

Gas chromatographic retention parameters database for refrigerant mixture composition management

Thomas J. Bruno*, Gregory M. Bachmeyer and Kelly H. Wertz¹

Physical and Chemical Properties Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Boulder, CO 80303, USA

Composition management of mixed refrigerant systems is a challenging problem in the laboratory, manufacturing facilities, and large refrigeration machinery. The issue of composition management is especially critical for the maintenance of machinery that utilizes zeotropic mixtures as working fluids. These are fluids in which the gas and liquid phases will generally have greatly different compositions. While there are many analytical techniques available for laboratory and on-line analyses, gas chromatography probably offers the greatest flexibility at the most reasonable cost. This paper describes a chromatographic database that provides for the identification of refrigerant components, and thereby facilitates composition management of zeotropic fluids. Prior to the description of the database is a description of the basic theory of chromatographic retention parameters and a description of the experimental techniques used in their measurement. © 1998 Elsevier Science Ltd and IIR. All rights reserved.

(Keywords: refrigerant; zeotropic mixtures; chemical composition; chromatography)

Base de données des paramètres de rétention en chromatographie gazeuse pour la gestion des mélanges de frigorigènes

La gestion des systèmes frigorifiques utilisant un mélange de frigorigènes est un défi dans le laboratoire, dans les installations de fabrication et dans des installations frigorifiques de grande taille. La gestion de la composition est particulièrement critique dans l'entretien des systèmes utilisant des mélanges non-azéotropiques comme fluides actifs. La composition des phases gazeuses et liquides de ces fluides est en général très variable. Il existe un bon nombre de techniques analytiques dans le laboratoire et en direct, mais la chromatographie gazeuse offre la plus grande souplesse au coût le plus raisonnable. Cet article décrit une base de données chromatographie qui permet l'identification des composants de frigorigènes, ce qui facilite la gestion de la composition des fluides non-azéotropiques. Avant de décrire la base de données elle-même, les auteurs décrivent la théorie de base des paramètres de rétention et les techniques expérimentales utilisées pour les obtenir. © 1998 Elsevier Science Ltd and IIR. All rights reserved.

(Mots clés: frigorigène; mélange zéotrope; composition chimique; chromatographie)

Introduction

Gas chromatography (GC) is one of the major quantitative analysis and qualitative identification methods that are applied to the study of alternative refrigerants and

related products. This stems from many important aspects of GC, not the least of which are simplicity, reliability, and economics of operation^{1,2}. A knowledge of the retention characteristics of important fluids on the more useful stationary phases is a valuable tool in the design of effective qualitative and quantitative chromatographic analyses. We have found that one of the best stationary phases for the analysis of alternative

* Corresponding author

¹ Present address: Hewlett Packard Corporation, 16339 West Bernardo Drive, San Diego, CA 92127, USA.

refrigerants and related fluids is a packed column of a 5% coating of hexafluoropropylene epoxide on graphitized carbon black. When applied to in-the-field instrumentation and on-line sensors on the plant floor, chromatographic retention can form the basis of an effective composition management strategy for working fluid application and manufacture. This is especially important for zeotropic fluids, in which the vapor and liquid compositions will usually be very different. The fluids that concern us in this respect include not only potential working fluids for heating, ventilation, air-conditioning, and refrigeration (HVAC and R) cycles, but also known synthetic precursors and potential decomposition reaction/decomposition products of these fluids.

Corrected retention parameters, such as the net retention volume, V_N , the adjusted net retention volume, V_N^0 (corrected to a column temperature of 0°C), and relative retentions, r_{alh} , provide the simplest avenue to achieving reliable qualitative identification by gas chromatography. In earlier work, we have presented such measurements as a function of temperature for many of the most important fluids³⁻¹⁰. These fluids are not only refrigerant mixture components, but also synthetic precursors and potential decomposition products. We have also presented some relevant experimental techniques that can be applied to gathering such measurements¹¹. In this paper, we present information on the development, structure, and application of an interactive database that contains retention parameters and relative response factors of alternative refrigerants and related compounds.

Theory

The typical chromatographic integrator (or chromatographic software package for a computer) will report, among many possible analytical parameters, the retention time, t_r , of each eluted 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):

$$V_R' = V_R - V_M \quad (1)$$

While it is possible to calculate the corresponding adjusted retention time, t_r' , by subtracting the retention time of the unretained peak, t_m , it is better to work with volumes since average flow rate variations between individual analyses are then taken into account.

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

$$V_N = jV_R' \quad (2)$$

where j is usually the Martin-James compressibility

factor:

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

In eqn (3), P_i is the inlet pressure (absolute) and P_o is the outlet pressure (usually atmospheric). The specific retention volume, V_g , corrects the net retention volume for the amount of stationary phase actually on the column, and the column temperature is adjusted or corrected to 0°C:

$$V_g = (273.15) \frac{V_N}{(W_s T_{col})} \quad (4)$$

In eqn (4), T_{col} is the column temperature, and W_s is the weight of stationary phase in the column. The specific retention volume 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 or a well-characterized mixture. If the weight of stationary phase is not known, or is not meaningful, one may use the net retention volume directly. Alternatively, one may 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).

It is also extremely valuable to calculate a relative retention, r_{alh} :

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

where the superscripts refer to the retention volumes of solutes a and b . In this case, solute a is a reference compound. 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. It can account for small differences in column temperature, stationary phase considerations, column history, and minor disturbances in carrier gas flow rate.

To extend the applicability of the retention parameters presented thus far, it is possible to account for column temperature by plotting the logarithm of the retention parameters against $1/T$, where T is the thermodynamic temperature of the column (and thus, the stationary phase). Column pressure is accounted for by variations in the volume measurement; therefore, there is no pressure dependence considered in these measurements. It is nonetheless of value to perform at least some measurements at several pressures to verify that the instrumentation is functioning properly. This will be reflected in the recovery of the same value for the retention parameter at each pressure.

The isothermal Kovats retention index goes beyond these simple retention parameters to incorporate a

logarithmic interpolation on a uniform scale¹⁰:

$$I_{\text{sample}}^{\text{st. phase}}(T) = 100 \left[\frac{\log X_S - \log X_L}{\log X_H - \log X_L} + n_L \right] \quad (6)$$

In the above equation, the value of the dimensionless retention index is represented by I . Since I is a function of both the temperature and the stationary phase employed, proper notation of I requires the specification of the sample name, stationary phase, and temperature. The terms represented by X are retention parameters of the sample and standards, as we will discuss fully below. The retention parameters that can be employed for X in eqn (6) above include all of the simple ones described earlier (t_r' , V_N , V_N' , V_E , r_{ab}). Following this convention, X_S is the retention parameter of the sample under consideration, X_L is the retention parameter of a normal alkane (that is, straight chain or unbranched) of carbon number n_L that elutes earlier than the sample, and X_H is the retention parameter of a normal alkane having a carbon number $n_L + 1$ that elutes after the sample. The retention index of a sample is, therefore, 100 multiplied by the carbon number of a hypothetical normal alkane that shows the same retention parameter on the stationary phase at that temperature. Thus, a sample that has a retention index of 785, for example, would coelute with a hypothetical normal alkane that has 7.85 carbon atoms.

By definition, the retention indices of the normal alkanes (on any stationary phase) are equal to 100 multiplied by the carbon number. Thus, for n -hexane, $I = 600$, and so on for the others in this homologous series. The zero point in the scale is defined for hydrogen, for which $I = 0$. For temperature programmed analyses, an expression similar to that in eqn (6) is employed, with the major difference being the replacement of the logarithms of the retention parameters in the X terms with emergent retention temperatures (the temperature at which the apex of the peak emerges from the column). It is possible to relate the isothermal and temperature programmed retention indices, a fact that greatly enhances the value of retention indices in qualitative analysis. Retention indices measured with the same stationary phase in both a capillary and a packed column will show differences. This is primarily due to differences in the onset, magnitude, and thermal behavior of adsorption phenomena.

The great utility of the retention index as a method of chromatographic identification is well known, and a number of large databases have been developed to exploit the retention index approach¹². The value of this method can be greatly expanded by a knowledge of the temperature dependence of I . It is known that this temperature dependence follows a hyperbolic form similar to the familiar Antoine equation used to represent vapor pressure¹⁰:

$$I_{\text{sample}}^{\text{st. phase}} = A + \frac{B}{T + C} \quad (7)$$

In this equation, A , B , and C are empirically determined constants, and T is the thermodynamic temperature of the column. When enough data are available, it is best to

determine these constants with a nonlinear fitting routine. The fitted value for A (that results from the nonlinear routine) approximates the mean value of the retention indices over the temperature range studied, while B and C provide the corrections needed to describe the structure of the data with respect to temperature.

A plot of retention index against temperature will often show a significant linearity. It is therefore also of value to report the temperature dependence as a slope coefficient, $\delta I/10^\circ\text{C}$, the variation of I for a sample on a particular stationary phase over a temperature change of 10°C ^{4-6,9,7,8}. When $\delta I/10^\circ\text{C}$ is reported, it is important to also report the temperature range over which the measurements are available, or the range over which linearity is observed to persist. The most commonly observed temperature dependence of the retention index is a slight to moderate increase in I with temperature¹¹⁻²¹. There are many instances, however, in which the slope is observed to be negative, and I decreases with temperature²¹. This has been the case with many halocarbon compounds.

The major source of uncertainty in retention parameters, especially when compared laboratory-to-laboratory, can be traced to the stationary phase. Some important considerations include stationary phase stability (chemical and physical), history (including such factors as oxygen exposure and water uptake), batch-to-batch coating nonuniformity, and the bleeding of volatile constituents from the stationary phase. The presence of active adsorptive sites on a support surface or capillary wall can be especially problematic. Adsorption isotherms of chromatographic sorbents are often highly nonlinear and not reproducible, and will show significant batch-to-batch differences. The supports used for packed columns should be as nearly inert as possible, and stationary phase coating thicknesses large enough to cover the most active sites must be applied. In general, Gibbs surface adsorption¹⁰ can be minimized by the use of as small a sample size as possible (that is, samples in the infinite dilution region), where the retention is independent of sample size.

Another consideration is the compatibility of the stationary phase and the solute. Polar solutes measured on nonpolar stationary phases, and nonpolar solutes measured on polar stationary phases are very often problematic. Related to this is the problem of solvent sensitivity, in which solvents that are incompatible with the stationary phase must be avoided.

For quantitative analysis, the analyst must apply a calibration to the raw detector response. The raw data used for quantitation are usually the integrated area of the chromatographic peak, but on rare occasions, the peak height is used. The simplest approach to quantitation is to measure relative response factors for each fluid of interest on appropriate detectors. One then applies for an n -component mixture:

$$\%A = \frac{A/F}{\sum_{i=1}^n A_i/F_i} \quad (8)$$

where %*A* is the corrected area percent of component *A* (the compound of interest), *A* is the total area of compound *A* having response factor *F*, and *A_i* and *F_i* are the areas and response factors, respectively, of all the components of the mixture.

Experimental

The measurements discussed 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 two 1.9 cm thick, 10 cm square copper plates surrounding (but not in contact with) the column to provide additional thermal mass for temperature stability. Additional insulation (in the form of mineral wool board and bubble wrap) was placed in appropriate locations around the oven compartment to further decrease heat flux into and out of the apparatus. The oven temperature was measured with a quartz-crystal oscillator thermometer (calibrated against a NIST standard platinum resistance thermometer) that had an uncertainty of $\pm 0.01^\circ\text{C}$. Injection was done with a syringe (either a liquid- or a gas-tight syringe) for less volatile fluids or with a thermostatted gas sampling valve (containing a sample loop of 0.05 mL volume) for the fluids that are gaseous at ambient temperature and pressure. The samples injected by syringe were introduced into a heated flash vaporization inlet maintained at 175°C . Samples were always injected individually and at infinite dilution to avoid the difficulties caused by nonuniform bracketing and Gibbs surface adsorption.

In order to correct for the gas holdup time, a quantity of air was injected as a minimally retained marker for each sample. In the case of the samples injected by syringe, air was injected with the sample. In the case of the samples injected by the sampling valve, five air injections were made before and five after the samples were injected.

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. The column outlet pressure was measured with an electronic barometer that had a resolution of 1.3 Pa (approximately 0.01 Torr). The column carrier gas flow rate was measured with a thermostatted electronic soap film flowmeter. Retention times were measured by a commercial integrator, which also provided a measure of peak quality. In general, only Gaussian-like (that is, highly symmetrical with no discernable tailing) peaks were considered acceptable.

Thermal conductivity detection (TCD) was used with a carrier gas of research grade helium. The helium was passed through oxygen and water traps before entering a thermostatted mass flow controller and finally the electronic pressure controller of the chromatograph. This was done to provide a highly uniform flow rate of high purity helium that would not cause stationary phase decomposition or degradation.

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 (Krytox 143 AC, E.I. duPont de Nemours and Co., Inc.²) on a 60/80 mesh carbon molecular sieve (Supelco)¹¹. This packed column was chosen for these measurements because field samples of alternative refrigerants commonly have acid gases such as hydrogen fluoride as impurities. This stationary phase is one of the few that is stable to routine exposure to such corrosive materials. A column was prepared by packing the phase into a cleaned, 2 m long section of copper tubing (0.65 cm outside diameter) plugged with sections of silanized Pyrex wool. Copper was chosen for the standard measurements because of its high thermal conductivity and thermal mass. The column was conditioned for 4 h in the chromatograph (not connected to the detector) by equilibration at 100°C with a gentle flow (between 3 and 6 mL min⁻¹) of helium carrier gas.

For each retention time measurement, five fluid injections were performed for each sample at each column temperature. The retention time of the sample was corrected for the gas holdup time by simply subtracting the air retention time from that of the sample. The carrier gas flow rate at the column exit was maintained at 45 ± 0.4 mL min⁻¹. Measurements were performed on at least four isotherms for each fluid, and the temperatures were chosen to minimize retention time uncertainty and to provide Gaussian-like peaks⁴⁻¹⁰.

For the measurement of relative response factors, the same instrumentation used for retention measurements was used to measure thermal conductivity integrated area counts for constant mass injections. These injections were done with the fixed volume gas sampling valve.

The uncertainty of the measurements of relative retention of all the compounds studied, at all temperatures, was approximately 0.6%⁴⁻⁹. The Kovats retention indices showed an overall standard deviation (with a coverage factor $k = 2$) of 0.54 retention index units¹⁰. This represents a coefficient of variation of between 0.1 and 0.3%. The overall uncertainty of the relative response factors is 0.2%. The values of the Kovats index that were fitted showed an average deviation from the experimental values of 0.26 retention index units¹⁰.

Chromatographic database

The relative retention and Kovats retention index information described in the theory section have been measured as a function of temperature for the fluids listed in Table 1, on the stationary phase described in the experimental section. Predictive models were developed for each parameter, which were assembled into an interactive database that provides assistance in fluid identification and analytical method development.

²Certain commercial equipment, instruments, or materials are identified in this paper to adequately describe the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment, instruments, or materials are the best available for the purpose.

Table 1 List of fluids included in the database

Tableau 1 Liste des fluides dans la base de données

trichlorofluoromethane, R-11	1,1,2-trichloro-1-fluoroethane, R-131a
dichlorodifluoromethane, R-12	1,2-dichloro-1,1-difluoroethane, R-132b
iodotrifluoromethane, R-13I,1	2-chloro-1,1,1-trifluoroethane, R-133a
chlorotrifluoromethane, R-13	1,1,2,2-tetrafluoroethane, R-134
tetrafluoroethane, R-14	1,1,1,2-tetrafluoroethane, R-134a
dichlorofluoromethane, R-21	1,2-dichloro-1-fluoroethane, R-141
chlorodifluoromethane, R-22	1,1-dichloro-1-fluoroethane, R-141b
trifluoromethane, R-23	1-chloro-1,1-difluoroethane, R-142b
difluoromethane, R-32	1,1,2-trifluoroethane, R-143
chloromethane, R-40	1,1,1-trifluoroethane, R-143a
fluoromethane, R-41	1,2-difluoroethane, R-152
1,1,2-trichlorotrifluoroethane, R-113	1,1-difluoroethane, R-152a
1,1,1-trichlorotrifluoroethane, R-113a	1-chloroethane, R-160
1,2-dichlorotetrafluoroethane, R-114	fluoroethane, R-161
1,1-dichlorotetrafluoroethane, R-114a	3,3,3-trifluoropropene, R-1243b
1-bromo-2-chlorotetrafluoroethane, R-114B1	1,2,2-trichloropentafluoropropane, R-215aa
chloropentafluoroethane, R-115	1,2,3-trichloropentafluoropropane, R-215ba
iodopentafluoroethane, R-115f-1	1,2-dichlorohexafluoropropane, R-216ba
hexafluoroethane, R-116	2-chloroheptafluoropropane, R-217ba
1,1,2,2-tetrachlorofluoroethane, R-121	1-bromo-1,1,2,2,3,3,3-heptafluoropropane, R-217caB1
1,2,2-trichloro-1,1-difluoroethane, R-122	1-iodoheptafluoropropane, R-217f-1
2,2-dichloro-1,1,1-trifluoroethane, R-123	3,3-dichloro-1,1,1,2,2-pentafluoropropane, R-225ca
1,2-dichloro-1,1,2-trifluoroethane, R-123a	1,3-dichloro-1,1,2,2,3-pentafluoropropane, R-225cb
2-bromo-2-chloro-1,1,1-trifluoroethane, R-123B1	1,1,1,2,2,3,3-heptafluoropropane, R-227ca
2-chloro-1,1,1,2-tetrafluoroethane, R-124	trifluoroethene, R-1123
pentafluoroethane, R-125	1,1-dichloroethene, R-1130a
1,2,3-trichloro-2-fluoroethane, R-131	cis-1,2-dichloroethene, R-1130c
1,1,1,2,3,3,3-heptafluoropropane, R-227ea	trans-1,2-dichloroethene, R-1130t
1,1,1,2,3,3-hexafluoropropane, R-226ea	1-chloro-1-fluoroethene, R-1131a
1,1,1,3,3,3-hexafluoropropane, R-236fa	1,1-difluoroethene, R-1132a
2,3-dichloro-1,1,1-trifluoropropane, R-243db	bromoethene, R-1140B1
1,1,2,3,3-pentafluoropropane, R-245ca	fluoroethene, R-1141
1,1,1,2,2-pentafluoropropane, R-245cb	1,1,2,2,3,3-hexafluoro oxetane, R-CE216
1,1,1,3,3-pentafluoropropane, R-245fa	pentafluorodimethyl ether, R-E125
3-chloro-1,1,1-trifluoropropane, R-253fb	bis-(difluoromethyl) ether, R-E134
1,1,2,2-tetrafluoropropane, R-254cb	methoxy-1,1,1-trifluoroethane, R-E143a
2-chloro-1,3-difluoropropane, R-262da	2-chloro-1,1,2-trifluoroethyl difluoromethyl ether, R-E235ca2
1,1,1-trifluoropropane, R-263fb	1-chloro-2,2,2-trifluoroethyl difluoromethyl ether, R-E235da1
2,2-dichloropropane, R-270aa	1,2,2,2-tetrafluoroethyl difluoromethyl ether, R-E236ea1
1,2-dichloropropane, R-270da	2-(difluoromethoxy)-1,1,1-trifluoroethane, R-E24fa1
1,3-dichloropropane, R-270fa	2,2,2-trifluoroethyl methyl ether, R-E263fb1
1,1-dichloropropane, R-270fb	2-chloroethyl methyl ether, R-E280
2-chloropropane, R-280da	fluoromethyl-2,2,2-trifluoro-1-(trifluoromethyl)ethyl ether, R-E347
tetrachloroethene, R-1110	
trichlorofluoroethene, R-1111	
1,1-dichloro-2,2-difluoroethene, R-1112a	
cis-1,2-dichloro-1,2-difluoroethene, R-1112c	
trans-1,2-dichloro-1,2-difluoroethene, R-1112t	
chlorotrifluoroethene, R-1113	
1,2,3-trichloroethene, R-1120	
cis-1,2-dichloro-1-fluoroethene, R-1121c	
trans-1,2-dichloro-1-fluoroethene, R-1121t	
2-chloro-1,1-difluoroethene, R-1122	
2-bromo-1,1-difluoroethene, R-1122B1	

Upon starting the database program, the user is provided with a schematic of the chromatograph used for the retention measurements, showing the features that are recommended for halocarbon analysis. The main menu is also provided on this screen. This menu provides buttons to access: (1) an introduction to the database, (2) a listing of appropriate references to the literature upon which the database is based, (3) a database entry search tool, (4) a database entry edit tool, (5) peak search tools, (6) method development tools, and (7) quantitative analysis tools.

Basic features

The introductory screen provides the user with a description of each button on the main menu. These buttons may be clicked on in this screen as well as in the main menu. The final screen of the introduction provides contact points for further information on the database.

Clicking on the references button provides the user with the choice of viewing literature references to experimental data upon which the database is based, or

Relative Retention Calculation (a)

Chemical/Fluid	f _a /f _b	
	R-14	Deviation
1,1-difluoroethane, R-1132a	4.63	-0.03
hexafluoroethane, R-116	5.07	0.40
fluoroethane, R-1141	4.09	-0.59
trifluoroethane, R-1123	5.91	1.24
chlorotrifluoromethane, R-13	6.06	1.39
1,1,1-trifluoroethane, R-143a	6.88	2.22
fluoroethane, R-161	7.37	2.71

Column Temperature: 80 °C

Peak Retention Time or Volume: 7.9 min

Air or Marker Retention Time or Volume: 2.3 min

Retention Time or Volume of R-14: 3.5 min

or/and

Retention Time or Volume of R-116: min

The Relative Retention of the Unknown in Relation to R-14: 4.67

CALCULATE Clear for New Calculation

PRINT Constraints

HELP Net Retention Calculation

EXIT Kovals Retention Index

Kovats Retention Index (b)

Chemical/Fluid	Kovats Retention Index	
	Index	Deviation
2,3-dichloro-1,1,1-trifluoropropane, R-243cb	554.25	0.68
1,1,2-trichloro-1-fluoroethane, R-131a	546.46	-7.11
1,3-dichloropropane, R-270fa	560.88	7.31
1,2-dichloropropane, R-270da	545.13	-8.44
fluoromethane, R-41	542.84	-10.73
1,2,2-trichloropentafluoropropane, R-215aa	564.43	10.86
1,2,2-trichloro-1,1-difluoroethane, R-122	542.25	-11.32
1,1-dichloropropane, R-270fb	542.21	-11.36

Column Temperature: 90 °C

Peak Retention Time or Volume: 13.7 min

Lower N-Alkane Retention Time or Volume: 11.6 min

Upper N-Alkane Retention Time or Volume: 15.9 min

Air or Marker Retention Time or Volume: 2.3 min

Carbon Number of Lower n-Alkane: 5

Kovats Retention Index for Unknown: 553.57

CALCULATE Clear for New Calculation

PRINT Constraints

HELP Net Retention Calculation

EXIT Relative Retention Calculation

Figure 1 (a) A reproduction of the relative retention calculation window, showing some sample data and results; (b) a reproduction of the Kovats retention index window, showing some sample data and results

Figure 1 (a) *Reproduction de la fenêtre de la rétention relative, avec un échantillon de données et de résultats; (b) reproduction de la fenêtre des indices de rétention de Kovats, avec un échantillon de données et de résultats*

references to the more unique aspects of the experimental techniques that were developed for or used in performing the measurements.

The database search tool allows the user to view essential physical property and spectroscopic information for each of the fluids listed in *Table 1*. The physical property screen includes basic thermal properties such as the normal boiling temperature, critical parameters, dipole moments, refractive indices, and chemical solubilities. In addition to these data, this screen also includes information for the safe handling of the fluid, including the flammable limits (if appropriate), threshold limit values, a brief description of the known toxicology, and any major known chemical incompatibilities. The user is then able to retrieve the mass spectrum (in tabular form and as a mass/charge histogram) and the infrared spectrum of the fluid. In some cases, both gas and liquid phase infrared spectra are provided.

The database entry edit tool is primarily intended to allow the users to enter data for new compounds, and to revise existing data on the basis of updates and/or results from their own measurements.

Chromatographic calculations

The most important part of the database is that which

provides the user with a chromatographic peak find-and-match capability, and with method development assistance (when using the stationary phase described in the experimental section). The quantitative analysis tool provided is, of course, independent of the stationary phase employed, and will work for all applications involving the thermal conductivity detector.

The *peak find-and-match* function is activated by clicking on the peak search button, which then allows the user to work with net retention volumes, relative retentions, and Kovats retention indices. For analytical purposes, the best parameters to work with are the relative retentions and the Kovats retention indices. Net retention volumes are best suited for calculations of thermodynamic functions.

For relative retention calculations, depicted in *Figure 1a*, the users are asked for the column temperature used for their analyses (which is constrained only by the limits of the stationary phase), the column holdup time (or volume), the peak retention time (or volume), and the retention time (or volume) for one or more reference compounds. At present, reference compounds are limited to R-14 and R-116. The program then calculates the relative retention, and matches that value with what would have been obtained under the experimental conditions of our measurements. A listing

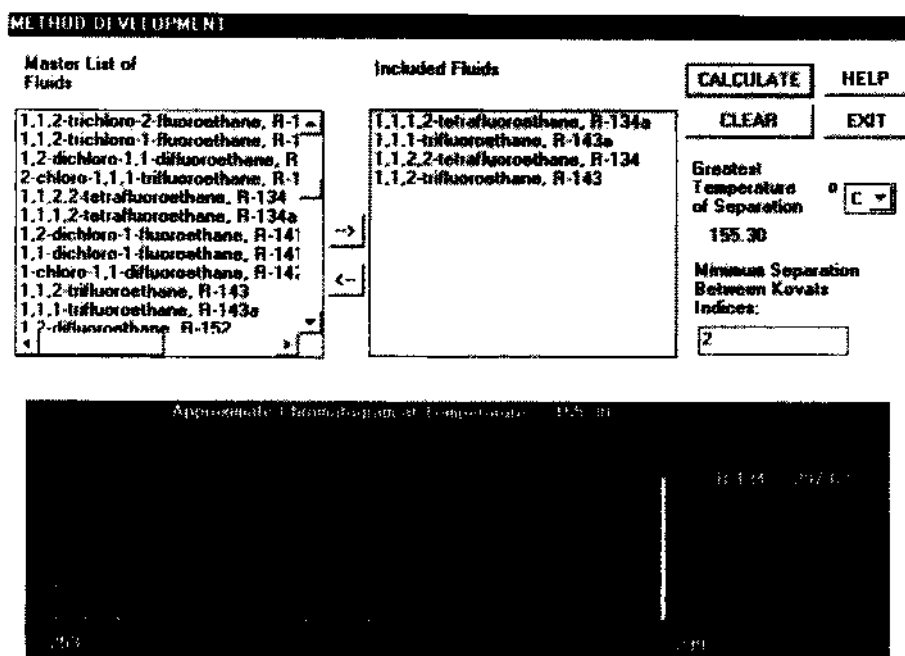


Figure 2 A reproduction of the methods development window, in which a hypothetical mixture has been constructed, and for which the database has calculated a maximum separation temperature, and provided a graphical representation of the retention indices of the components

Figure 2 Reproduction de la fenêtre du développement des méthodes dans laquelle un mélange théorique a été préparé; la base de données a permis de calculer la température de séparation maximale pour ce mélange et montre une représentation graphique des indices de rétention des composants

is provided that includes the relative retentions of all compounds in the database (at the user's column temperature), and the deviations (in units of relative retention) of these relative retentions with those of the user's compound.

For calculations based on Kovats retention indices, depicted in *Figure 1b*, the user is asked for the retention times (or volumes) for the upper and lower *n*-alkanes, and the carbon number of the lower *n*-alkane, in addition to column temperature and peak and marker retention times (or volumes). The program then calculates the Kovats retention index (using correlations based upon eqn (7) of the user's compound) and provides the same match table as is provided with the relative retention calculation.

With all of the peak find-and-match screens (net retention volume, relative retention, and Kovats retention index methods), it is a simple matter to repeat the calculations for different peaks or at different column temperatures. The results from each calculation may be printed from each window. Conversion between methods is also a simple matter, as is the return to the main menu window. Since the user's column temperature must be entered for each calculation, the program will advise the user if the temperature that has been entered is physically reasonable and within the limits of the stationary phase.

It is important to note that the retention parameter measurements upon which this program is based were performed at infinite dilution. Users must be aware of the possibility that the sample size can change retention parameters. Such sample size effects are well known, and are minimized at infinite dilution of the solute.

The *methods development* function, depicted in *Figure 2*, allows the user to develop a list of up to 20 components for which a chromatographic separation is desired. The compounds are chosen by highlighting the entries in a window that lists all of the compounds shown in *Table 1*. The selected compounds are clicked into the methods development list window. The user then selects the desired minimum degree of separation of the compounds. At present, this is done by entering a value of the Kovats retention index difference that is required (or could be tolerated) between each component. At this point, the program will calculate the highest isothermal column temperature at which the desired separation is possible. In addition, a graphical representation of the separation, in units of *I*, is then displayed in another window.

Some discussion about the desired degree of separation is in order. If the user selects a minimum separation of, for example, 1 retention index unit, the resulting peaks are close together, thus minimizing analysis time.

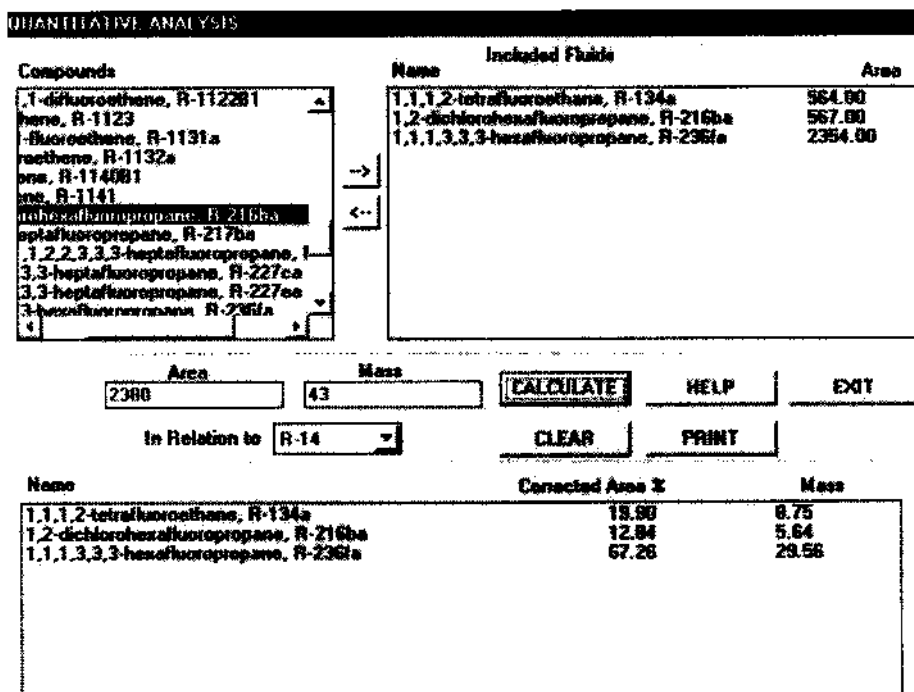


Figure 3 A representation of the quantitative analysis window, in which a hypothetical mixture has been constructed, and for which a quantitative analysis calculation has been performed

Figure 3 Représentation de la fenêtre d'analyse quantitative, dans laquelle un mélange théorique a été préparé et pour lequel on a effectué de l'analyse quantitative

Selecting a value of 30 units forces the program to impose a much greater degree of separation between components, which would require a lower temperature and a longer analysis time. Prediction of separation on the basis of Kovats retention index is somewhat unusual, but a look at the temperature dependence of these values shows that it is in fact very effective as a first approximation¹⁰. Naturally, this approach considers only thermodynamic factors that affect separation. Kinetic factors that influence peak width and shape are not considered in this approach. Work on incorporating peak widths (on important stationary phases) into the separation criteria is ongoing.

For many of the fluids listed in *Table 1*, relative response factors for the thermal conductivity detector (TCD) have been determined with respect to R-14 and R-116. This allows the users to perform *quantitative analysis calculations* based only on their measurement of the peak area(s) of the mixture constituent components and a reference compound (either R-14 or R-116). The use of this feature is similar to that of the methods development window. The user is provided with a window containing a listing of the compounds for which relative response factors have been determined. The compounds of interest are highlighted and clicked into the quantitation list window. The integrated area of each peak is entered, and then the area of the reference compound is entered. The resulting calculation provides a listing of the corrected area percents of each compound on the quantitation list. The results of a sample calculation are shown in *Figure 3*.

The response factor measurements were performed by injecting equal volumes of the sample and reference compound. Significant departures from this measurement technique could result in changes in the response factors because of detector nonlinearity.

The database described in this paper will be available through the National Institute of Standards and Technology (Physical and Chemical Properties Division) and the Environmental Protection Agency (National Risk Management Research Laboratory, Air Pollution Prevention and Control Division).

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Simulation of the transient response of heat driven refrigerators with continuous temperature control

J. V. C. Vargas^{a,*}, I. Horuz^b, T. M. S. Callander^c, J. S. Fleming^d
and J. A. R. Parise^e

^aDept. of Mech. Engineering, Universidade Federal do Paraná,
Curitiba, PR 81531-990, Brazil

^bDept. of Mech. Engineering, Uludag Universitesi, 16059,
Gorukle/Bursa, Turkey

^cDept. of Design Mf. Eng. Mng., University of Strathclyde,
Glasgow G1 1XJ, UK

^dDept. of Mech. Engineering, University of Strathclyde,
Glasgow G1 1XJ, UK

^eDept. of Mech. Engineering, Pontificia Universidade Católica,
Rio de Janeiro, RJ 22453-900, Brazil

A theoretical and experimental study is presented and a mathematical model is introduced for a heat driven refrigeration system operating with continuous temperature control. The model consists of a refrigerated space, an absorption refrigerator, operating irreversibly, a temperature sensor and a reference signal, and a power law control action. The steady-state behavior of the absorption refrigerator model is validated by direct comparison between theoretical results and experimental data. The model is then used to identify an optimal thermal conductance allocation, for a fixed total thermal conductance inventory, such that the refrigeration rate is maximized and the 'pull-down' time is minimized. A simulation of the system operating in a transient mode is carried out to show that closed-loop operation results in a large reduction of fuel consumption, with respect to the 'on-off' operation. Appropriate dimensionless groups are identified and the generalized results reported in charts using dimensionless variables. © 1998 Elsevier Science Ltd and IIR. All rights reserved.

(Keywords: refrigerating system; absorption system; heat exchange)

Simulation de la réponse transitoire des réfrigérateurs utilisant une source de chaleur avec maîtrise de la température en continu

Dans cet article, on présente une étude théorique et expérimentale ainsi qu'un modèle mathématique pour un système frigorifique utilisant une source de chaleur, avec maîtrise de température en continu pendant son fonctionnement. Le modèle comprend un espace frigorifique, un réfrigérateur à absorption fonctionnant de façon irréversible, un capteur de température, un signal de référence et un système de vérification de la loi énergétique. Le comportement du modèle de réfrigérateur à absorption en régime permanent est validé en utilisant une comparaison directe entre les résultats théoriques et les données expérimentales. Le modèle est ensuite utilisé pour identifier des conditions de transfert de chaleur optimaux, de telle manière que la vitesse de réfrigération soit rendue maximale et le temps d'abaissement de température soit minimisé. On effectue une simulation de système fonctionnant dans un mode transitoire afin de montrer que le fonctionnement en boucle fermée permet de diminuer

* To whom correspondence should be addressed.