Retention of halocarbons on a hexafluoropropylene epoxide modified graphitized carbon black
I. Methane-based compounds ✩

Thomas J. Bruno *, Michael Caciari ✩✩

Thermophysics Division, National Institute of Standards and Technology, Boulder, CO 80303, USA

Abstract

The retention characteristics of eight methane-based chlorofluorocarbon and fluorocarbon fluids have been studied as a function of temperature on a stationary phase consisting of a 5% (w/w) coating of a low-molecular-mass polymer of hexafluoropropylene epoxide on a graphitized carbon black. The fluids that were studied include chlorotrifluoromethane (R-13), tetrafluoromethane (R-14), dichlorofluoromethane (R-21), chlorodifluoromethane (R-22), trifluoromethane (R-23), difluoromethane (R-32), chloromethane (R-40), and fluoromethane (R-41). Measurements were made at −20, 0, 20 and 40°C for all fluids except dichlorofluoromethane, which was measured at 40, 60, 80 and 100°C. Net retention volumes, corrected to a column temperature of 0°C, were calculated from retention time measurements, the logarithms of which were fitted against reciprocal thermodynamic temperature. The relative retentions, also as a function of temperature, were calculated with respect to the retention of tetrafluoromethane. Qualitative features of the data are examined, and trends are identified. In addition, the data were fit to linear models for the purpose of predicting retention behavior of these compounds to facilitate chromatographic analysis.

1. Introduction

Many laboratories are engaged in a comprehensive research program geared toward the development of new fluids for use as refrigerants, blowing and foaming agents, and propellants. These new materials are needed to replace the fully halogenated materials that are believed to contribute to atmospheric ozone depletion, and which will be phased out of production by law. The research that comprises this large scale effort includes thermophysical properties measurements and correlation, materials compatibility testing, chemical stability measurement, and cycle suitability studies [1,2]. An important part of all of these research programs is the chemical analysis of new fluids that are tested [3–6].

Gas chromatography is one of the major chemical analysis methods that is applied to the study of alternative refrigerants for several important reasons, not the least of which are simplicity and economics of operation [7,8]. It is used both as a qualitative identification tool and for quantitative analysis of impurities that are

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* Corresponding author.
✩ Contribution of the United States Government.
✩✩ Permanent address: Fort Lupton High School, Fort Lupton, CO 80621, USA.

known to be present in a sample [7,9]. A knowledge of the retention characteristics of important fluids on the more useful stationary phases is an important component in the design of effective qualitative and quantitative chromatographic analyses. Such information would fill two very important analytical needs. First, we would like to identify unknown or unfamiliar peaks that appear on a chromatogram obtained from, for example, the analysis of a field sample of a new refrigerant fluid. Second, we would like to optimize chromatographic separations by being able to predict the response of elution times and separation factors to controllable instrumental parameters.

It is well known that the use of chromatographic retention characteristics as a means of compound identification must be approached with extreme caution, since the results are indirect [7,9]. For example, the equality of retention times of two materials (measured under the same conditions of column temperature, carrier gas flow-rate and stationary phase identity and quantity) does not constitute absolute proof that the materials are in fact the same. One must consider (1) the possibility of coincidence, and (2) the possibility of a chromatographic peak being caused by multiple compounds that co-elute. The coincidence of retention times of two or more peaks, in the absence of any other data, must therefore be viewed as supporting evidence only. The "other data" to which we refer may be the results from other analytical tests, or simply a knowledge of the sample history or synthetic route. One can generally make the contrary statement about retention time coincidence, however. In this respect, if the retention times of two materials are different under the same instrumental conditions (and the instrument is functioning properly), then the materials are indeed very likely different.

There are a number of measures that one can take to significantly increase the utility and reliability of retention data as a qualitative identification tool. The first method we shall mention involves the measurement of retention times on two different columns having stationary phases of different polarity. A close match of the

two retention times with the retention times of a standard compound provides much more confidence in identification. One may also route the effluent of a single column to different but appropriate detectors. For example, the consistency of the response ratio from a thermal conductivity detector and a flame ionization detector for a standard and an unknown is good evidence of identity. Both of these methods are somewhat difficult to implement, however. The first suffers from inconvenience and from being very time-consuming. The second approach suffers from difficulty in reproducibly controlling the split pneumatics. The need for two detectors instead of one increases both the complexity and implementation cost. Moreover, it is sometimes difficult to select two distinct yet appropriate detectors for a given analyte.

Corrected retention parameters, although indirect, provide a very useful and well known method to overcome some of the difficulties and complexities of peak identification in chromatographic analysis. The use of such parameters (which have been corrected for controllable instrumental variables) will minimize many of the pitfalls caused by the day-to-day variation in chromatographic performance. An example of this is the use of net retention volumes (which themselves may be further corrected for column temperature). The calculation of relative retention volumes is a useful way to minimize instrument to instrument (or column to column) variations. This is important when multiple instruments operating at somewhat different conditions and using separate columns (but the same stationary phase and column type) are to be compared. It is then possible to rationally compare the retentions obtained from an unknown sample with retentions measured from pure materials. When one further measures the temperature dependence of these parameters for unknown peaks and compares these results with such data measured on pure materials, a far greater level of confidence is achieved. This is especially true if more than one compound elutes under a single peak at a given temperature, since changing column temperature will often resolve such species.

In this paper, we present temperature-depen-

dent measurements of the net retention volume, corrected to a column temperature of 0°C, of eight methane-based fluids that are commonly encountered in alternative refrigerant research and testing. The fluids we have studied are all gaseous at room temperature and pressure. To facilitate the data analysis and comparison, one measurement each (at 40°C) is also provided for trichlorofluoromethane (R-11), dichlorofluoromethane, (R-12) and methane (R-50). A listing of all the fluids studied is provided in the left-hand column of Table 2, along with the accepted code numbers. An explanation of the numbering system for these compounds is provided in the appendix. The measurements were made on the packed-column stationary phase that is most commonly used for refrigerant analysis; a 5% coating of a low-molecular-mass polymer of hexafluoropropylene epoxide (HPE) on a graphitized carbon black [10]. Other stationary phases have been used for these types of analyses [11–13], but the HPE has proven to be the most chemically stable. This modifier has a usable temperature range of −35 to 290°C. The relative retentions were then calculated with respect to tetrafluoromethane. In addition to the discussion of qualitative trends in the data, fits to simple linear models are presented of the logarithms of the net retention volumes and the relative retentions against thermodynamic temperature. These fits provide a predictive capability.

2. Theory

The typical chromatographic integrator (or chromatographic software package for a computer) will report, among many possible analytical parameters, the retention time of each peak. If the volumetric carrier gas flow-rate (at the column exit) is measured and multiplied by the retention time, the retention volume, V_R, is obtained. The adjusted retention volume, V'_R, is the retention volume corrected for the void volume (or mobile phase holdup) of the column. It is obtained by simply subtracting the retention volume of an unretained solute (V_M) such as air:

$$V'_R = V_R - V_M \tag{1}$$

The net retention volume, V_N, is obtained by applying a factor, j, to account for the pressure drop across the column:

$$V_N = jV'_R \tag{2}$$

where j is usually[a] the Martin–James compressibility factor:

$$j = \frac{3}{2} \left[\frac{\left(\frac{P_i}{P_0}\right)^2 - 1}{\left(\frac{P_i}{P_0}\right)^3 - 1} \right] \tag{3}$$

where P_i is the inlet pressure (absolute) and P_0 is the outlet pressure (usually atmospheric pressure). The specific retention volume, V_g^0, corrects the net retention volume for the amount of stationary phase, and the column temperature is adjusted to 0°C:

$$V_g^0 = (273.15) \frac{V_N}{(W_s T_{col})} \tag{4}$$

where T_{col} is the column temperature, and W_s is the mass of stationary phase in the column. This value is a characteristic for a particular solute on a particular stationary phase in a particular carrier gas, and is instrument independent. This is a quantity that may be compared from instrument to instrument, and laboratory to laboratory with a high level of confidence provided the stationary phase used is a single, pure compound. If the mass of stationary phase is not known, or is not meaningful, it is still of value to correct the net retention volume to a column temperature of 0°C (represented by V_N^0) by simply not including the term for W_s (that is, setting it equal to unity). In the present study, the stationary phase is a solid sorbent modified with a liquid coating. Since the retention in this case is not caused exclusively by either adsorption or absorption processes, we will use the net retention volume, V_N^0, corrected to 0°C (that is, V_g^0, with $W_s = 1$).

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[a] Other expressions or approximations have been used as well. One of the most reliable approximations to the Martin–James compressibility factor is due to Halasz and Heine: $j_{approx.} = 3/[2(P_i/P_0) + 1]$.

It is also extremely valuable to calculate a relative retention, $r_{a/b}$:

$$r_{a/b} = \left(\frac{V_g^b}{V_g^a}\right) = \left(\frac{V_N^b}{V_N^a}\right) \qquad (5)$$

where the numerical superscripts refer to the retention volumes of solutes a and b. In this case, solute a is a reference. The relative retention is dependent only on the column temperature and the type of stationary phase. For reasons of operational simplicity, this parameter is usually one of the best to use for qualitative analysis [7,9]. It can account for small differences in column temperature, stationary phase considerations, column history, and minor disturbances in carrier gas flow-rate. Some of the stationary phase considerations for packed columns include differences in liquid loadings, purities and packing density, coiling effects, and residual activity of the solid support. The last concern is very important when the stationary phase is an adsorbent or an adsorbent modified by a coating. For capillary columns, these considerations include differences in coating thicknesses, purity, and irregularities in split ratios. When measurements are performed carefully, the relative retention varies only with column temperature and stationary phase, and thus forms a reasonable basis for qualitative identification.

To extend the applicability of relative retention data, it is possible to account for temperature by plotting $\ln(r_{a/b})$ against $1/T$, where T is the thermodynamic temperature. Such plots are approximately linear (especially in gas–liquid chromatography), and allow comparisons at many column temperatures. The plots can become very non-linear when measured with unmodified solid sorbents as the stationary phase, depending upon the detailed characteristics of the adsorption isotherms. The use of a surface modifier (as was done in the present study) on a solid phase will often increase the linearity of the plots, and shorten retention times.

Although it is not generally considered good practice to extrapolate the plot beyond the temperature range for which experimental data

are available, we have found with this class of compounds that extrapolation to temperatures 50°C higher than that used in the correlation can provide acceptable predictions. Naturally, interpolation within the region covered by the experimental data provides very good predictions of both the relative retentions and the net retention volumes. These data can even provide the basis for scaling isothermal analyses to temperature-programmed analyses.

3. Experimental

The measurements presented in this paper were performed on a commercial gas chromatograph that had been modified to provide high-precision retention data. The column oven was modified by the addition of 1.9 cm thick, 10×10 cm square aluminum plates surrounding the column to provide additional thermal mass for stability, and also to integrate out temperature variations in different locations within the oven. Additional insulation (in the form of mineral wool board and bubble-wrap) was placed in appropriate locations around the oven compartment. The oven temperature was measured with a quartz-crystal oscillator thermometer (calibrated against a NIST-standard platinum resistance thermometer) that was accurate to within ± 0.01°C. Injection was done with a valve containing a sample loop of 0.1 ml volume. The valve was pneumatically actuated with pilot valves using helium as the actuation gas to inject very rapidly and thereby minimize the injection pressure pulse. The injection valve and loop were maintained at 50°C for all measurements. The carrier gas line to the injection valve was modified to allow the column head pressure to be measured with a calibrated Bourdon tube gauge. This gauge was calibrated with an electronic Bourdon tube transfer standard that was itself calibrated against a NIST-standard dead mass pressure balance. The column outlet pressure was measured with an electronic barometer that had a resolution of 1.3 Pa (approximately 0.01 mm Hg). This barometer was calibrated against a dead mass pressure balance. The col-

umn carrier gas flow-rate was measured with an electronic soap-bubble flow meter, the temperature of which was referenced to the oven temperature with a pair of type-j thermocouple junctions operated in differential mode. The electromotive force of the pair was measured with a nanovoltmeter. This measurement allowed the flow-rate to be corrected for the vapor pressure of water. Retention times were measured by a commercial integrator. A Ranque–Hilsch vortex tube was used to provide cooling in the column oven for the subambient temperature measurements [13]. Thermal conductivity detection (TCD) was used with a carrier gas of research-grade helium. The TCD was maintained at 50°C for all measurements.

The stationary phase was a commercially prepared packing consisting of a 5% (mass/mass) coating of a low-molecular-mass polymer of hexafluoropropylene epoxide modifier on a 60/80 mesh (250–177 μm) graphitized carbon black [10]. Some representative properties of this modifier are presented in Table 1. A column was prepared by packing the phase into a cleaned, 2 m long section of copper tubing (0.65 cm O.D.). The column was conditioned for 4 h in the chromatograph by equilibration at 100°C with a gentle flow of helium carrier gas.

For each retention time measurement, five fluid injections were performed at each column temperature. Each series of injections was preceded and followed by five measurements of the

carrier gas flow-rate, and the injection of five aliquots of air. The air was injected separately, before and after the injection of fluid, to measure the void volume of the column without introducing air as an impurity into the fluid containers. The corrected retention time was simply obtained by subtracting the average air retention time. At the start of each of these fifteen injections (five air, five fluid, five air), the requisite temperatures (column, flowmeter, and barometer) and pressures (column head and column exit) were recorded. These replicate measurements furnished the uncertainties used for the error propagation that provided the overall experimental uncertainties that are reported. The column head pressure was maintained uniformly at 137.9 ± 0.3 kPa (approximately 20 p.s.i.g.) for the measurements, although measurements were initially performed at several other pressures to verify consistency in the operation of the chromatograph. The carrier gas flow-rate at the column exit was maintained at 45 ± 0.3 ml/min.

Measurements were performed on four isotherms for each fluid. Most of the fluids were measured at −20, 0, 20 and 40°C, but the less volatile fluids were measured at 40, 60, 80 and 100°C.

The chlorofluorocarbon samples used for these measurements were all obtained from commercial sources in the highest purity available, and were used without any further purification.

Table 1
Properties of hexafluoropropylene epoxide modifier

$$F \text{---}(\!\!- CF \text{------} CF_2 \text{------} O \rightarrow)_{\!n}\ CF_2CF_3$$

$$\overset{|}{CF_3}$$

n = 10 - 60
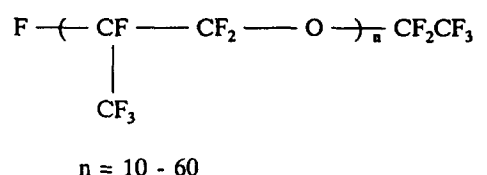
Number average molecular mass	6250
Vapor pressure	$1 \cdot 10^{-8}$ kPa (38°C)
	$1 \cdot 10^{-4}$ kPa (260°C)
Density (24°C)	1.86–1.91 g/ml
Refractive index (n_D^{25})	1.296–1.301

4. Results and discussion

The corrected net retention volumes, V_N^0, for each fluid are presented in Table 2. The reported uncertainties are the result of an error propagation performed with the standard deviations obtained from replicate measurements of each experimental parameter. The errors were added in quadrature since all variables are essentially uncorrelated (as determined by examination of Spearman's ρ and Kendall's τ), and the deviations were found to fit a normal distribution and were therefore treated as being random. In addition to the uncertainty, the coefficient of

Table 2
The net retention volume, V_N^0 (ml), and their logarithms, of the fluids measured in this study

Name	V_N^0 (ml)				$\log (V_N^0)$			
	− 20°C (253.15 K)	0°C (273.15 K)	20°C (293.15 K)	40°C (313.15 K)	− 20°C (253.15 K)	0°C (273.15 K)	20°C (293.15 K)	40°C (313.15 K)
Chlorotrifluoromethane, R-13	243.5 ± 2.84 1.17%	108.9 ± 1.42 1.30%	57.3 ± 0.53 0.92%	30.9 ± 0.54 1.76%	2.39	2.04	1.76	1.49
Tetrafluoromethane, R-14	18.4 ± 0.16 0.87%	9.9 ± 0.10 1.04%	6.5 ± 0.06 0.87%	4.0 ± 0.06 1.49%	1.27	1.00	0.81	0.60
Chlorodifluoromethane, R-22	474.2 ± 3.78 0.86%	201.6 ± 2.16 1.07%	101.3 ± 0.89 0.88%	52.4 ± 0.62 1.48%	2.68	2.31	2.01	1.72
Trifluoromethane, R-23	38.5 ± 0.41 1.05%	20.5 ± 0.32 1.55%	12.1 ± 0.11 0.88%	7.4 ± 0.11 1.49%	1.59	1.31	1.08	0.87
Difluoromethane, R-32	46.5 ± 0.63 0.74%	23.6 ± 0.26 1.11%	12.5 ± 0.16 1.31%	8.3 ± 0.06 0.77%	1.67	1.37	1.10	0.92
Chloromethane, R-40	413.8 ± 4.16 1.00%	179.7 ± 2.20 1.22%	91.0 ± 0.79 0.86	47.3 ± 0.14 0.70%	2.62	2.26	1.96	1.68
Fluoromethane, R-41	30.1 ± 0.15 0.51%	16.6 ± 0.24 1.42%	10.0 ± 0.08 0.85%	6.3 ± 0.09 1.48%	1.48	1.22	1.00	0.80

	V_N^0 (ml)				$\log (V_N^0)$			
	40°C (313.15 K)	60°C (333.15 K)	80°C (353.15 K)	100°C (373.15 K)	40°C (313.15 K)	60°C (333.15 K)	80°C (353.15 K)	100°C (373.15 K)
Trichlorofluoromethane, R-11	774.3 ± 2.3 0.30%				2.89			
Dichlorodifluoromethane, R-12	149.2 ± 1.3 0.86%				2.17			
Dichlorofluoromethane, R-21	309.8 ± 4.72 1.52%	156.9 ± 1.18 0.75%	87.6 ± 0.57 0.65%	51.3 ± 0.82 1.60%	2.49	2.20	1.94	1.71
Methane, R-50	17.54 ± 0.01 0.05%				1.24			

The uncertainties cited are propagated from replicate measurements of the experimental parameters.

variation in percent is provided. The uncertainty of the measurements is generally between 0.5 and 1.5%, with the average precision of all the measurements being 1.04%. This figure compares very well with the precision of typical measured retention parameters (generally between 1 and 2%) obtained in other physico-chemical gas chromatographic studies [15]. A plot of $\log (V_N^0)$ against $(1/T)$ is provided in Fig. 1. These temperature-dependent data were then fit with the best linear model (simple linear, logarithmic, power or exponential) [16]. The results of these fits are provided in Table 3. Included with each fluid are the coefficients, the Pearson correlation coefficient of the fit, and the temperature range over which the fit was taken.

Most of the measurements are represented very well (within experimental error) with the simple linear model:

$$\log (V_N^0) = m/T + b \qquad (6)$$

where m is the slope and b is the intercept. In one instance, with difluoromethane (R-32), the power model was slightly better able to account for all of the structure in the data, and therefore provides a somewhat more accurate representation of the measurements. The form of this model is:

$$\log^2 (V_N^0) = m[\log (1/T)] + b \qquad (7)$$
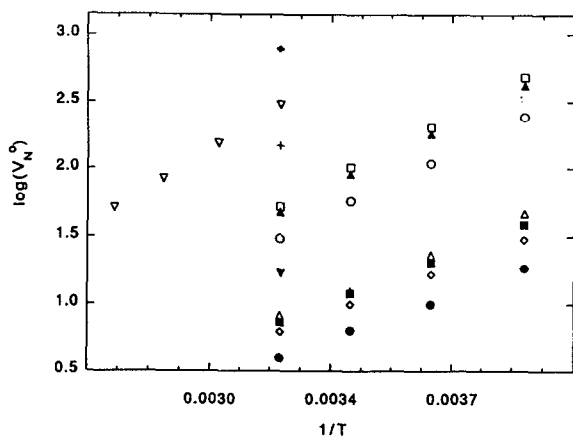
where m is the slope and b is the intercept. To

Fig. 1. A plot of the logarithm of the net retention volume, $\log(V_N^0)$, against $1/T$, for each fluid. $\bigcirc$ = R-13, $\bullet$ = R-14, $\square$ = R-22, $\blacksquare$ = R-23, $\triangle$ = R-32, $\blacktriangle$ = R-40, $\Diamond$ = R-41, $\blacklozenge$ = R-11, $+$ = R-12, $\triangledown$ = R-21, $\blacktriangledown$ = R-50.

recover the V_N^0 value from this model, one must take the antilogarithm (that is, 10^x) twice.

The relative retentions, $r_{a/b}$, were calculated with tetrafluoromethane (R-14) as the reference. This fluid was chosen because it is the least retained of all the fluids examined. These results are summarized in Table 4, along with their respective common logarithms. A plot of $\log(r_{a/b})$ against $1/T$ is provided in Fig. 2. The expected trend with temperature is observed,

and the plot and fits can be used for prediction of retention behavior on other columns containing the same stationary phase.

In addition to the quantitative relationships and correlations presented above, the retention parameters we have measured appear to fit an important qualitative scheme that is useful in understanding the behavior of chlorofluorocarbons and fluorocarbons. One can construct a kind of "periodic chart" or property diagram for these types of compounds. The chart has a triangular format that groups the fluids according to their molecular structures and properties. We present in Fig. 3 such a chart for one-carbon fluids. The top of the chart represents compounds rich in hydrogen (with methane the extreme member); the right-hand side represents compounds rich in fluorine (with tetrafluoromethane being the extreme member); and the left-hand side represents compounds rich in chlorine (with carbon tetrachloride being the extreme member). Such charts have been successful in systematizing, in a semiquantitative manner, properties such as normal boiling point, atmospheric lifetime, flammability, and toxicity [2]. The retention parameters measured in this study fit this scheme qualitatively, with expected minima in the fluorine-rich section, and expected

Table 3
Coefficients of the fits of $\log(V_N^0)$ against $1/T$, with the respective correlation coefficients

Name	m	b	r	Temperature range
Chlorotrifluoromethane, R-13	1176.28	−2.26	0.99981	−20–40°C
Tetrafluoromethane, R-14	860.50	−2.14	0.99919	−20–40°C
Dichlorofluoromethane, R-21	1518.77	−2.36	0.99998	40–100°C
Chlorodifluoromethane, R-22	1256.10	−2.29	0.99986	−20–40°C
Trifluoromethane, R-23	948.39	−2.16	0.99995	−20–40°C
Difluoromethane, R-32	2.83	7.04	0.99932	−20–40°C
Chloromethane, R-40	1243.33	−2.29	0.99979	−20–40°C
Fluoromethane, R-41	896.44	−2.06	0.99998	−20–40°C

Note that for difluoromethane, R-32, the coefficients are for the power model rather than the simple linear model.

Table 4
Relative retentions, $r_{a/b}$, of each fluid with respect to tetrafluoromethane, R-14

Name	$r_{a/b}$				$\log(r_{a/b})$			
	−20°C (253.15 K)	0°C (273.15 K)	20°C (293.15 K)	40°C (313.15 K)	−20°C (253.15 K)	0°C (273.15 K)	20°C (293.15 K)	40°C (313.15 K)
Chlorotrifluoromethane, R-13	13.23	11.00	8.82	7.73	1.12	1.04	0.95	0.89
Dichlorofluoromethane, R-21	*281.94*	*183.53*	*97.90*	77.45	2.45	2.26	1.99	1.89
Chlorodifluoromethane, R-22	25.77	20.36	15.58	13.10	1.41	1.31	1.19	1.12
Trifluoromethane, R-23	2.09	2.07	1.86	1.85	0.32	0.32	0.27	0.27
Difluoromethane, R-32	2.53	2.38	1.92	2.08	0.40	0.38	0.28	0.32
Chloromethane, R-40	22.49	18.15	14.00	11.83	1.35	1.26	1.15	1.07
Fluoromethane, R-41	1.64	1.68	1.54	1.58	0.21	0.23	0.19	0.20

The values in italics were calculated from the fit from 40–100°C data.

maxima predicted to occur in the chlorine-rich section. This chart can provide guidance in the design of analyses of (1) compounds not measured in this study, and (2) analyses done with somewhat different modifier concentration on the stationary phase.

5. Conclusions

Measurements of the corrected net retention volume and relative retentions of eight halocar-
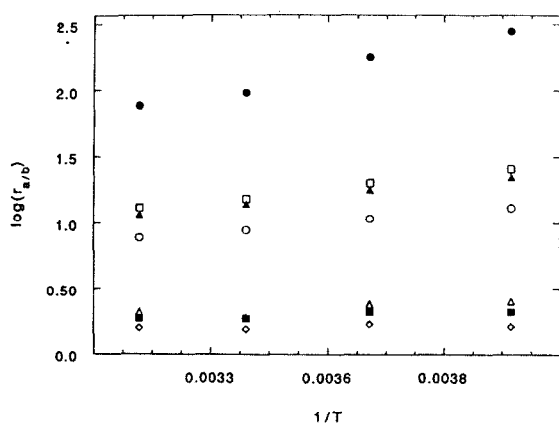
bons relevant to research on alternative refrigerants have been presented. The logarithms of these data were fitted against reciprocal thermodynamic temperature to several linear models. In most cases, a simple linear relationship accounts for all structure in the data; in one case, a power model is slightly better. These derived equations can be used for the prediction of the retention behavior of these fluids on this important stationary phase (hexafluoropropylene epoxide modified graphitized carbon black), and therefore can be used for solute identification and analytical

Fig. 2. A plot of the logarithm of the relative retention, $\log(r_{a/b})$, with respect to tetrafluoromethane, against $1/T$. $\bigcirc$ = R-13, $\bullet$ = R-21, $\square$ = R-22, $\blacksquare$ = R-23, $\triangle$ = R-32, $\blacktriangle$ = R-40, $\diamond$ = R-41.
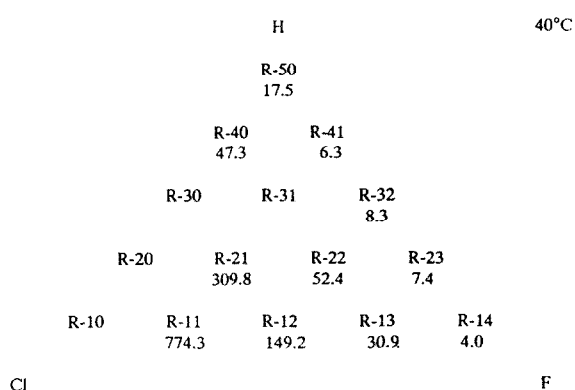
Fig. 3. A triangular diagram that provides a semiquantitative representation of refrigerant properties correlated with molecular structure. In this diagram, we have listed the net retention volumes (ml), V_N^0, for each of the indicated fluids measured at 40°C (313.15 K).

separation design. In addition, we note that the retention parameters also fit the triangular diagram scheme that successfully describes the normal boiling point, flammability, atmospheric lifetime and toxicity of these compounds.
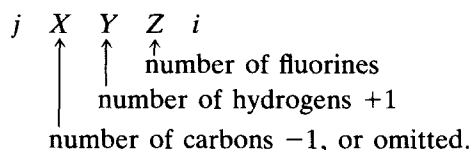
6. Acknowledgements

7. Appendix

The code numbering system used for the systematic designation of refrigerant fluids and related products follows the appropriate ANSI/ASHRAE standard [17]. The code number is built up from the right-hand side of the designation.

Refrigerant numbering:

$$j \quad X \quad Y \quad Z \quad i$$

$\uparrow$ $\uparrow$ $\uparrow$ number of fluorines

number of hydrogens +1

number of carbons −1, or omitted.

where X = number of carbons − 1, or omitted; Y = number of hydrogens + 1; Z = number of fluorines. Number of chlorines = [2 + 2(number of carbon bonds)] − (F + H) − 2(number of double bonds); i = isomer designation: a, b . . . ; j = cyclic designation, C; ether designation, E; or else it is omitted.

For example, R-152a:

$$H - \overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}} - CH_3$$
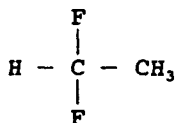
1. The first digit on the right is the number of fluorine atoms on the molecule. When there are no fluorines on the molecule, such as in methylene chloride, a zero is assigned to this position as a place-holder.
2. The second digit from the right is one more than the number of hydrogen atoms on the molecule.
3. The third number from the right is one less than the number of carbon atoms in the compound. When this digit is zero, as in the case of methane-based fluids, it is omitted.
4. The number of chlorines is found by subtracting the sum of the number of fluorine and hydrogen atoms from the total of the number of atoms that can be connected to the carbon atoms. 5. For cyclic compounds, an upper case C is placed before the identifying number.
6. In those instances where bromine is present, the same rules apply except that the upper case letter B after the number for the parent refrigerant shows the presence of bromine. The number to the right of the B indicates the number of bromine atoms present. When isomers of brominated compounds exist, the position of the bromine atoms are indicated by the Greek letters α and β. The Greek letters indicate the carbon atoms of the backbone chain, starting from the end carbon having the largest sum of atomic masses bonded to it. If more than one bromine is bonded to the same carbon, the Greek letter identifying that carbon is repeated for each bromine atom. It should be noted that the isomerization of brominated compounds is not explicitly addressed in the ANSI/ASHRAE standard 34-1992. The extension of this system of nomenclature to include bromine isomers according to the format presented here is very commonly used, however.
7. In the case of ethane-based isomers, each isomer carries the same number. The different isomers are then indicated by appending lower case a, b, c, etc., to the extreme right-hand side of the code. The most symmetrical isomer does not have a letter appended. The letters are appended to the isomers as they become more and more unsymmetrical. The symmetry is determined by adding the atomic masses of the atoms bonded to each carbon, and subtracting one sum from another.
8. Unsaturated compounds are indicated by a

the fourth number from the right, which indicates the number of double bonds.

9. The code number generated by rules 1–8 is prefixed with a letter or name. The preferred prefix in the standard is R (or R- or Refrigerant) (*e.g.*, R134a, R-134a, or Refrigerant 134a). The use of composition-designating prefixes is also allowed (*e.g.*, CFC-12, HCFC-22, HFC-134a).

10. For compounds that contain an ether linkage (–O–), rules 1–8 are applied as they would be in the absence of oxygen. The presence of the ether linkage is then indicated by the code number being preceded by an upper case E. For example, bis(difluoromethyl) ether, E-134:

$$
\begin{array}{ccccc}
 & F & & F & \\
 & | & & | & \\
H - & C & - O - & C & - H \\
 & | & & | & \\
 & F & & F &
\end{array}
$$
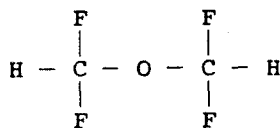
The extension to ethers is not part of the ANSI/ASHRAE standards; at present there is no standard (or even unofficial method) for designating isomers with more than two carbons.

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