Using Kovats Indices
to Identify Hydrocarbon Peaks in a Chromatogram

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Determining the identity of a hydrocarbon peak in a chromatogram of vehicle exhaust or ambient air is a difficult task, as the detector of choice - flame ionization detector - cannot provide any indication of the analyte's structure. Mass spectrometry can help, but many hydrocarbons have similar spectra, and this detector does not yield even responses across the range of hydrocarbons anticipated, necessitating a calibration standard for each compound.

Kovats Indices were developed to provide a listing of the expected elution of hydrocarbons based on their relative retention to the n-Alkanes. The formula for temperature programmed chromatograms is:

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

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. For example, Ethene has an index of 251.1, which places it just over midway between Ethane and Propane. Remarkably, this computation for similar column phases is nearly independent of column parameters (such as length and diameter), flow rate and column temperature programming.

If retention times are measured for known peaks, their Kovats Indices are computed in Microsoft Excel by the following formulae:

Analyte	Retention Time	Kovats Index Formula	Calculated Kovats Index
Ethane	3.582	=200	200.0
Ethene	7.482	=(B3-B$2)/(B$4-B$2)*(C$4-C$2)+C$2	251.1
Propane	11.216	=300	300.0
Propene	15.071	=(B5-B$4)/(B$8-B$4)*(C$8-C$4)+C$4	370.4
Methylpropane	16.256	=(B6-B$4)/(B$8-B$4)*(C$8-C$4)+C$4	392.0
Ethyne	16.470	=(B7-B$4)/(B$8-B$4)*(C$8-C$4)+C$4	395.9
Butane	16.693	=400	400.0

In the converse calculation, if the Kovats Index is known from a tabulated series[1,2], the expected retention time can be estimated from the formula:

Known Kovats Index	Expected Retention Time	Calculated Retention Time		n-Alkane	Retention Time	Kovats Index
370.4	=(A2-F3)*(E4-E3)/(F4-F3)+E3	15.072		Ethane	3.582	200
				Propane	11.216	300
				Butane	16.693	400

For illustration purposes, only a few n-Alkanes are shown here, but the same process can be applied to others.

[1] Bramston-Cook, Randall, "Kovats Indices for C_2-C_9 Hydrocarbons with Alumina PLOT Capillary Columns", Lotus Consulting, 2010.

[2] Bramston-Cook, Randall, "Kovats Indices for C_2-C_{13} Hydrocarbons and Selected Oxygenates/Halocarbons with 100% Dimethylpolysiloxane Columns", Lotus Consulting, 2010.

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