Enthalpy of Solution and Kováts Retention Indices for Nitroaromatic Compounds on Stationary Phases Using Gas Chromatography

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Worldwide terrorism has recently resulted in increased efforts to detect and identify explosive residues. Availability of experimentally determined thermochemical data for explosive compounds and their degradation products is limited, however. Gas chromatography was used to determine the enthalpy of solution, $\Delta_{\text{sol}}H$, for a series of nitroaromatic explosives and explosive degradation products including nitrobenzene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 1,2-dinitrobenzene, 1,3-dinitrobenzene, 1,4-dinitrobenzene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 3,4-dinitrotoluene, 3,5-dinitrotoluene, 1,3,5-trinitrobenzene, and 2,4,6-trinitrotoluene. Four polar stationary phases (by mass composition), namely, 80 % dimethyl + 20 % diphenyl polysiloxane, 14 % cyanopropylphenyl + 86 % dimethyl polysiloxane, 50 % phenyl + 50 % methyl polysiloxane, and 100 % polyethylene glycol, were evaluated with the 13 nitroaromatic compounds. Isothermal Kováts retention indices are also reported for the nitroaromatics as well as the $\Delta_{\text{sol}}H$ of several *n*-alkanes. Enthalpies reported herein were computed over a wide temperature range, thus net retention volumes are also tabulated to facilitate the specific needs of interested readers.

Introduction

Terrorist attacks worldwide have increased national and international efforts to stem the violence. These efforts have amplified the need for robust and sensitive detection of highly energetic materials. A wide variety of analytical techniques have been used for the detection of such materials and have been compiled in recent review articles.[1−5] To date, however, no single technology has been able to meet the extensive list of requirements for the rapid and reliable detection of explosives. Perhaps the most challenging facet of this field lies in the difficulty of detecting explosives from the vapor phase at ambient conditions. Many common explosives, such as 2,4,6-trinitrotoluene (TNT), exhibit vapor pressures on the order of 0.1 Pa at room temperature; however, many explosives have vapor pressures orders of magnitude lower than that of TNT.[1] With such low vapor pressures and current limitations in the detection limits of many analytical techniques, vapor phase detection will typically require either large sample volumes or a preconcentration step before analysis.[1]

While the vapor pressure of many explosives has been determined (at least at higher temperatures), we must understand that vapor pressure is a pure component property and has no meaning when one discusses mixtures of components. Often, the relevant property is then the volatility, as expressed by the vapor−liquid equilibrium. Another situation that commonly arises is that of a substance deposited or presented on a surface, where the surface energetics plays a significant role. It is therefore unlikely that the vapor pressure alone will be a representative indicator of the material's behavior outside of a controlled laboratory. An understanding of the interactions of these energetic materials as they adsorb on surfaces and absorb into solvating materials would be extremely useful. A fundamental thermodynamic parameter describing adsorption and absorption phenomena is the enthalpy of interaction, $\Delta_{\text{int}}H$. The specific process for adsorption and absorption can be represented by the enthalpy of adsorption, $\Delta_{\text{ads}}H$, and the enthalpy of solution, $\Delta_{\text{sol}}H$, respectively.[6−9]

Gas chromatography (GC) theory and techniques can be employed to describe the $\Delta_{\text{ads}}H$ and $\Delta_{\text{sol}}H$ parameters specific to their respective analyte and matrix.[6−15] Despite the need to understand the fundamental interactions between explosives and various media, and the availability of a variety of GC stationary phases, little data are currently available. This study experimentally determines the $\Delta_{\text{sol}}H$ for several nitroaromatic compounds on four bonded-polymer stationary phases. These data provide insight into the molecular interactions between the explosives and polymers that will be useful for development of preconcentrating materials and predicting the vapor phase concentration of explosives in real-world environments.

Theory

The retention of an analyte under isothermal column conditions can be used to determine the $\Delta_{\text{sol}}H$ between the analyte and column stationary phase. The most direct measurement of retention is the adjusted retention time, t'_{R}, described by

$$t'_{\text{R}} = t_{\text{R}} - t_{\text{m}} \tag{1}$$

where t_{R} is the retention time and t_{m} is the elution time of a nonretained compound. Variations in experimental conditions, such as column flow rate and ambient pressure, can contribute to inconsistencies in t'_{R}, thus the more fundamental parameter of adjusted retention volume, V'_{R}, is commonly used. Equation 2 shows the retention volume equation in an analogous form

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Table 1. Chemical IUPAC Name, Abbreviated Name, and Stated Purity of All Chemicals Used in This Study

IUPAC name	abbreviated name	stated purity	IUPAC Name	abbreviated name	stated purity
acetonitrile	ACN	HPLC grade	undecane	C11	>99 %
nitrobenzene	NB	>99 %	dodecane	C12	>99 %
2-nitrotoluene	2-NT	>99 %	tridecane	C13	>99 %
3-nitrotoluene	3-NT	99 %	tetradecane	C14	>99 %
4-nitrotoluene	4-NT	99 %	pentadecane	C15	>99 %
1,2-dinitrobenzene	1,2-DNB	>99 %	hexadecane	C16	99 %
1,3-dinitrobenzene	1,3-DNB	97 %	heptadecane	C17	99 %
1,4-dinitrobenzene	1,4-DNB	98 %	octadecane	C18	97 %
2,4-dinitrotoluene	2,4-DNT	97 %	nonadecane	C19	99 %
2,6-dinitrotoluene	2,6-DNT	98 %	eicosane	C20	99 %
3,4-dinitrotoluene	3,4-DNT	99 %	docosane	C22	99 %
3,5-dinitrotoluene	3,5-DNT	1000 $\mu g \cdot mL^{-1}$ ACN std.	tricosane	C23	99 %
1,3,5-trinitrobenzene	TNB	1000 $\mu g \cdot mL^{-1}$ ACN std.	tetracosane	C24	99 %
2,4,6-trinitrotoluene	TNT	1000 $\mu g \cdot mL^{-1}$ ACN std.	pentacosane	C25	99 %
methane	---	98 %	hexacosane	C26	99 %
hexane	---	>99 %	heptacosane	C27	99 %
			octacosane	C28	99 %
			nonacosane	C29	>99.5 %
			triacontane	C30	99 %
			hentriacotane	C31	>99.5 %

as eq 1, which can be obtained by multiplying the retention time by the volumetric flow rate of the column, F_c.

$$V'_R = V_R - V_m \tag{2}$$

Measurements of F_c, when made with a bubble flow meter, include a correction of the measured flow rate, F_m, for the column temperature and vapor pressure of water.[16] Equation 3 shows the correction terms, where T_C represents column temperature, T_a the ambient temperature, P_a the ambient pressure, and P_w the vapor pressure of water at ambient temperature.

$$F_c = F_m\left(\frac{T_C}{T_a}\right)\frac{P_a - P_w}{P_a} \tag{3}$$

The net retention volume, V_N, is obtained by correcting for the pressure drop between the column inlet and outlet using the compressibility factor, j.[16] The equation relating the terms can be seen in eq 4, where the pressures at the inlet and outlet of the column are represented by p_i and p_o, respectively.

$$V_N = \frac{3}{2}\left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1}\right]V'_R = jV'_R \tag{4}$$

Assuming the solute is infinitely dilute and the activity coefficients for the mobile and stationary phase remain constant, the net retention volume and the enthalpy of solution can be related by

$$\ln V_N = -\frac{\Delta_{sol}G}{RT_C} + C \tag{5}$$

Note that R is the universal gas constant and C is a general constant often used to simplify the equations.[6] Alternatively, the equation can be written as

$$\ln V_N = -\frac{\Delta_{sol}H}{RT_C} + C' \tag{6}$$

to show the relationship between the enthalpy of solution and ln V_N. Entropic information is now included in C'. Thus, the slope multiplied by the gas constant reveals $-\Delta_{sol}H$ or $\Delta_{vap}H$ when plotting ln V_N against inverse temperature ($1/T_C$) under isobaric conditions with respect to p_i and p_o.

In addition to evaluating $\Delta_{sol}H$ for the various analytes, it is also useful to identify the isothermal Kováts retention indices, $I(T)$. The Kováts retention index goes beyond the simpler retention parameters discussed above to present a logarithmic interpolation on a uniform scale. Kováts indices can provide a nearly unequivocal means to identify chromatographic peaks since these parameters are invariant at a particular temperature on a particular stationary phase. They are not subject to instrumental and diurnal variations. The most usual scale interpolates the retention data between that of n-alkanes, whose Kováts indices are fixed. Equation 7 shows the calculation for determining these indices where the subscript A refers to the analyte and n is the number of carbon atoms in n-alkanes. The n and $n + 1$ alkanes are selected so that $(V_N)_n$ and $(V_N)_{n+1}$ bracket $(V_N)_A$.[6]

$$I(T) = 100n + 100\frac{[(\log V_N)_A - (\log V_N)_n]}{[(\log V_N)_{n+1} - (\log V_N)_n]} \tag{7}$$

Embedded within eq 7, there is a flow rate term in each of the net retention volumes. Since those flow rates cancel, eq 7 can be rewritten in the form of eq 8.

$$I(T) = 100n + 100\frac{[(\log jt'_R)_A - (\log jt'_R)_n]}{[(\log jt'_R)_{n+1} - (\log jt'_R)_n]} \tag{8}$$

Experiment

Chemicals and Materials. Table 1 shows the explosives, nitroaromatic surrogates, and n-alkanes used in this experiment. The table indicates the appropriate IUPAC names for the compounds as well as abbreviated names which will be used throughout this text. All compounds were obtained through commercial sources as near pure substances, with purities ranging from 97 % to greater than 99.5 %. 3,5-Dinitrotoluene (3,5-DNT), 1,3,5-trinitrobenzene (TNB), and TNT were obtained as 1000 $\mu g \cdot mL^{-1}$ chemical standards dissolved in acetonitrile (ACN). Stock solutions of explosive and nitroaromatics com-

Table 2. V_N with (2σ Uncertainty) for Nitroaromatics Using (a) 80 % Dimethyl + 20 % Diphenyl Polysiloxane (DM80.DP), (b) 14 % Cyanopropylphenyl + 86 % Dimethyl Polysiloxane (CP14.DM), (c) 50 % Phenyl + 50 % Methyl Polysiloxane (P50.M), and (d) 100 % Polyethylene Glycol (PEG) Stationary Phases by Mass

(a)	NB	2-NT	3-NT	4-NT		1,2-DNB	1,3-DNB	1,4-DNB
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3
60	26.74 (0.38)	48.07 (0.69)	61.41 (0.88)	70.12 (1.00)	100	66.80 (1.01)	56.07 (0.84)	51.21 (0.77)
70	16.16 (0.23)	28.00 (0.40)	35.51 (0.51)	40.33 (0.58)	110	40.35 (0.62)	33.82 (0.52)	30.98 (0.47)
80	10.18 (0.15)	17.07 (0.25)	21.48 (0.31)	24.27 (0.35)	120	24.99 (0.39)	21.07 (0.33)	19.35 (0.30)
90	6.61 (0.10)	10.75 (0.16)	13.44 (0.20)	15.11 (0.22)	130	15.99 (0.25)	13.53 (0.22)	12.46 (0.20)
100	4.42 (0.07)	6.99 (0.11)	8.69 (0.13)	9.71 (0.15)	140	10.49 (0.17)	8.93 (0.14)	8.23 (0.13)
110	3.03 (0.05)	4.67 (0.07)	5.76 (0.09)	6.43 (0.10)	150	7.07 (0.12)	6.04 (0.10)	5.59 (0.09)
120	2.13 (0.03)	3.19 (0.05)	3.92 (0.06)	4.35 (0.07)	160	4.90 (0.08)	4.19 (0.07)	3.88 (0.06)
130	1.53 (0.02)	2.25 (0.04)	2.74 (0.04)	3.03 (0.05)	170	3.44 (0.06)	2.96 (0.05)	2.74 (0.05)
140	1.10 (0.02)	1.59 (0.03)	1.94 (0.03)	2.14 (0.03)	180	2.48 (0.04)	2.13 (0.04)	1.98 (0.03)
150	0.82 (0.01)	1.16 (0.02)	1.41 (0.02)	1.55 (0.03)	190	1.81 (0.03)	1.56 (0.03)	1.46 (0.03)
160	0.61 (0.01)	0.87 (0.01)	1.04 (0.02)	1.15 (0.02)	200	1.36 (0.02)	1.17 (0.02)	1.09 (0.02)
170	0.47 (0.01)	0.64 (0.01)	0.77 (0.01)	0.84 (0.01)	210	1.03 (0.02)	0.89 (0.02)	0.83 (0.01)
					220	0.79 (0.01)	0.68 (0.01)	0.63 (0.01)

	2,4-DNT	2,6-DNT	3,4-DNT	3,5-DNT		TNB	TNT
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	t/°C	V_N/cm^3	V_N/cm^3
110	52.01 (0.80)	36.47 (0.56)		57.59 (0.88)	140	34.82 (0.56)	34.39 (0.56)
120	31.72 (0.49)	22.50 (0.35)	46.36 (0.72)	34.95 (0.55)	150	21.70 (0.36)	21.43 (0.35)
130	19.95 (0.32)	14.31 (0.23)	28.74 (0.46)	21.88 (0.35)	160	13.93 (0.23)	13.75 (0.23)
140	12.91 (0.21)	9.35 (0.15)	18.34 (0.30)	14.09 (0.23)	170	9.17 (0.16)	9.06 (0.15)
150	8.58 (0.14)	6.28 (0.10)	12.03 (0.20)	9.32 (0.15)	180	6.22 (0.11)	6.13 (0.11)
160	5.85 (0.10)	4.32 (0.07)	8.10 (0.14)	6.33 (0.11)	190	4.28 (0.07)	4.23 (0.07)
170	4.07 (0.07)	3.03 (0.05)	5.57 (0.09)	4.39 (0.07)	200	3.04 (0.05)	2.99 (0.05)
180	2.90 (0.05)	2.19 (0.04)	3.94 (0.07)	3.11 (0.05)	210	2.19 (0.04)	2.16 (0.04)
190	2.09 (0.04)	1.60 (0.03)	2.83 (0.05)	2.24 (0.04)	220	1.60 (0.03)	1.58 (0.03)
200	1.56 (0.03)	1.18 (0.02)	2.06 (0.04)	1.66 (0.03)	230	1.19 (0.02)	1.17 (0.02)
210	1.16 (0.02)	0.89 (0.02)	1.55 (0.03)	1.23 (0.02)	240	0.90 (0.02)	0.88 (0.02)
220	0.89 (0.02)	0.68 (0.01)	1.17 (0.02)	0.93 (0.02)	250	0.69 (0.01)	0.69 (0.01)
230	0.67 (0.01)	0.52 (0.01)	0.88 (0.02)	0.70 (0.01)	260	0.53 (0.01)	0.53 (0.01)
240	0.53 (0.01)	0.42 (0.01)	0.70 (0.01)	0.56 (0.01)			

(b)	NB	2-NT	3-NT	4-NT		1,2-DNB	1,3-DNB	1,4-DNB
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3
70	20.50 (0.34)	33.88 (0.56)	45.25 (0.75)	52.99 (0.88)	120	44.96 (0.79)	31.82 (0.56)	27.33 (0.48)
80	12.81 (0.21)	20.49 (0.34)	27.19 (0.45)	31.61 (0.52)	130	28.18 (0.50)	20.22 (0.36)	17.46 (0.31)
90	8.26 (0.14)	12.83 (0.21)	16.89 (0.28)	19.52 (0.33)	140	18.18 (0.33)	13.22 (0.24)	11.48 (0.21)
100	5.49 (0.09)	8.31 (0.14)	10.84 (0.18)	12.46 (0.21)	150	12.06 (0.22)	8.88 (0.16)	7.74 (0.14)
110	3.73 (0.06)	5.51 (0.09)	7.15 (0.12)	8.18 (0.14)	160	8.20 (0.15)	6.10 (0.11)	5.35 (0.10)
120	2.62 (0.05)	3.77 (0.07)	4.85 (0.08)	5.52 (0.10)	170	5.69 (0.11)	4.28 (0.08)	3.77 (0.07)
130	1.85 (0.03)	2.62 (0.05)	3.36 (0.06)	3.81 (0.07)	180	4.05 (0.08)	3.06 (0.06)	2.71 (0.05)
140	1.36 (0.02)	1.89 (0.03)	2.38 (0.04)	2.69 (0.05)	190	2.92 (0.06)	2.23 (0.04)	1.97 (0.04)
150	1.00 (0.02)	1.36 (0.03)	1.73 (0.03)	1.94 (0.04)	200	2.14 (0.04)	1.65 (0.03)	1.47 (0.03)

	2,4-DNT	2,6-DNT	3,4-DNT	3,5-DNT		TNB	TNT
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	t/°C	V_N/cm^3	V_N/cm^3
130	30.11 (0.54)	18.98 (0.34)	52.82 (0.94)	33.99 (0.61)	160	29.82 (0.56)	26.10 (0.49)
140	19.26 (0.35)	12.35 (0.22)	33.11 (0.60)	21.66 (0.39)	170	19.22 (0.37)	16.86 (0.32)
150	12.68 (0.23)	8.24 (0.15)	21.38 (0.39)	14.19 (0.26)	180	12.72 (0.25)	11.18 (0.22)
160	8.56 (0.16)	5.63 (0.11)	14.17 (0.27)	9.55 (0.18)	190	8.62 (0.17)	7.58 (0.15)
170	5.91 (0.11)	3.95 (0.08)	9.62 (0.18)	6.57 (0.13)	200	5.97 (0.12)	5.27 (0.10)
180	4.17 (0.08)	2.82 (0.05)	6.68 (0.13)	4.63 (0.09)	210	4.21 (0.08)	3.74 (0.08)
190	2.99 (0.06)	2.04 (0.04)	4.73 (0.09)	3.31 (0.06)	220	3.04 (0.06)	2.69 (0.06)
200	2.19 (0.04)	1.51 (0.03)	3.42 (0.07)	2.41 (0.05)	230	2.23 (0.05)	1.99 (0.04)
210	1.63 (0.03)	1.14 (0.02)	2.51 (0.05)	1.80 (0.04)	240	1.67 (0.04)	1.50 (0.03)
220	1.24 (0.03)	0.87 (0.02)	1.88 (0.04)	1.36 (0.03)	250	1.26 (0.03)	1.13 (0.02)
					260	0.98 (0.02)	0.88 (0.02)

(c)	NB	2-NT	3-NT	4-NT		1,2-DNB	1,3-DNB	1,4-DNB
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3
70	19.94 (0.25)	33.78 (0.43)	43.20 (0.55)	49.34 (0.63)	110	60.64 (0.81)	50.32 (0.67)	46.13 (0.62)
80	12.35 (0.16)	20.23 (0.26)	25.70 (0.33)	29.17 (0.37)	120	36.80 (0.50)	30.56 (0.42)	28.14 (0.38)
90	7.87 (0.10)	12.54 (0.16)	15.80 (0.21)	17.84 (0.23)	130	23.02 (0.32)	19.17 (0.27)	17.71 (0.25)
100	5.20 (0.07)	8.03 (0.11)	10.05 (0.13)	11.30 (0.15)	140	14.83 (0.21)	12.36 (0.18)	11.46 (0.16)
110	3.51 (0.05)	5.29 (0.07)	6.57 (0.09)	7.36 (0.10)	150	9.81 (0.14)	8.20 (0.12)	7.62 (0.11)
120	2.43 (0.03)	3.58 (0.05)	4.41 (0.06)	4.92 (0.07)	160	6.65 (0.10)	5.56 (0.08)	5.18 (0.08)
130	1.72 (0.02)	2.49 (0.03)	3.04 (0.04)	3.38 (0.05)	170	4.62 (0.07)	3.86 (0.06)	3.61 (0.05)
140	1.24 (0.02)	1.75 (0.02)	2.13 (0.03)	2.37 (0.03)	180	3.27 (0.05)	2.75 (0.04)	2.57 (0.04)
150	0.90 (0.01)	1.27 (0.02)	1.53 (0.02)	1.69 (0.02)	190	2.35 (0.04)	1.98 (0.03)	1.86 (0.03)
160	0.67 (0.01)	0.93 (0.01)	1.12 (0.02)	1.22 (0.02)	200	1.72 (0.03)	1.45 (0.02)	1.35 (0.02)
170	0.51 (0.01)	0.69 (0.01)	0.83 (0.01)	0.91 (0.01)	210	1.29 (0.02)	1.08 (0.02)	1.02 (0.02)
180	0.40 (0.01)	0.53 (0.01)	0.63 (0.01)	0.69 (0.01)	220	0.97 (0.02)	0.81 (0.01)	0.77 (0.01)

Table 2 Continued

	2,4-DNT	2,6-DNT	3,4-DNT	3,5-DNT		TNB	TNT
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	t/°C	V_N/cm^3	V_N/cm^3
130	27.06 (0.38)	19.33 (0.27)	40.62 (0.57)	29.76 (0.41)	150	33.48 (0.48)	31.56 (0.46)
140	17.13 (0.24)	12.39 (0.18)	25.40 (0.36)	18.75 (0.27)	160	20.90 (0.31)	19.86 (0.29)
150	11.16 (0.16)	8.16 (0.12)	16.36 (0.24)	12.16 (0.18)	170	13.44 (0.20)	12.77 (0.19)
160	7.45 (0.11)	5.51 (0.08)	10.80 (0.16)	8.08 (0.12)	180	8.88 (0.13)	8.45 (0.13)
170	5.10 (0.08)	3.80 (0.06)	7.31 (0.11)	5.51 (0.08)	190	6.02 (0.09)	5.72 (0.09)
180	3.57 (0.05)	2.69 (0.04)	5.07 (0.08)	3.84 (0.06)	200	4.16 (0.06)	3.97 (0.06)
190	2.54 (0.04)	1.93 (0.03)	3.57 (0.05)	2.72 (0.04)	210	2.97 (0.05)	2.83 (0.04)
200	1.83 (0.03)	1.41 (0.02)	2.57 (0.04)	1.96 (0.03)	220	2.14 (0.03)	2.05 (0.03)
210	1.37 (0.02)	1.05 (0.02)	1.88 (0.03)	1.44 (0.02)	230	1.59 (0.03)	1.52 (0.02)
220	1.01 (0.02)	0.78 (0.01)	1.40 (0.02)	1.07 (0.02)	240	1.21 (0.02)	1.16 (0.02)
230	0.77 (0.01)	0.61 (0.01)	1.05 (0.02)	0.82 (0.02)	250	0.92 (0.02)	0.89 (0.01)

(d)	NB	2-NT	3-NT	4-NT		1,2-DNB	1,3-DNB	1,4-DNB
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3
60	92.89 (2.70)				160	30.04 (1.05)	17.18 (0.60)	16.26 (0.57)
70	52.98 (1.56)				170	19.80 (0.70)	11.63 (0.41)	11.01 (0.39)
80	31.33 (0.94)				180	13.36 (0.48)	8.05 (0.29)	7.63 (0.27)
90	19.33 (0.59)	24.79 (0.76)	30.57 (0.93)	36.49 (1.11)	190	9.24 (0.34)	5.71 (0.21)	5.41 (0.20)
100	12.30 (0.38)	15.48 (0.48)	19.08 (0.59)	22.66 (0.71)	200	6.54 (0.24)	4.15 (0.15)	3.95 (0.15)
110	8.07 (0.26)	10.03 (0.32)	12.30 (0.39)	14.52 (0.46)				
120	5.45 (0.18)	6.65 (0.22)	8.16 (0.27)	9.58 (0.31)				
130	3.81 (0.13)	4.55 (0.15)	5.58 (0.19)	6.50 (0.22)				
140	2.65 (0.09)							
150	1.93 (0.07)							
160	1.43 (0.05)							
170	1.07 (0.04)							
180	1.01 (0.04)							

	2,4-DNT	2,6-DNT	3,4-DNT	3,5-DNT		TNB	TNT
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	t/°C	V_N/cm^3	V_N/cm^3
160	19.77 (0.69)	14.43 (0.50)	40.07 (1.40)	19.90 (0.70)	180	33.50 (1.20)	26.96 (0.97)
170	13.30 (0.47)	9.76 (0.35)	26.20 (0.93)	13.36 (0.47)	190	21.85 (0.79)	17.59 (0.64)
180	9.11 (0.33)	6.74 (0.24)	17.45 (0.63)	9.15 (0.33)	200	14.66 (0.54)	11.85 (0.44)
190	6.43 (0.23)	4.79 (0.17)	11.98 (0.43)	5.05 (0.18)	210	10.10 (0.38)	8.17 (0.31)
200	4.63 (0.17)	3.47 (0.13)	8.40 (0.31)	4.64 (0.17)	220	7.12 (0.27)	5.79 (0.22)

pounds were prepared by use of high-performance liquid chromatography (HPLC) grade ACN as the solvent, whereas the *n*-alkanes were dissolved in HPLC grade hexane. GC capillary columns were obtained through commercial sources. Four distinct stationary phases were used in this experiment. Their mass fractions were 80 % dimethyl + 20 % diphenyl polysiloxane (DM80.DP), 14 % cyanopropylphenyl + 86 % dimethyl polysiloxane (CP14.DM), 50 % phenyl + 50 % methyl polysiloxane (P50.M), and 100 % polyethylene glycol (PEG). All columns were cut to approximately 10 m in length and had an inner diameter and stationary phase thickness of 250 μm and 0.5 μm, respectively. Simple mixtures of solutes were analyzed, thus the 10 m column length provided us with sufficient efficiency and provided a good compromise between retention and elution speed.

Gas Chromatography. Data generated from these experiments were obtained with commercially available GC systems, outfitted with automatic samplers and flame ionization detectors (FID). Dry, research grade nitrogen was used for the carrier and makeup gases for both the capillary column and FID, respectively. Nitrogen carrier and makeup gases were used to maximize the sensitivity of the FID.[17] A 68.9 kPa constant head pressure (103.4 kPa for the PEG column) was applied to the head of the column. Research grade hydrogen and high purity (zero) air (formulated with low hydrocarbon content) were used as jet gases for the FID. Injector systems were operated in split injection mode with 1 μL injections. The split ratio was varied to achieve optimal chromatographic conditions. Injector and detector temperatures were held constant and were generally a minimum of 20 °C higher than the oven temperature for the PEG column. For the DM80.DP, CP14.DM, and P50.M columns, the injector and detector temperatures were held constant at 260 °C and 270 °C, respectively. Ambient pressure and temperature were recorded at a minimum of once a day (typically two to three times daily) to allow fluctuations to be monitored and accounted for in the data processing. Ambient pressure was monitored either via the standard fixed cistern mercury barometer located at the National Institute of Standards & Technology (NIST) facilities in Boulder, CO, or a commercially available hand-held vacuum gauge. The hand-held device was found to agree within 0.5 % of the standard NIST pressure.

Procedures. Analyte retention times resulting from isothermal chromatographic conditions were recorded. The nitroaromatic test compounds were injected five times at each oven temperature, while the *n*-alkanes were injected in triplicate. Nitroaromatics were injected individually or in mixtures of two to four compounds. Indeed, one of the ancillary advantages of the chromatographic approach is the ability to inject mixtures since the technique is also a separation method. The *n*-alkanes were dissolved in hexane and injected in mixtures of two to seven consecutive carbon numbers (for example: C23, C24, C25, and C26) with three to four compounds being typical. All analyte mixtures injected were verifiably resolved to the baseline. Analyte concentrations were adjusted so that peak heights were not excessively large to justify the assumption of infinite dilution conditions. The elution time of methane was measured for all conditions used in this experiment and was assumed to have negligible retention; thus, it was used as a marker to determine void volume. Carrier gas flow rates were measured at all conditions by use of a water-jacketed soap bubble flow meter.

Table 3. V_N with (2σ Uncertainty) for Alkanes Using (a) 80 % Dimethyl + 20 % Diphenyl Polysiloxane (DM80.DP), (b) 14 % Cyanopropylphenyl + 86 % Dimethyl Polysiloxane (CP14.DM), (c) 50 % Phenyl + 50 % Methyl Polysiloxane (P50.M), and (d) 100 % Polyethylene Glycol (PEG) Stationary Phases by Mass

(a)	C11	C12	C13	C14	C15
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3
60	14.83 (0.21)	33.57 (0.48)	75.67 (1.08)		
70	8.86 (0.13)	19.19 (0.28)	41.37 (0.60)		
80	5.52 (0.08)	11.49 (0.17)	23.74 (0.35)	48.90 (0.71)	
90	3.55 (0.05)	7.12 (0.11)	14.15 (0.21)	28.04 (0.42)	55.35 (0.82)
100	2.35 (0.04)	4.55 (0.07)	8.74 (0.13)	16.71 (0.25)	31.87 (0.48)
110	1.61 (0.02)	3.00 (0.05)	5.57 (0.09)	10.31 (0.16)	18.99 (0.29)
120	1.10 (0.02)	2.02 (0.03)	3.65 (0.06)	6.55 (0.10)	11.70 (0.18)
130	0.79 (0.01)	1.40 (0.02)	2.45 (0.04)	4.29 (0.07)	7.45 (0.12)
140	0.56 (0.01)	0.98 (0.02)	1.68 (0.03)	2.86 (0.05)	4.86 (0.08)
150		0.69 (0.01)	1.18 (0.02)	1.97 (0.03)	3.26 (0.05)
160		0.51 (0.01)	0.86 (0.01)	1.39 (0.02)	2.25 (0.04)
170		0.37 (0.01)	0.61 (0.01)	0.98 (0.02)	1.55 (0.03)
180					1.12 (0.02)
190					0.80 (0.01)
200					0.60 (0.01)
210					0.45 (0.01)

	C16	C17	C18	C19	C20
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3
100	60.53 (0.91)				
110	34.91 (0.53)	63.83 (0.98)			
120	20.86 (0.33)	36.99 (0.58)	65.29 (1.02)		
130	12.90 (0.21)	22.21 (0.35)	38.03 (0.60)		
140	8.20 (0.13)	13.74 (0.22)	22.93 (0.37)	38.20 (0.62)	63.36 (1.02)
150	5.37 (0.09)	8.77 (0.14)	14.27 (0.23)	23.17 (0.38)	37.47 (0.62)
160	3.61 (0.06)	5.76 (0.10)	9.15 (0.15)	14.50 (0.24)	22.92 (0.38)
170	2.47 (0.04)	3.86 (0.07)	6.01 (0.10)	9.32 (0.16)	14.41 (0.24)
180	1.74 (0.03)	2.66 (0.05)	4.05 (0.07)	6.16 (0.11)	9.33 (0.16)
190	1.23 (0.02)	1.86 (0.03)	2.78 (0.05)	4.15 (0.07)	6.18 (0.11)
200	0.90 (0.02)	1.33 (0.02)	1.96 (0.03)	2.87 (0.05)	4.20 (0.07)
210	0.67 (0.01)	0.97 (0.02)	1.41 (0.03)	2.03 (0.04)	2.91 (0.05)
220	0.50 (0.01)	0.71 (0.01)	1.03 (0.02)	1.46 (0.03)	2.06 (0.04)
230	0.37 (0.01)	0.53 (0.01)	0.75 (0.01)	1.05 (0.02)	1.47 (0.03)
240	0.28 (0.01)	0.40 (0.01)	0.57 (0.01)	0.79 (0.01)	1.08 (0.02)
250	0.23 (0.00)	0.32 (0.01)	0.44 (0.01)	0.60 (0.01)	0.81 (0.02)
260		0.24 (0.00)	0.33 (0.01)	0.46 (0.01)	0.61 (0.01)

(b)	C12	C13	C14	C15
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3
70	17.09 (0.28)	36.44 (0.60)	77.37 (1.28)	
80	10.27 (0.17)	21.01 (0.35)	42.63 (0.71)	
90	6.38 (0.11)	12.56 (0.21)	24.61 (0.41)	48.06 (0.80)
100	4.10 (0.07)	7.80 (0.13)	14.76 (0.25)	27.81 (0.47)
110	2.70 (0.05)	4.99 (0.09)	9.14 (0.16)	16.65 (0.29)
120	1.84 (0.03)	3.29 (0.06)	5.84 (0.10)	10.34 (0.18)
130	1.27 (0.02)	2.22 (0.04)	3.83 (0.07)	6.60 (0.12)
140	0.91 (0.02)	1.54 (0.03)	2.60 (0.05)	4.35 (0.08)
150	0.64 (0.01)	1.09 (0.02)	1.79 (0.03)	2.92 (0.05)

	C16	C17	C18	C19	C20	C22
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3
120	18.35 (0.32)	32.05 (0.56)	56.07 (0.98)			
130	11.36 (0.20)	19.34 (0.34)	32.86 (0.58)	55.57 (0.99)		
140	7.28 (0.13)	12.06 (0.22)	19.94 (0.36)	32.91 (0.60)	53.87 (0.98)	
150	4.79 (0.09)	7.74 (0.14)	12.49 (0.23)	20.11 (0.37)	32.09 (0.59)	
160	3.25 (0.06)	5.12 (0.10)	8.06 (0.15)	12.67 (0.24)	19.68 (0.37)	47.87 (0.90)
170	2.24 (0.04)	3.46 (0.07)	5.34 (0.10)	8.21 (0.16)	12.47 (0.24)	28.96 (0.55)
180	1.58 (0.03)	2.40 (0.05)	3.63 (0.07)	5.46 (0.11)	8.13 (0.16)	18.16 (0.35)
190	1.13 (0.02)	1.69 (0.03)	2.51 (0.05)	3.71 (0.07)	5.43 (0.11)	11.64 (0.23)
200	0.82 (0.02)	1.21 (0.02)	1.78 (0.04)	2.58 (0.05)	3.71 (0.07)	7.69 (0.15)
210	0.61 (0.01)	0.89 (0.02)	1.28 (0.03)	1.83 (0.04)	2.59 (0.05)	5.19 (0.10)
220	0.46 (0.01)	0.67 (0.01)	0.94 (0.02)	1.33 (0.03)	1.85 (0.04)	3.59 (0.07)
230					1.34 (0.03)	2.53 (0.05)
240					0.99 (0.02)	1.82 (0.04)
250					0.73 (0.02)	1.33 (0.03)
260					0.56 (0.01)	0.99 (0.02)

Table 3 Continued

(c)	C12	C13	C14	C15
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3
70	8.88 (0.11)	18.75 (0.24)	39.46 (0.50)	82.42 (1.05)
80	5.45 (0.07)	11.05 (0.14)	22.30 (0.29)	44.93 (0.58)
90	3.43 (0.04)	6.72 (0.09)	13.12 (0.17)	25.44 (0.33)
100	2.24 (0.03)	4.25 (0.06)	8.00 (0.11)	14.99 (0.20)
110	1.49 (0.02)	2.76 (0.04)	5.03 (0.07)	9.14 (0.12)
120	1.03 (0.01)	1.84 (0.03)	3.27 (0.04)	5.76 (0.08)
130	0.72 (0.01)	1.26 (0.02)	2.19 (0.03)	3.74 (0.05)
140	0.50 (0.01)	0.87 (0.01)	1.48 (0.02)	2.47 (0.03)
150	0.34 (0.00)	0.59 (0.01)	1.02 (0.01)	1.68 (0.02)
160			0.72 (0.01)	1.16 (0.02)
170			0.50 (0.01)	0.83 (0.01)
180				0.61 (0.01)

	C16	C17	C18	C19	C20	C22
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3
90	49.07 (0.64)					
100	27.96 (0.37)					
110	16.56 (0.22)	29.86 (0.40)	53.44 (0.72)	95.49 (1.28)		
120	10.12 (0.14)	17.72 (0.24)	30.80 (0.42)	53.37 (0.73)		
130	6.39 (0.09)	10.86 (0.15)	18.38 (0.26)	30.98 (0.43)	52.01 (0.72)	
140	4.14 (0.06)	6.87 (0.10)	11.30 (0.16)	18.57 (0.26)	30.40 (0.43)	
150	2.75 (0.04)	4.47 (0.06)	7.18 (0.10)	11.51 (0.17)	18.37 (0.26)	46.39 (0.67)
160	1.87 (0.03)	2.97 (0.04)	4.68 (0.07)	7.33 (0.11)	11.52 (0.17)	27.83 (0.41)
170	1.31 (0.02)	2.04 (0.03)	3.13 (0.05)	4.80 (0.07)	7.40 (0.11)	17.13 (0.26)
180	0.93 (0.01)	1.42 (0.02)	2.15 (0.03)	3.22 (0.05)	4.89 (0.07)	10.87 (0.16)
190	0.67 (0.01)	1.00 (0.02)	1.49 (0.02)	2.21 (0.03)	3.31 (0.05)	7.09 (0.11)
200	0.48 (0.01)	0.72 (0.01)	1.05 (0.02)	1.54 (0.02)	2.28 (0.04)	4.74 (0.07)
210	0.37 (0.01)	0.53 (0.01)	0.76 (0.01)	1.09 (0.02)	1.61 (0.03)	3.26 (0.05)
220	0.26 (0.00)	0.39 (0.01)	0.56 (0.01)	0.79 (0.01)	1.16 (0.02)	2.27 (0.04)
230			0.42 (0.01)	0.58 (0.01)	0.88 (0.01)	1.64 (0.03)
240					0.69 (0.01)	1.21 (0.02)
250					0.53 (0.01)	0.90 (0.02)

(d)	C16	C17	C18	C19	C20
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3
90	10.53 (0.32)	18.90 (0.58)	33.92 (1.03)	60.75 (1.85)	
100	6.53 (0.20)	11.37 (0.35)	19.69 (0.61)	34.12 (1.06)	
110	4.19 (0.13)	7.06 (0.22)	11.88 (0.38)	19.96 (0.64)	33.58 (1.07)
120	2.77 (0.09)	4.54 (0.15)	7.44 (0.24)	12.23 (0.40)	19.94 (0.65)
130	1.89 (0.06)	3.03 (0.10)	4.83 (0.16)	7.69 (0.26)	12.21 (0.41)

	C20 cont.	C22	C23	C24	C25
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3
160	3.40 (0.12)	7.47 (0.26)	11.04 (0.39)	16.26 (0.57)	23.95 (0.84)
170	2.36 (0.08)	4.97 (0.18)	7.22 (0.26)	10.42 (0.37)	15.05 (0.53)
180	1.67 (0.06)	3.39 (0.12)	4.84 (0.17)	6.87 (0.25)	9.71 (0.35)
190	1.21 (0.04)	2.38 (0.09)	3.34 (0.12)	4.64 (0.17)	6.47 (0.23)
200	0.90 (0.03)	1.70 (0.06)	2.35 (0.09)	3.22 (0.12)	4.42 (0.16)

	C26	C27	C28	C29	C30	C31
t/°C	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3	V_N/cm^3
160	35.12 (1.23)	51.16 (1.79)	74.54 (2.61)			
170	21.65 (0.77)	31.00 (1.10)	44.61 (1.58)			
180	13.75 (0.49)	19.41 (0.70)	27.34 (0.98)	38.52 (1.38)	53.99 (1.93)	75.58 (2.71)
190	9.01 (0.33)	12.51 (0.45)	17.31 (0.63)	23.74 (0.86)	33.04 (1.20)	45.56 (1.65)
200	6.04 (0.22)	8.26 (0.30)	11.28 (0.41)	15.37 (0.56)	20.81 (0.76)	28.41 (1.04)
210			7.53 (0.28)	10.09 (0.38)	13.56 (0.51)	18.21 (0.68)
220			5.19 (0.20)	6.90 (0.26)	9.08 (0.35)	11.97 (0.46)

Results

We note that there is some variation among researchers regarding the preferred manner to treat chromatographic data of this sort. In an effort to provide the most useful data set to the stakeholder community, the net retention volumes determined in this study are provided in addition to $\Delta_{sol}H$ and $I(T)$. Table 2 shows the calculated net retention volumes for all nitroaromatic compounds used in this study. Table 3 shows analogous data for the *n*-alkanes investigated. The tables are categorized according to the stationary phase where DM80.DP, CP14.DM, P50.M, and PEG are assigned the letters A, B, C, and D respectively. Uncertainty analysis revealed that the primary contributing factor to uncertainty in V_N was the uncertainty of F_m (eq 3). While T_C, T_a, P_a, and P_w could also contribute uncertainty, the relatively high precision of those measurements rendered their error contribution negligible compared to F_m. A second-order polynomial was used to fit F_c as a function of T_C. The 95 % certainty values for F_c were

Table 4. $\Delta_{sol}H$ of Nitroaromatics with the Temperature Range of Data Used for the Regression[a]

	DM80.DP		CP14.DM		P50.M		PEG	
	$\Delta_{sol}H$	t_{low} to t_{high}	$\Delta_{sol}H$	t_{low} to t_{high}	$\Delta_{sol}H$	t_{low} to t_{high}	$\Delta_{sol}H$	t_{low} to t_{high}
molecule	$kJ \cdot mol^{-1}$	°C	$kJ \cdot mol^{-1}$	°C	$kJ \cdot mol^{-1}$	°C	$kJ \cdot mol^{-1}$	°C
NB	−45.1 (0.2)	60 to 160	−45.5 (0.2)	70 to 150	−46.3 (0.2)	70 to 170	−49.5 (0.3)	60 to 180
2-NT	−47.9 (0.2)	60 to 170	−48.5 (0.2)	70 to 150	−48.8 (0.2)	70 to 180	−51.6 (0.3)	90 to 130
3-NT	−48.6 (0.2)	60 to 170	−49.3 (0.2)	70 to 150	−49.7 (0.2)	70 to 180	−51.8 (0.3)	90 to 130
4-NT	−49.1 (0.2)	60 to 170	−49.9 (0.2)	70 to 150	−50.2 (0.2)	70 to 180	−52.5 (0.2)	90 to 130
1,2-DNB	−56.5 (0.3)	100 to 220	−58.8 (0.3)	120 to 200	−58.9 (0.3)	110 to 220	−64.9 (0.3)	160 to 200
1,3-DNB	−56.2 (0.3)	100 to 220	−57.2 (0.2)	120 to 200	−58.8 (0.3)	110 to 220	−60.6 (0.4)	160 to 200
1,4-DNB	−55.9 (0.3)	100 to 220	−56.5 (0.2)	120 to 200	−58.4 (0.3)	110 to 220	−60.4 (0.4)	160 to 200
2,4-DNT	−57.9 (0.3)	110 to 230	−58.6 (0.3)	130 to 220	−59.9 (0.3)	130 to 230	−61.9 (0.4)	160 to 200
2,6-DNT	−56.7 (0.3)	110 to 220	−56.5 (0.3)	130 to 220	−58.4 (0.3)	130 to 230	−60.7 (0.4)	160 to 200
3,4-DNT	−58.6 (0.3)	120 to 240	−61.3 (0.3)	130 to 220	−61.5 (0.3)	130 to 230	−66.6 (0.3)	160 to 200
3,5-DNT	−58.3 (0.3)	110 to 240	−59.1 (0.3)	130 to 220	−60.6 (0.3)	130 to 230	−62.1 (0.4)	160 to 200
TNB	−64.0 (0.4)	140 to 250	−65.7 (0.4)	160 to 260	−66.2 (0.5)	150 to 250	−71.9 (0.5)	180 to 220
TNT	−63.9 (0.4)	140 to 250	−65.2 (0.4)	160 to 260	−65.8 (0.6)	150 to 250	−71.5 (0.5)	180 to 220

[a] The uncertainty 2σ is in parentheses.

Table 5. $\Delta_{sol}H$ of *n*-Alkanes with the Temperature Range of Data Used for the Regression[a]

	DM80.DP		CP14.DM		P50.M		PEG	
	$\Delta_{sol}H$	t_{low} to t_{high}	$\Delta_{sol}H$	t_{low} to t_{high}	$\Delta_{sol}H$	t_{low} to t_{high}	$\Delta_{sol}H$	t_{low} to t_{high}
molecule	$kJ \cdot mol^{-1}$	°C	$kJ \cdot mol^{-1}$	°C	$kJ \cdot mol^{-1}$	°C	$kJ \cdot mol^{-1}$	°C
C11	−46.7 (0.3)	60 to 130						
C12	−50.3 (0.3)	60 to 150	−49.5 (0.3)	70 to 140	−48.1 (0.2)	70 to 140		
C13	−53.6 (0.3)	60 to 170	−52.9 (0.4)	70 to 150	−51.8 (0.6)	70 to 150		
C14	−56.4 (0.3)	80 to 170	−56.8 (0.4)	70 to 150	−54.8 (0.2)	70 to 170		
C15	−58.8 (0.3)	90 to 200	−59.6 (0.4)	90 to 150	−57.7 (0.4)	70 to 180		
C16	−61.0 (0.3)	100 to 210	−59.5 (0.2)	120 to 200	−59.7 (0.3)	90 to 200	−52.2 (0.3)	90 to 130
C17	−63.9 (0.3)	110 to 220	−62.4 (0.3)	120 to 220	−61.9 (0.4)	110 to 210	−55.8 (0.3)	90 to 130
C18	−66.2 (0.3)	120 to 240	−65.9 (0.4)	120 to 220	−64.8 (0.3)	110 to 220	−59.4 (0.3)	90 to 130
C19	−68.1 (0.4)	140 to 250	−68.6 (0.4)	140 to 220	−67.8 (0.3)	110 to 230	−63.1 (0.5)	90 to 130
C20	−69.6 (0.5)	140 to 260	−68.9 (0.3)	140 to 260	−67.5 (0.5)	130 to 250	−60.8 (0.7)	110 to 130, 160 to 200
C21								
C22			−74.2 (0.4)	160 to 260	−72.7 (0.5)	150 to −250	−63.0 (0.6)	160 to 200
C23							−65.9 (0.3)	160 to 200
C24							−69.0 (0.3)	160 to 200
C25							−72.1 (0.3)	160 to 200
C26							−75.0 (0.3)	160 to 200
C27							−77.6 (0.4)	160 to 200
C28							−79.0 (0.6)	160 to 220
C29							−79.9 (0.9)	180 to 220
C30							−82.8 (0.8)	180 to 220
C31							−85.6 (0.6)	180 to 220

[a] The uncertainty 2σ is in parentheses.

propagated through to V_N and used to generate the uncertainty presented for V_N. As a result, it can be seen in Tables 2 and 3 that the absolute uncertainty generally scales with the retention volume.

The calculated $\Delta_{sol}H$ for the 13 nitroaromatic compounds evaluated in this study can be seen in Table 4. The data are arranged by stationary phase so that the strongest interactions (i.e., largest $\Delta_{vap}H$ or most negative $\Delta_{sol}H$) between the polymers and analytes increased from left to right. Only data that had a corresponding retention factor of greater than 1.0 were used in the regression for determining enthalpy. The uncertainty of the enthalpy of solution is shown in parentheses next to the calculated values and represents a 95 % confidence level from the linear regression. Generally, the strength of interaction for a particular analyte follows the trend: DM80.DP < CP14.DM < P50.M < PEG, although based on uncertainty some values are considered to be statistically identical.

The temperature range from which enthalpies were calculated can also be seen in Table 4. The plotting of ln V_N against $1/T_C$ can produce deviations from linearity due to changes in the heat capacity of the stationary phase and activity coefficients.[6−9] Thus, direct comparisons of enthalpy data measured over different temperature ranges should be done with appropriate caution. The addition of V_N data in Tables 2 and 3 was, in part, included so that interested readers could recalculate enthalpies over a desired temperature range.

Table 5 shows $\Delta_{sol}H$ for the alkanes used in this study. Enthalpies generally increase as the molecular weight of the alkane increases. When comparing a particular alkane across the four stationary phases, generally the strength of interaction is DM80.DP > CP14.DM > P50.M > PEG, the reverse of the trend of the nitroaromatics.

Table 6 shows the Kováts retention indices for the 13 nitroaromatics on all columns. The uncertainty in retention index was found to arise primarily from the uncertainty in the corrected retention time. Kováts retention indices are a comparison between the retention of a particular analyte, in this case, a nitroaromatic compound, and similarly retained *n*-alkanes. Data collection in this study was conducted so that at a given temperature the three replicate alkane chromatograms were collected immediately after the five replicate nitroaromatic chromatograms. One benefit to this strategy is that pressure fluctuations can be minimized between the nitroaromatics and their respective alkanes. In addition, analysis of uncertainty propagation showed that the uncertainty contribution of j was small compared to the contributions of t'_R. The uncertainty values reported here were generated by propagating two standard deviations (2σ, that is, a coverage factor $k = 2$) of the measured

Table 6. A Isothermal Kováts Retention Indices, $I(T)$, of Nitroaromatics with (2σ Uncertainty) on (a) 80 % Dimethyl + 20 % Diphenyl Polysiloxane (DM80.DP), (b) 14 % Cyanopropylphenyl + 86 % Dimethyl Polysiloxane (CP14.DM), (c) 50 % Phenyl + 50 % Methyl Polysiloxane (P50.M), and (d) 100 % Polyethylene Glycol (PEG) Stationary Phases by Mass

(a)	NB	2-NT	3-NT	4-NT		1,2-DNB	1,3-DNB	1,4-DNB
t/°C	$I(T)$	$I(T)$	$I(T)$	$I(T)$	t/°C	$I(T)$	$I(T)$	$I(T)$
60	1172.2 (0.4)	1244.2 (0.5)	1274.3 (0.3)	1290.6 (0.3)	100		1588.0 (0.6)	1573.9 (0.5)
70	1177.8 (0.3)	1249.2 (0.2)	1280.1 (0.3)	1296.7 (0.3)	110	1624.3 (0.8)	1595.0 (0.7)	1580.6 (0.5)
80	1183.5 (0.4)	1254.6 (0.4)	1286.2 (0.5)	1303.1 (0.6)	120	1631.9 (0.6)	1602.1 (0.8)	1587.3 (0.4)
90	1189.4 (0.5)	1260.0 (0.4)	1292.5 (0.4)	1309.6 (0.5)	130	1639.8 (0.7)	1609.1 (1.0)	1593.9 (0.7)
100	1195.5 (0.7)	1265.7 (0.5)	1299.0 (0.5)	1316.3 (0.5)	140	1648.1 (0.5)	1616.9 (0.6)	1601.3 (0.7)
110	1201.3 (0.2)	1271.6 (0.5)	1305.5 (0.5)	1323.3 (0.5)	150	1656.4 (0.6)	1624.2 (0.6)	1608.4 (0.7)
120	1209.0 (0.5)	1277.3 (0.7)	1312.3 (0.4)	1329.9 (0.4)	160	1665.8 (0.7)	1632.5 (0.6)	1616.1 (0.6)
130	1215.4 (1.7)	1284.5 (1.3)	1319.5 (0.2)	1337.5 (0.3)	170	1674.3 (0.8)	1641.6 (0.5)	1624.5 (0.3)
140	1221.7 (3.5)	1289.8 (2.1)	1327.5 (0.9)	1345.4 (0.8)	180	1684.7 (1.3)	1648.9 (0.9)	1631.7 (0.8)
150	1230.4 (6.3)	1296.6 (3.3)	1334.5 (2.1)	1353.0 (1.8)	190	1694.1 (2.5)	1658.1 (2.0)	1642.1 (2.1)
160	1235.7 (10.2)	1304.1 (6.1)	1341.2 (4.1)	1360.7 (3.4)	200	1706.2 (2.4)	1667.6 (3.5)	1650.2 (4.4)
170	1249.0 (15.2)	1311.3 (10.4)	1351.4 (6.9)	1368.9 (5.7)	210	1717.3 (4.7)	1677.1 (6.0)	1658.3 (6.3)
					220	1729.1 (7.9)	1687.1 (10.0)	1666.5 (11.4)

	2,4-DNT	2,6-DNT	3,4-DNT	3,5-DNT		TNB	TNT
t/°C	$I(T)$	$I(T)$	$I(T)$	$I(T)$	t/°C	$I(T)$	$I(T)$
110	1665.9 (0.5)	1607.0 (0.8)		1682.7 (0.5)	140	1881.9 (0.6)	1879.4 (0.3)
120	1673.0 (0.7)	1612.9 (0.4)	1739.6 (0.8)	1689.9 (0.6)	150	1886.2 (0.5)	1883.7 (0.4)
130	1680.0 (0.4)	1618.7 (0.5)	1747.6 (0.8)	1697.0 (0.4)	160	1891.2 (0.5)	1888.4 (0.6)
140	1687.8 (0.5)	1625.4 (0.6)	1756.2 (0.4)	1704.8 (0.5)	170	1896.4 (0.7)	1893.4 (0.7)
150	1695.5 (0.7)	1631.9 (0.6)	1764.9 (0.5)	1712.5 (0.7)	180	1902.0 (0.9)	1898.7 (0.9)
160	1703.1 (0.7)	1638.2 (0.6)	1773.8 (0.7)	1720.3 (0.7)	190	1907.2 (0.8)	1904.3 (0.8)
170	1711.6 (0.6)	1646.0 (0.5)	1783.2 (0.8)	1728.9 (0.6)	200	1914.5 (0.5)	1910.5 (0.4)
180	1720.9 (0.3)	1654.1 (1.0)	1793.1 (1.0)	1737.2 (0.5)	210	1921.1 (0.4)	1917.0 (0.4)
190	1729.0 (0.6)	1662.8 (1.9)	1804.4 (0.3)	1746.0 (0.8)	220	1927.0 (1.6)	1924.1 (1.6)
200	1740.5 (1.8)	1670.0 (3.6)	1813.1 (0.5)	1756.1 (1.7)	230	1934.5 (3.7)	1931.3 (4.0)
210	1749.0 (3.6)	1677.1 (6.0)	1826.6 (1.7)	1763.6 (3.3)	240	1940.6 (6.6)	1935.1 (6.9)
220	1759.5 (6.0)	1687.1 (10.0)	1837.3 (3.6)	1773.7 (5.5)	250	1946.7 (10.7)	1946.7 (10.7)
230	1768.1 (10.0)	1691.8 (14.6)	1849.4 (6.9)	1781.3 (9.3)	260	1953.6 (17.2)	1953.6 (17.2)
240	1776.0 (14.2)	1710.7 (24.4)	1861.0 (10.0)	1792.2 (13.2)			

(b)	NB	2-NT	3-NT	4-NT		1,2-DNB	1,3-DNB	1,4-DNB
t/°C	$I(T)$	$I(T)$	$I(T)$	$I(T)$	t/°C	$I(T)$	$I(T)$	$I(T)$
70	1224.0 (0.5)	1290.4 (0.7)	1328.8 (1.5)	1349.7 (1.3)	120	1760.5 (0.3)	1698.7 (0.4)	1671.4 (0.8)
80	1230.9 (0.4)	1296.5 (0.5)	1336.4 (0.9)	1357.7 (1.0)	130	1770.8 (0.6)	1708.3 (0.5)	1680.6 (0.4)
90	1238.0 (0.4)	1303.2 (0.5)	1344.1 (0.4)	1365.6 (0.5)	140	1781.4 (0.4)	1718.0 (0.6)	1689.9 (0.5)
100	1245.5 (0.4)	1309.9 (0.6)	1351.6 (0.4)	1373.5 (0.4)	150	1792.2 (0.5)	1728.2 (0.7)	1699.5 (0.8)
110	1252.3 (0.4)	1316.4 (0.5)	1359.3 (0.5)	1381.6 (0.5)	160	1803.3 (0.8)	1738.0 (0.7)	1709.2 (0.7)
120	1260.9 (0.7)	1323.8 (0.4)	1367.7 (0.5)	1390.1 (0.6)	170	1814.4 (0.8)	1748.4 (0.7)	1719.3 (0.6)
130	1267.7 (1.1)	1330.5 (0.3)	1375.8 (0.8)	1398.9 (1.0)	180	1826.4 (0.7)	1758.8 (0.7)	1729.1 (0.4)
140	1276.5 (2.2)	1338.5 (0.8)	1383.7 (1.0)	1407.2 (0.2)	190	1837.9 (0.6)	1769.3 (1.1)	1738.3 (0.8)
150	1284.2 (3.9)	1344.3 (2.1)	1392.7 (1.8)	1415.9 (0.6)	200	1849.1 (0.8)	1779.6 (1.9)	1749.5 (1.8)

	2,4-DNT	2,6-DNT	3,4-DNT	3,5-DNT		TNB	TNT
t/°C	$I(T)$	$I(T)$	$I(T)$	$I(T)$	t/°C	$I(T)$	$I(T)$
130	1783.8 (1.0)	1696.7 (0.5)	1890.4 (1.1)	1806.7 (2.0)	160	2093.8 (1.6)	2064.0 (2.1)
140	1793.5 (0.5)	1705.1 (0.6)	1902.0 (1.2)	1817.0 (0.8)	170	2103.0 (1.2)	2071.9 (1.1)
150	1803.7 (0.7)	1713.6 (0.7)	1913.8 (0.5)	1827.5 (0.6)	180	2111.5 (1.2)	2079.7 (1.0)
160	1813.8 (0.7)	1721.6 (0.7)	1925.8 (0.6)	1838.2 (0.7)	190	2121.2 (1.0)	2087.8 (0.9)
170	1824.3 (0.7)	1730.6 (0.6)	1938.3 (0.7)	1849.1 (0.7)	200	2130.8 (1.1)	2096.6 (0.9)
180	1834.7 (0.7)	1739.0 (0.5)	1950.5 (0.7)	1860.0 (0.8)	210	2140.2 (0.9)	2105.6 (0.8)
190	1845.3 (0.6)	1749.0 (0.8)	1963.0 (0.9)	1871.2 (0.9)	220	2150.7 (1.2)	2114.4 (0.9)
200	1856.2 (0.9)	1758.2 (1.9)	1976.5 (1.1)	1882.3 (1.3)	230	2162.0 (1.5)	2125.7 (1.3)
210	1868.8 (1.8)	1769.3 (3.4)	1989.1 (1.7)	1895.4 (2.2)	240	2172.2 (2.7)	2136.6 (2.6)
220	1879.4 (3.2)	1778.0 (6.2)	2003.3 (2.5)	1906.5 (2.0)	250	2181.5 (3.8)	2145.5 (4.1)
					260	2195.1 (6.0)	2157.2 (6.2)

(c)	NB	2-NT	3-NT	4-NT		1,2-DNB	1,3-DNB	1,4-DNB
t/°C	$I(T)$	$I(T)$	$I(T)$	$I(T)$	t/°C	$I(T)$	$I(T)$	$I(T)$
70	1308.3 (0.8)	1379.1 (0.5)	1412.3 (1.2)	1430.3 (1.0)	110	1821.8 (2.3)	1789.7 (0.8)	1774.8 (0.6)
80	1315.8 (0.7)	1386.2 (0.3)	1420.3 (0.4)	1438.3 (0.4)	120	1832.4 (1.1)	1798.5 (0.9)	1783.7 (1.1)
90	1323.6 (0.5)	1393.2 (0.4)	1428.1 (0.5)	1446.5 (0.4)	130	1843.2 (0.5)	1808.1 (0.7)	1792.9 (0.7)
100	1331.7 (0.5)	1400.6 (0.6)	1436.3 (0.5)	1455.0 (0.4)	140	1854.6 (0.5)	1818.0 (0.6)	1802.6 (0.7)
110	1340.0 (0.4)	1408.6 (0.5)	1444.7 (0.5)	1463.8 (0.5)	150	1866.2 (0.6)	1828.0 (0.6)	1812.4 (0.7)
120	1348.5 (0.5)	1416.1 (0.4)	1453.0 (0.5)	1472.3 (0.6)	160	1878.3 (0.7)	1838.4 (0.7)	1822.8 (0.7)
130	1356.8 (1.3)	1424.2 (0.3)	1461.4 (0.6)	1481.2 (0.7)	170	1890.8 (1.0)	1849.2 (0.6)	1833.4 (0.6)
140	1367.1 (2.6)	1432.6 (1.1)	1471.5 (1.0)	1491.9 (1.2)	180	1903.6 (0.6)	1860.8 (0.8)	1844.4 (0.6)
150	1377.2 (12.0)	1442.6 (2.7)	1480.7 (2.2)	1501.3 (1.1)	190	1916.4 (0.2)	1871.9 (1.6)	1855.2 (1.3)
160		1453.6 (4.6)	1493.1 (3.9)	1511.2 (2.7)	200	1930.5 (1.1)	1883.7 (2.6)	1866.4 (2.6)
170	1404.2 (14.2)	1462.5 (7.4)	1500.0 (6.3)	1520.7 (5.2)	210	1946.3 (2.6)	1896.2 (4.6)	1880.3 (4.5)
180			1506.1 (11.0)	1529.2 (8.9)	220	1960.0 (5.4)	1907.3 (8.1)	1890.9 (8.1)

Table 6 Continued

	2,4-DNT	2,6-DNT	3,4-DNT	3,5-DNT		TNB	TNT
t/°C	*I*(*T*)	*I*(*T*)	*I*(*T*)	*I*(*T*)	*t*/°C	*I*(*T*)	*I*(*T*)
130	1873.9 (0.8)	1809.6 (1.7)	1952.2 (0.9)	1892.1 (1.6)	150	2129.7 (0.6)	2116.9 (0.9)
140	1883.7 (0.5)	1818.4 (0.9)	1963.6 (0.8)	1901.9 (1.2)	160	2134.8 (0.6)	2123.1 (0.7)
150	1893.5 (0.5)	1827.1 (0.7)	1975.2 (0.5)	1911.7 (0.6)	170	2141.7 (0.8)	2129.4 (0.6)
160	1903.6 (0.8)	1836.4 (0.7)	1987.1 (0.5)	1922.0 (0.8)	180	2148.9 (0.8)	2136.1 (0.7)
170	1914.5 (0.8)	1845.6 (0.6)	1999.4 (0.7)	1932.4 (0.7)	190	2156.5 (0.8)	2143.0 (0.8)
180	1925.3 (0.6)	1855.9 (0.7)	2011.8 (0.8)	1943.1 (0.7)	200	2163.8 (1.0)	2150.5 (1.0)
190	1936.8 (0.6)	1866.8 (1.5)	2024.4 (0.6)	1954.2 (0.8)	210	2173.2 (1.5)	2159.1 (1.4)
200	1946.8 (1.1)	1877.2 (2.5)	2037.4 (0.3)	1965.6 (1.3)	220	2181.1 (1.9)	2167.0 (1.8)
210	1962.3 (2.5)	1888.3 (4.5)	2050.5 (0.8)	1977.4 (2.5)	230	2190.7 (3.1)	2174.6 (3.0)
220	1971.8 (4.5)	1900.0 (7.9)	2063.7 (2.3)	1988.3 (4.5)	240	2200.0 (5.0)	2186.6 (5.0)
230	1983.7 (7.4)	1914.5 (12.2)	2073.2 (4.4)	2000.0 (7.4)	250	2205.9 (7.8)	2194.0 (7.8)

(d)	NB	2-NT	3-NT	4-NT		1,2-DNB	1,3-DNB	1,4-DNB
t/°C	*I*(*T*)	*I*(*T*)	*I*(*T*)	*I*(*T*)	*t*/°C	*I*(*T*)	*I*(*T*)	*I*(*T*)
90	1703.7 (2.7)	1746.8 (1.3)	1782.7 (1.5)	1813.0 (2.3)	160	2559.5 (1.5)	2414.4 (2.0)	2400.1 (1.4)
100	1714.0 (0.9)	1756.6 (0.9)	1794.7 (1.6)	1825.9 (0.8)	170	2575.6 (2.0)	2430.0 (1.6)	2415.1 (0.9)
110	1726.1 (0.7)	1766.8 (0.8)	1806.1 (1.0)	1838.3 (1.0)	180	2592.4 (1.6)	2445.8 (0.9)	2430.5 (0.7)
120	1737.6 (0.5)	1776.5 (0.5)	1818.0 (0.5)	1850.5 (0.9)	190	2608.4 (1.8)	2462.5 (0.7)	2446.6 (0.6)
130	1749.0 (0.5)	1787.8 (0.7)	1831.4 (0.5)	1864.0 (0.6)	200	2625.5 (0.7)	2480.3 (0.3)	2464.8 (0.2)

	2,4-DNT	2,6-DNT	3,4-DNT	3,5-DNT		TNB	TNT
t/°C	*I*(*T*)	*I*(*T*)	*I*(*T*)	*I*(*T*)	*t*/°C	*I*(*T*)	*I*(*T*)
160	2450.3 (3.2)	2368.9 (2.2)	2635.0 (4.1)	2452.1 (2.1)	180	2859.1 (1.6)	2795.6 (2.9)
170	2466.1 (1.4)	2381.6 (0.8)	2653.0 (1.9)	2467.5 (1.2)	190	2874.0 (1.9)	2805.8 (3.5)
180	2480.2 (0.8)	2393.4 (1.6)	2668.1 (2.1)	2484.1 (2.4)	200	2884.8 (1.7)	2816.8 (0.8)
190	2497.3 (0.9)	2408.2 (0.2)	2686.3 (0.9)	2498.7 (1.5)	210	2900.3 (1.7)	2827.8 (2.1)
200	2514.9 (0.4)	2423.2 (0.4)	2704.8 (1.5)	2516.5 (0.5)	220	2911.4 (1.4)	2838.5 (1.1)

retention times, through eq 8. In the event that all replicate retention times were identical (a relatively common occurrence), a standard deviation of 0.005 min was conservatively assumed (retention times were recorded to the 1/100 min) rather than assuming no variance. Uncertainty remains relatively constant until the upper temperatures are obtained. This outcome is to be expected since corrected retention times were small (less than 1 min in some cases) at high temperatures and a small variance in retention time would have large impacts.

Generally, when considering a particular nitroaromatic at a selected temperature, the Kováts retention indices consistently follow the trend: DM80.DP < CP14.DM < P50.M < PEG. Retention indices on the PEG column are typically much higher than those corresponding to the other three columns. This is likely a manifestation of strong and weak interactions between the PEG column with nitroaromatics and alkanes, respectively.

We have shown that useful thermodynamic information for explosives and other nitroaromatic compounds can be efficiently obtained by use of commercially available GC instrumentation. These data will be valuable to researchers interested in the development and improvements in analytical instrumentation to combat terrorism.

Literature Cited

(1) Moore, D. S. Instrumentation for trace detection of high explosives. *Rev. Sci. Instrum.* **2004**, *75*, 2499–2512.

(2) Toal, S. J.; Trogler, W. C. Polymer sensors for nitroaromatic explosives detection. *J. Mater. Chem.* **2006**, *16*, 2871–2883.

(3) Kolla, P. The application of analytical methods to the detection of hidden explosives and explosive devices. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 800–811.

(4) Nambayah, M.; Quickenden, T. I. A quantitative assessment of chemical techniques for detecting traces of explosives at counter-terrorist portals. *Talanta* **2004**, *63*, 461–467.

(5) Yinon, J. Detection of explosives by electronic noses. *Anal. Chem.* **2003**, *75*, 99A–105A.

(6) Laub, R. J.; Pescok, R. L. *Physicochemical applications of gas chromatography*; John Wiley & Sons: New York, 1978.

(7) Poole, C. F. *The essence of chromatography*; Elsevier Science: Amsterdam, 2003.

(8) Kaiser, M. A.; Dybowski, C. R. Physicochemical Measurements by Gas Chromatography. In *Modern practice of gas chromatography*, 4th ed.; Grob, R. L., Barry, E. F., Eds.; John Wiley & Sons: NJ, 2004; pp 605−627.

(9) Cazes, J.; Scott, R. P. W. *Chromatography theory*; Marcel Dekker: New York, 2002.

(10) Atkinson, D.; Curthoys, G. The determination of heats of adsorption by gas-solid chromatography. *J. Chem. Educ.* **1978**, *55*, 564−566.

(11) Atkinson, D.; Curthoys, G. The determination of entropies of adsorption by gas-solid chromatography. *J. Chem. Educ.* **1979**, *56*, 802–804.

(12) Ellison, H. R. Enthalpy of vaporization by gas chromatography. *J. Chem. Educ.* **2005**, *82*, 1086–1088.

(13) Bruno, T. J.; Lewandowski, A.; Tsvetkov, F.; Hanley, H. J. M. Determination of heats of adsorption of hydrocarbons on a synthetic clay by gas-solid chromatography using a wall coated open tubular approach. *J. Chromatogr. A* **1999**, *844*, 191–199.

(14) Bruno, T. J.; Lewandowski, A.; Tsvetkov, F.; Miller, K. E.; Hanley, H. J. M. Wall-coated open-tubular column chromatography on an organo-clay stationary phase. *J. Chromatogr. A* **2002**, *973*, 143−149.

(15) Miller, K. E.; Bruno, T. J. Enthalpy of fuel gas odorants on surrogate soil surfaces by gas chromatography. *J. Chromatogr. A* **2002**, *975*, 311–318.

(16) Grob, R. L. *Modern practice of gas chromatography*; John Wiley & Sons: NJ, 2004.

(17) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Basic Tables for Chemical Analysis*; CRC Press: Boca Raton, 2004.

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