		cis-But-2-ene	481	-	1
14	Isopentane	Methylbutane	490	-	1
15		**PENTANE**	500	=0	1
16		Buta-1,3-ene	525	-	1
17		trans-Pent-2-ene	539	-	1
18		Pent-1-ene	551	-	1
19		cis-Pent-2-ene	561	-	1
20		**HEXANE**	600	=0	1

Notes:

1. Suggested column conditions - Column: Varian CP-Alumina/MAPD, 50 meters, 0.53 mm ID; temperature program: 30 ^oC, hold for 5 minutes, 20 ^oC/minute to 200^oC; column flow: 5.0 ml/minute.

Alumina PLOT - Na_2SO_4

	Common Name	IUPAC Name	Average Kovats Index	Standard Deviation	Number of Chromatogram Sources
1		**ETHANE**	200	=0	5
2	Ethylene	Ethene	259	13	5
3		**PROPANE**	300	=0	5
4		Cyclopropane	376	-	1
5	Propylene	Propene	378	±6	5
6	Isobutane	Methylpropane	391	±2	5
7		**BUTANE**	400	=0	5
8	Acetylene	Ethyne	425	±8	5
9		trans-But-2-ene	457	±4	5
10		But-1-ene	463	±4	5
11	Isobutylene	Methylpropene	471	±5	2
12		cis-But-2-ene	477	±4	5
13		Cyclopentane	484	-	1
14	Isopentane	Methylbutane	490	-	1
15		**PENTANE**	500	=0	1
16		Buta-1,2-diene	504	-	1
17		Buta-1,3-diene	527	±4	3
18	Methylacetylene	Propyne	529	-	1
19		Cyclopentene	535	-	1
20		3-Methylbut-1-ene	536	-	1
21		trans-Pent-2-ene	539	-	1
22		Methylbut-2-ene	547	-	1
23		Pent-1-ene	552	-	1
24		2-Methylbut-1-ene	555	-	1
25		cis-Pent-2-ene	560	-	1
26		But-2-yne	574	-	1
27		But-1-ene-3-yne	569	-	1
28		But-1-yne	583	-	1
29		2-Methylpentane	585	-	1
30		3-Methylpentane	587	-	1
31		**HEXANE**	600	=0	1
32	Isoprene	Methylbuta-1,3,-diene	621	-	1

Notes:

1. Listed compound names follow IUPAC protocol (see: en.wikipedia.org/wiki/ IUPAC_nomenclature). For example: Isobutane or 2-Methylpropane is simply Methylpropane, as the methyl group can only be substituted in the second position with propane.
2. Suggested column conditions - Column: Varian CP-Al_2O_3/Na_2SO_4, 50 meters, 0.32 mm ID, 5 micron film thickness; temperature program: -30 ^oC, hold for 1.1 minutes, 5 ^oC/minute to 70 ^oC, 10 ^oC/min to 200 ^oC, hold for 3.90 minutes; column flow: 2.0 ml/minute.

Lotus Consulting
310/569-0128 Fax 714/898-7461
email ebramstoncook@msn.com

5781 Campo Walk
Long Beach, California 90803