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Journal of Chromatography A, 1019 (2003) 261–272
JOURNAL OF CHROMATOGRAPHY A
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Standardized test mixture for the characterization of comprehensive two-dimensional gas chromatography columns: the Phillips mix

Jean-Marie D. Dimandja [a,*], Garrick C. Clouden [b], Ivelisse Colón [c], Jean-François Focant [d], Whitney V. Cabey [a], Ritchard C. Parry [e]

[a] *Department of Chemistry, Spelman College, 350 Spelman Lane, SW Box 279 Atlanta, GA 30314, USA*
[b] *Meharry Medical College, 1005 Dr. D. B. Todd Jr. Blvd., Nashville, TN 37208, USA*
[c] *Pfizer Global Research and Development, Eastern Point Road, Groton, CT 06340, USA*
[d] *Centers for Disease Control and Prevention, 4770 Buford Highway NE, Atlanta, GA 30041, USA*
[e] *LECO Corporation, 3000 Lakeview Avenue, St. Joseph, MI 49085, USA*

Abstract

A novel column characterization test mixture is developed for use in comprehensive two-dimensional gas chromatography (GC × GC). This mixture has been named the "Phillips mix" in honor of the late professor John B. Phillips, the father of GC × GC. The mixture comprises a series of homologous compounds from structural groups that cover a volatility and polarity range that is similar to the Grob mix, and includes saturated hydrocarbons (alkanes), unsaturated hydrocarbons (alkenes and alkynes), carbonyls (ketones and aldehydes), primary alcohols, fatty acid methyl esters, alkyl ethers, carboxylic acids, aromatics, as well as other unique functional groups (such as amines, etc.). Similarly to the Grob mix in conventional one-dimensional GC, the Phillips mix can be used as a standardized test for performance characterization of GC × GC column sets. Unlike the Grob mix, however, the Phillips mix's most important use is as a practical guideline for column users. This paper addresses some qualitative aspects of the use of the Phillips mix through an investigation of the chromatographic fingerprints of two different GC × GC column combinations.

Keywords: Phillips mix; Grob mix; Column characterization; Stationary phases; GC × GC; Gas chromatography, comprehensive two-dimensional

1. Introduction

Analytical techniques typically follow an evolutionary pattern that involves four different phases, which include the invention of the technology and its initial development in a single laboratory, the early adoption of the technology by a small group of enthusiasts, the commercialization of the instrumentation and the maturation of the technique [1,2]. The first two phases are mainly focused on instrument development, while in the latter two phases the focus shifts towards the development of a host of methods based on the analytical instrument. Comprehensive two-dimensional gas chromatography [3–9] (GC × GC) is currently in transition from the instrument development phase to the method development phase. As GC × GC instrumentation becomes more accessible and more researchers

* Corresponding author. Tel.: +1-404-270-5743.
E-mail address: jdimandja@spelman.edu (J.-M.D. Dimandja).

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doi:10.1016/j.chroma.2003.09.027

start using the technology, an emerging issue is the normalization of several operational and methodological parameters of importance [10,11].

Even though the modulator is the central piece to the successful operation of a GC × GC system, the separation column nevertheless plays the most significant role in any GC-based instrument, and its efficient use will ultimately be the key factor behind the power and versatility of GC × GC applications. Simply connecting two columns and placing modulation between them does not produce a good GC × GC separation. The optimization process, as in 1D GC, involves a combination of factors, such as modulation frequency and efficiency, differential migration tuning through the relative amounts of the coupled stationary phase set, temperature and/or flow programming, etc. [11–14].

So far the use of test mixtures for characterization of GC × GC column sets has not actively been pursued in spite of isolated research efforts [7,15–17], and no consensus exists on a normalized process to determine column performance in spite of the great variety of column sets, as summarized from the peer-reviewed literature in Table 1. Standardized one-dimensional column test procedures have successfully been applied to the evaluation of GC columns for over two decades since the introduction of the Grob test mixture [18]. As Grob initially proposed, the basic column test requirements involve the completion of the test in a single chromatographic run, the inclusion in the mixture of all components necessary to provide qualitative and quantitative information pertaining to column performance, and the use of the same test and conditions to all column stationary phases for comparison of test results.

The Grob mix has been applied to the characterization of GC × GC columns [15], but its routine use as a performance test is limited for three reasons. First, GC × GC column sets are coupled column ensembles that are most often assembled from two separate stationary phases, and their behavior is thus a composite of several different effects. The evaluation of the differences between two GC × GC column combinations is thus more complex because it involves the combined mechanisms of at least two physicochemical properties. Second, Grob mix test procedures are primarily designed for column making rather than practical guidelines for column users. In the early development of column manufacturing, the primary goal was the acquisition of knowledge on how to make good quality columns. Conventional column quality tests therefore focused on a better understanding of the column making process [19–22]. The situation in GC × GC is different, in the sense that it does not involve the preparation of new specialized stationary phases but rather just the serial assembly of two existing one-dimensional GC columns in the appropriate proportions. Although conventional column tests would still be useful for column manufacturers to improve the development of low bleed, high temperature stationary phases, it is more practical to perform the characterization test to gain information on the merits of a particular column combination for an application from a column user's perspective. Third, the Grob mix contains a limited number of sample components. While it may cover a reasonable range of chemical functionalities for testing various column qualitative aspects such as adsorption, thermostability and inertness, it does not give detailed information on the stationary phase behavior towards the many varieties of chemical functional groups and their possible combinations in a real sample. This limitation is primarily due to the limited peak capacity of 1D GC, which requires that the test chromatogram be free of co-elutions in order to study chromatographic behavior such as peak tailing, adsorption, and enhance qualitative identification of the test mixture components as well as quantitative determinations.

The goal of this work is the development of a test mixture for GC × GC that addresses the need for a standardized set of compounds that will help the growing number of practitioners to learn the intricacies of multi-dimensional operational parameters. The main difference in the optimization of 1D and 2D GC methods is the active use of compound class structure as a useful parameter in the separation process. In 1D GC structure is present in the chromatogram, but it is not as easily decipherable because the dimensionality of the analyzer. In GC × GC, however, the chemical structure parameter becomes a useful parameter that can be exploited in several ways to the advantage of the researcher [4,23,24]. This parameter was not previously available to chromatographers, and learning its optimization in relation to the other operational parameters of GC × GC is likely to be a key factor in the increase of the versatility of this promising technique.

Table 1
Survey of the variety of GC × GC column sets

Proponent (year)	Primary phase	Secondary phase	Modulator	Temperature program	Application (number of peaks)	Reference number
Liu and Phillips (**1991**)	Polar (25, 250)	Non-polar (1, 100)	Thermally resistive paint	Iso-ramping	Liquid coal (50)	[3]
Ledford and Billesbach (2000)	Non-polar (**100**, 250)	Polar (**1**, 100)	Quad jet	**Temperature lagging**	Kerosene (5,000+)	[5]
Beens et al. (1998)	Semi-polar (**2**, 100)	Semi-polar (**0.5**, 100)	Sweeper	Iso-ramping	Quantitative analysis (25)	[25]
Lewis et al. (2000)	Non-polar (50, **530**)	Polar (2.2, **150**)	LMCS	Iso-ramping	VOCs (500)	[6]
Harju and Haglund (2001)	**Shape** (10, 100)	**Shape** (1, 100)	LMCS	Temperature leading	PCBs (75)	[26]
Dimandja et al. (2000)	Non-polar (**1**, 100)	Polar (**2**, 100)	Sweeper	Temperature leading	Essential oils (90)	[27]
Bruckner et al. (1998)	Non-polar (9.2, 530)	Polar (0.89, 180)	**Valve**	Isothermal	Jet fuel (N/A)	[28]
Marriott et al (2000)	Non-polar (30, 250)	Semi-polar (0.8, 100)	LMCS	Various	**Miscellaneous** (50–1000+)	[8,14]

Primary and secondary phase dimensions in parentheses correspond to the column length (m) and the column i.d. (μm). Temperature program lexicon: iso-ramping means identical temperature programs in the first and second dimension, temperature leading means that the second dimension temperature proceeds ahead of the temperature programming of the primary column. Isothermal means that both columns were operated at one temperature throughout the run, and temperature lagging indicates that the secondary column's temperature program is below the temperature program of the primary column. In bold are the highlights of each system. Liu and Phillips represents the first GC × GC system ever used; the Ledford and Billesbach system employs the longest column set and uses temperature lagging instead of temperature leading; the Beens et al. set-up is the shortest column set reported; the Lewis system uses the widest first to second dimension column i.d. restriction (530–150 μm), etc.

2. Experimental

2.1. Column sets

The first column set that was assembled was a non-polar (HP-1; 30 m, 250 μm i.d., 0.25 μm film thickness) column obtained from Agilent (Palo Alto, CA) that was coupled to a semi-polar second dimension column (Rtx-35; 2 m, 100 μm i.d., 0.1 μm film thickness) column from Restek through a universal press-fit connector. This column combination is the one most utilized in the reported literature, as shown in Fig. 1. The ends of the two columns to be placed in the press-fit were cleaned with ethyl acetate, and the connection was cured in an oven for 1 h (temperature program: 30–80 °C at 1 °C/min, then isothermal at 80 °C for 35 min). This process was followed to avoid using the polyimide resin that is generally used with press-tight connectors, as it may introduce unwanted traces of compounds in the chromatogram. The second column ensemble was a polar column (SP-2331; 30 m length, 250 μm i.d., 0.25 mm film thickness) that was coupled to a non-polar column (Rtx-5, 2 m length, 100 μm i.d., 0.1 μm film thickness).

2.2. Chemicals

A commercial Grob mix sample was obtained from Restek Corporation (Bellefonte, PA). The Phillips mix compounds, which are listed in Table 2, were purchased from Sigma–Aldrich (St. Louis, MO). Hexane was used as the solvent for the Phillips mix. Each homologous series was prepared individually, and was spiked with the alkanes. These individual mixtures were then run on the conventional GC × GC column set with no modulation at the same temperature

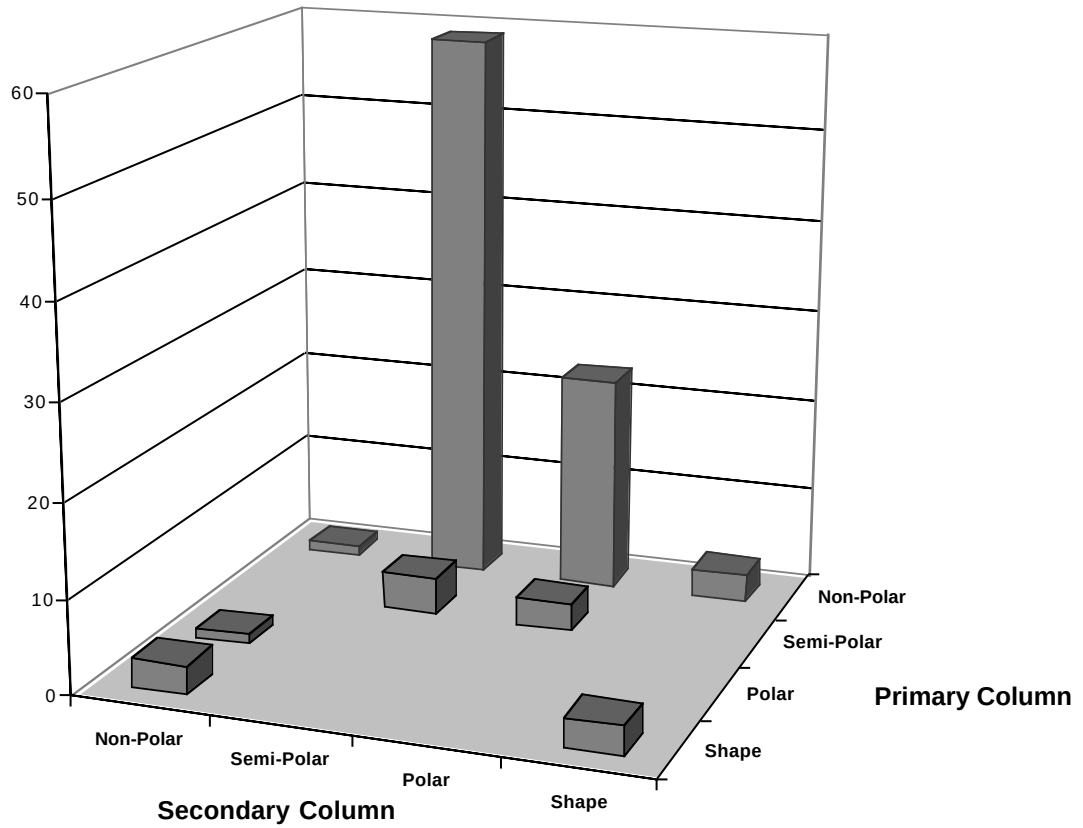

Fig. 1. Survey of GC × GC column sets. The *z*-axis represents the percentage of column sets relative to the total number of column sets reported in peer-reviewed literature.

Table 2
Phillips mix compound list, with temperature programmed retention index values

Compound	TPRI value	Compound	TPRI value	Compound	TPRI value
Alkanes		Alcohols		Grob mix compounds	
Heptane	700	1-Pentanol	763	2,3-Butanediol	787
Octane	800	1-Hexanol	868	2-Ethylhexanoic acid	1118
Nonane	900	1-Heptanol	972	2,6-Dimethylphenol	1136
Decane	1000	1-Octanol	1075	2,6-Dimethylaniline	1207
Undecane	1100	1-Nonanol	1179	Dicyclohexylamine	1464
Dodecane	1200	1-Decanol	1284		
Tridecane	1300	1-Undecanol	1389		
Tetradecane	1400	1-Dodecanol	1496		
Pentadecane	1500	Methyl esters			
Hexadecane	1600	Methyl butanoate	719		
Heptadecane	1700	Methyl pentanoate	823		
Alkenes		Methyl hexanoate	924		
Octene	791	Methyl heptanoate	1025		
Nonene	892	Methyl octanoate	1126		
Decene	992	Methyl nonanoate	1226		
Undecene	1093	Methyl decanoate	1329		
Dodecene	1194	Methyl undecanoate	1430		
Tridecene	1295	Methyl dodecanoate	1532		
Tetradecene	1395	Carboxilic acids			
Pentadecene	1496	Butanoic acid	758		
Hexadecene	1597	Pentanoic acid	863		
Alkynes		Hexanoic acid	966		
Heptyne	720	Heptanoic acid	1066		
Octyne	822	Alkylbenzenes			
Nonyne	924	Ethylbenzene	875		
Decyne	1025	Propylbenzene	970		
Aldehydes		Butylbenzene	1076		
Pentanal	701	Alkylethers			
Hexanal	804	Dibutylether	882		
Heptanal	908	Dipentylether	1079		
Octanal	1011	Dihexylether	1276		
Nonanal	1115	Cycloalkanes			
Decanal	1220	Cyclohexane	686		
Undecanal	1326	Cycloheptane	813		
Dodecanal	1432	Cyclooctane	942		
Ketones		Naphthalenes			
2-Pentanone	696	Naphthalene	1232		
2-Hexanone	792	1-Methylnaphthalene	1349		
2-Heptanone	894	2-Methylnaphthalene	1372		
2-Octanone	997	Xylenes			
2-Nonanone	1099	*m*-Xylene	882		
2-Decanone	1202	*p*-Xylene	882		
2-Undecanone	1307	*o*-Xylene	910		

program that was later used for modulated runs. This was done to obtain temperature programmed retention index values (listed in Table 2) for each compound that would be helpful in the confirmation of the identity of the each compound in the GC × GC chromatogram.

2.3. GC × GC instrumentation

A Pegasus 4D GC × GC/TOF MS (LECO Corporation, St. Joseph, MI) equipped with a two-stage four-jet (quad-jet) modulator that has recently been described elsewhere [9] was used. The carrier gas was

helium, which was delivered at a constant flow rate of 1 ml/min. The inlet temperature was 280 °C, and the inlet volume was 0.1 μl (200:1 split). The temperature program of the primary column started at 50 °C for 0.2 min, then was ramped to 245 °C at a rate of 5 °C/min, with a final hold time of 0.8 min for a total run time of 40 min. The secondary column was programmed in positive temperature iso-ramping mode, which meant that its temperature program sequence was identical to that of the first column except for the fact that it was 5 °C higher than the first dimension oven throughout the course of the run. The transfer line into the TOF MS source was operated at 280 °C and the electron impact ionization source itself operated at 200 °C. The data acquisition rate was 200 Hz over a mass range of 40–450 amu. The modulator period was 4 s.

3. Results and discussion

3.1. Selection of Phillips mix compounds

At the outset of this project, the requirements for the Phillips mix were selected based on those outlined by Grob et al. [18] for characterization of 1D GC columns, namely:

- the test consists of a single chromatographic run;
- the test mixture contains all the components necessary to provide all the basic information needed;
- the same test should be applicable to all types of stationary phase combinations;
- operating conditions should be standardized to make test results comparable;
- some quantitative aspects should be included.

Fig. 2A shows a raw trace chromatogram of a Grob mix run on the non-polar/semi-polar GC × GC column set. The profile chromatogram is consistent with the expected profile from a non-polar first dimension column, since the primary stationary phase provides the broad outline of the separation. Fig. 2B shows a contour plot of the same trace, in which the polarity of each sample component is revealed. This "volatility × polarity" plot reveals the judicious selection of the Grob mix compounds for use in the characterization of 1D GC columns, as they adequately monitor the performance of the stationary phase vis-a-vis a variety of structural functionalities. As such, the Grob mix constitutes an excellent backbone upon which to build a characterization mixture for GC × GC.

The Phillips mix fingerprint on the non-polar/semi-polar column set is shown in Fig. 3. The GC × GC chromatogram is presented in terms of the peak apex data obtained from the coordinates of the retention times for each compound in the mixture in order to simplify the visualization of the data. The homologous series of paraffins (heptane through heptadecane) were chosen to bracket the volatility range of the Grob mix, and provide the marker points necessary for calculation of retention index values. Three other homologous series were also chosen based on the Grob mix: the *n*-alcohols (pentanol through dodecanol), the aldehydes (pentanal through dodecanal) and the fatty acid methyl esters (methyl butanoate through methyl dodecanoate). The remaining components of the Grob mix (2,3-butanediol, 2-ethylhexanoic acid, 2,6-dimethylphenol, 2,6-dimethylaniline and dicyclohexylamine) do not belong to homologous series that can easily be obtained from commercial sources. They were nevertheless included in the Phillips mix as individual compounds. As a result, all Grob mix compounds are present in the Phillips mix, and performance evaluations on the coupled column ensemble can be undertaken on the basis of these compounds. Additional series of compounds were added to test the effect of separation conditions and stationary phase combinations on the resolution of specifically chosen related compounds. Thus, the alkenes and the alkynes were added to test the separation power of the column set with regards to the alkanes, and the ketones were added as close eluters to the aldehydes. A number of aromatic compounds such as the alkylbenzenes and the naphthalenes were included as well.

The overall fingerprint of the mixture run at set conditions is visually recognizable, and distinct from that of other sets. Fig. 4A shows a subset of the Phillips mix fingerprint from the non-polar/semi-polar column set shown in Fig. 3. This peak apex plot focuses on the homologous series in the congested area of the chromatogram. The fingerprint for the same compounds is shown in Fig. 4B for the polar/non-polar column set. The compound series display a very different fingerprint, as the retention in the second dimension is practically reversed. The naphthalenes, for instance, which elute later in the second dimension in Fig. 4A

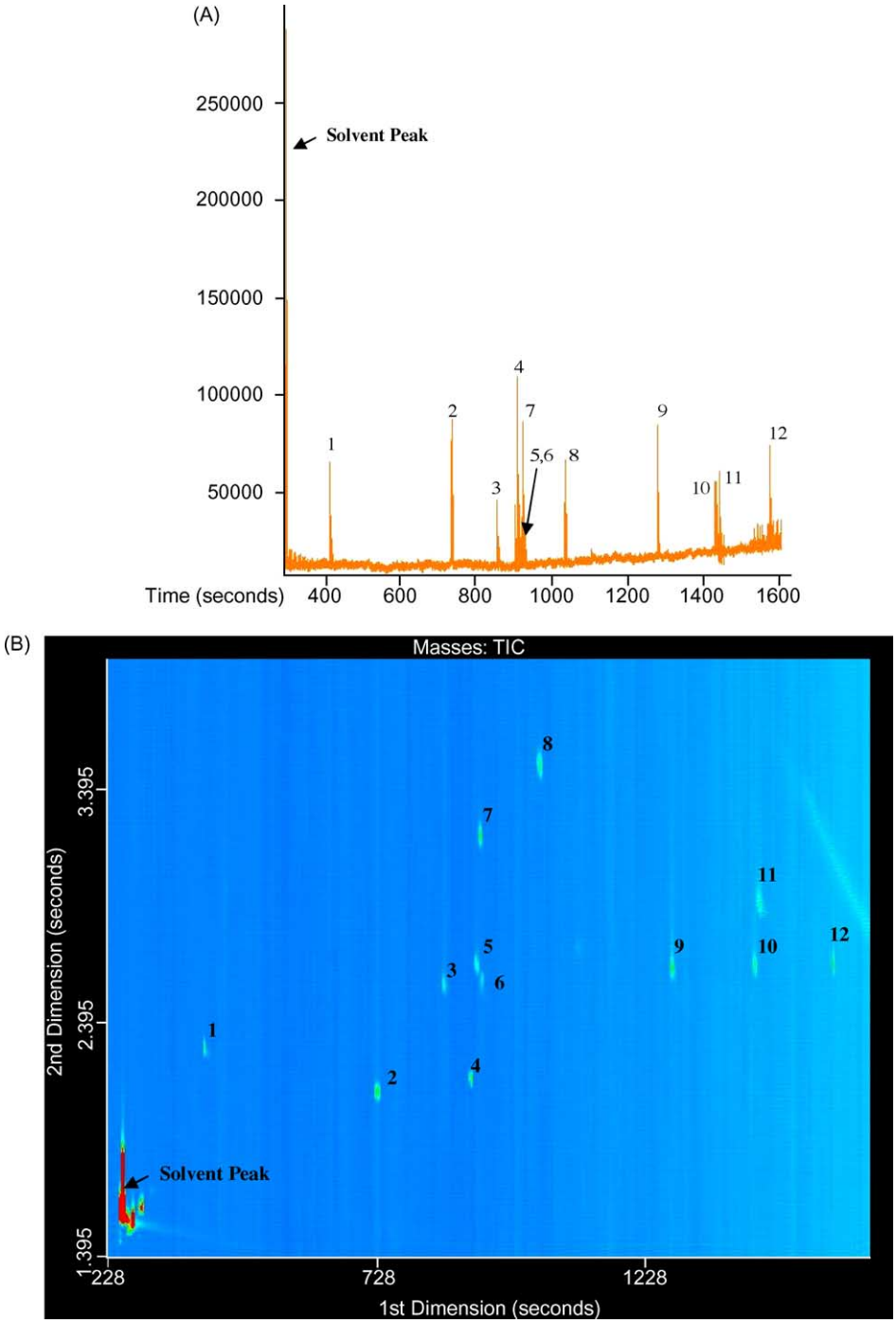

Fig. 2. (A) Raw GC × GC trace of Grob mix. Compound identification: (1) 2,3-butanediol; (2) *n*-decane; (3) 1-octanol; (4) *n*-undecane; (5) 1-nonanal; (6) 2,6-dimethylphenol; (7) 2-ethylhexanoic acid; (8) 2,6-dimethylaniline; (9) methyl decanoate; (10) methyl undecanoate; (11) dicyclohexylamine; and (12) methyl dodecanoate. (B) GC × GC contour plot chromatogram of the Grob mix. Peak assignments are the same as in (A).

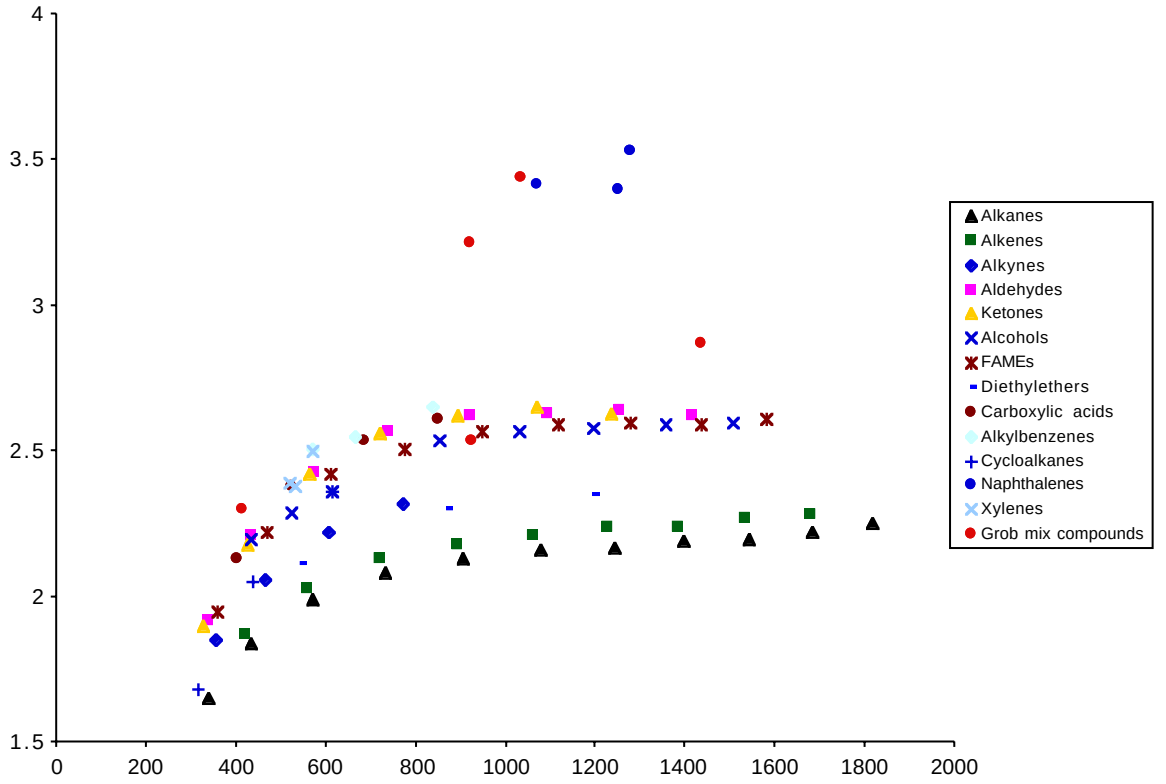

Fig. 3. GC × GC peak apex plot of the Phillips mix. First (*x*-axis) and second dimensions (*y*-axis) retention times are in seconds. The Grob mix compounds that do not belong to a particular homologous series class are labeled as a group.

are early second-dimension eluters in Fig. 4B. As different column combinations are examined and their characteristic fingerprints are known, the mixture will be a valuable asset in assessing the general regions of a GC × GC chromatogram, and help orient the researcher across the retention map [29].

3.2. GC × GC *optimization tuning*

The optimization of a GC × GC chromatogram requires a tuning process that involves a set of operational parameters such as modulation frequency, temperature programming rate, carrier gas linear velocity, etc. [11,14]. The Phillips mix can be useful as a practical guideline for end-users in assessing the effect of a given operational parameter on retention in both dimensions of a GC × GC separation. Fig. 5 illustrates the use of the Phillips mix in an optimization example where the analysis time of a separation was sought to be reduced. Fig. 5A shows the contour plot of a 30 min GC × GC Phillips mix run on a non-polar/semi-polar column set. A special fingerprint zone was created (an indicated by the circle in Fig. 5A) to aid in the visualization of the sample. This zone was created by removing one compound from the mixture out of the homologous series of the fatty acid methyl esters (methyl octanoate).

In Fig. 5B, the column ratio has been reduced from a 30 m primary column/2 m secondary column (denoted as 30:2) to 10:2 column ratio, and the temperature programming rate has been increased from 5 to 10 °C/min. Due to the increase of carrier velocity in the first dimension, the net effect of this change is a compression of the chromatogram in the first dimension (from 30 to 14 min), but an expansion of the chromatogram in the second dimension. Retention times in the secondary column are increased because of reduced elution temperatures in the primary column. As

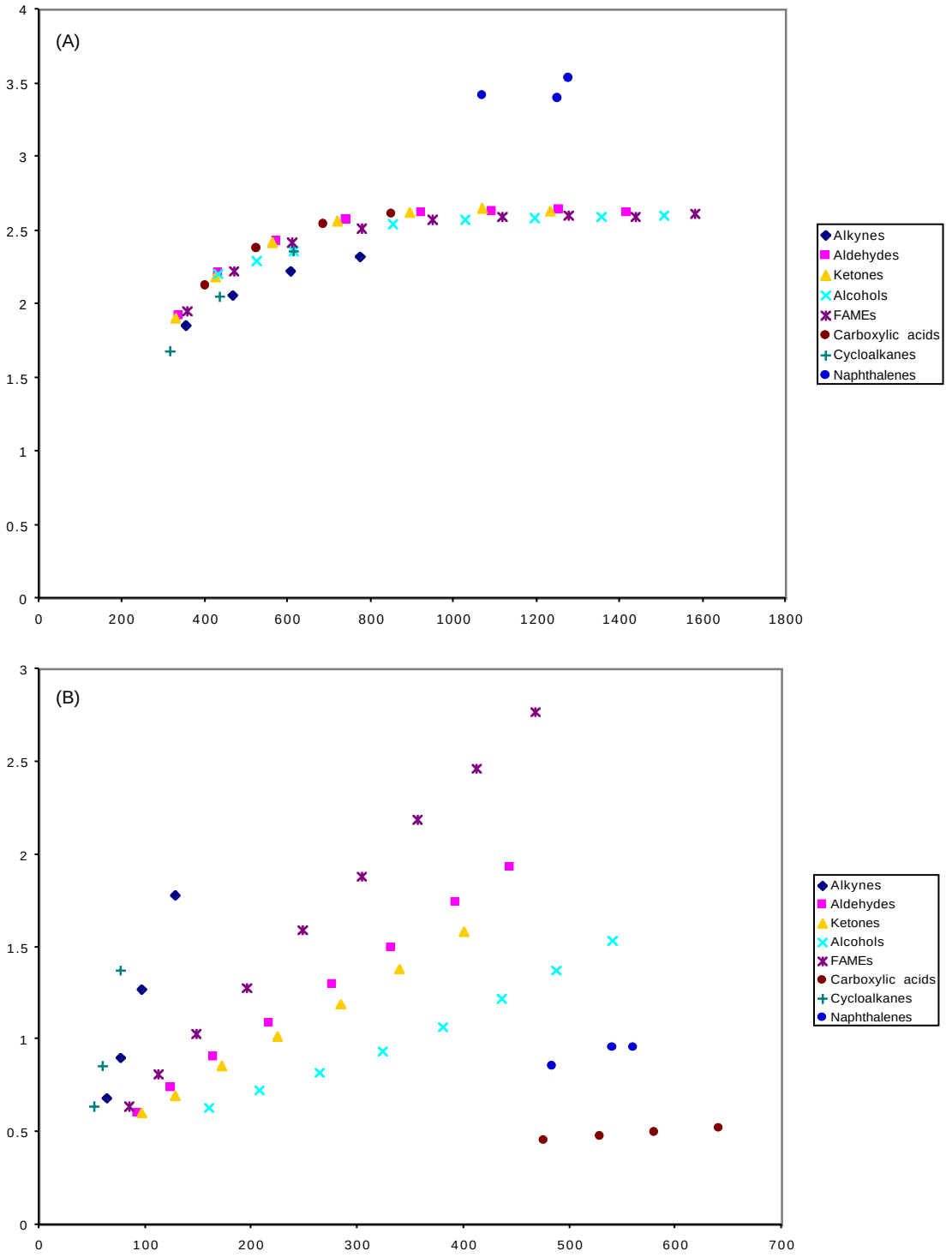

Fig. 4. Phillips mix fingerprints: (A) non-polar/semi-polar GC × GC column set and (B) polar/non-polar GC × GC column set. First (*x*-axis) and second dimensions (*y*-axis) retention times are in seconds.

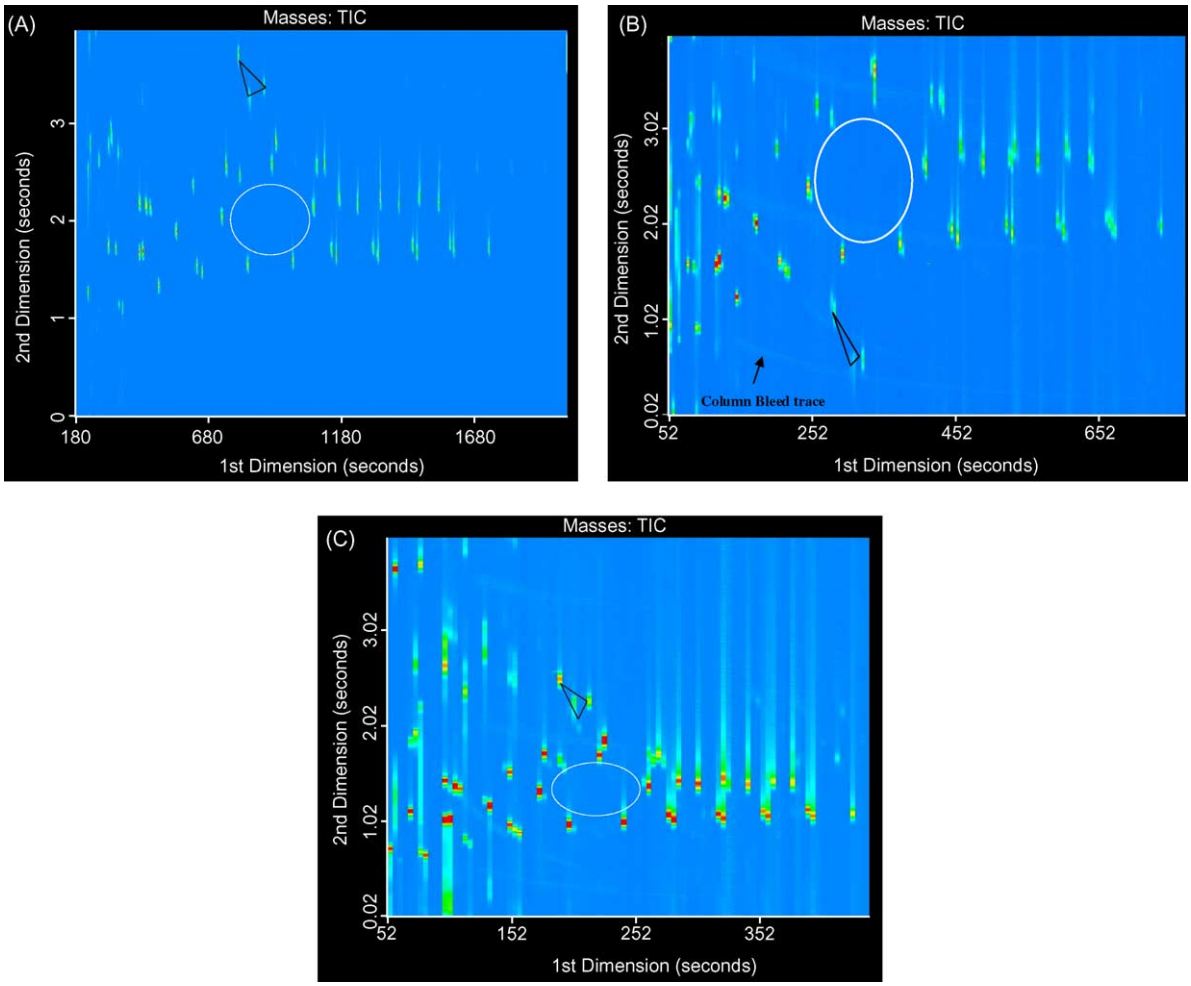

Fig. 5. GC × GC time-compression optimization: (A) 30:2 column ratio, 5 °C/min temperature program; (B) 10:2 column ratio, 10 °C/min temperature program; and (C) 10:2 column ratio, 20 °C/min temperature program (see text for details on the circle and triangle fingerprinted regions).

a result, the late eluting substances in the secondary column (peaks in the triangle shown in Fig. 5B) are now "wrapped around," i.e., their elution time exceeds the modulation period [14]. While wrap-around is not a problem so long as the peaks are not overlapping other peaks in the chromatogram, it should be avoided whenever possible. Thus, the shortening of the primary column to reduce analysis time requires that the programming rate be further increased to allow substances eluting from the end of the primary column to elute in the secondary column at a duration appropriate to the modulation frequency.

In Fig. 5C, the temperature program has been increased from 10 to 30 °C/min. The GC × GC chromatogram is further reduced in the first dimension (from 13 to 7 min), but the more significant effect on this change is the reduction of the secondary column retention times. The peaks that were wrapped-around in the previous chromatogram are now compressed. The resolution power of this column-set at these conditions is less than the original 30:2 column set, but the speed of the separation has been significantly improved. A primary column can be shorter than it would be in a one-dimensional separation of a given sample

because the second dimension provides substantial resolving power and peak capacity.

3.3. Monitoring of miscellaneous effects

The monitoring of column performance should include an assessment of column bleed, which gives an indication of column wear and tear. In one-dimensional GC column bleed is noticeable through the rise in the baseline level due to the production of polysiloxane bleed products that are released from the stationary phase into the mobile phase stream. In GC × GC, the progressive leaching of these breakdown products is visible in the form of a continuous trace as identified in Fig. 5B for example. The trace slopes down because of the temperature program, which slowly reduces the retention time of the same product in the secondary column during the course of the run. Primary column bleed is also distinguishable from secondary column bleed, as they appear in separate regions of the chromatogram. The monitoring of parameters such as column bleed are important in any chromatogram, and can be useful as a quality control measure to decide when to replace a column. One of the main areas of column development research of interest to GC × GC is the development of high temperature polar stationary phases. The testing of such phases should include an assessment of column bleed over a given operation time range. These investigations can be undertaken through the use of a GC × GC system now that the bleed factor can be localized in the GC × GC retention plane. It is important to note that the monitoring of column bleed does not require the use of the Phillips mix since it involves products emanating from the column and not the test mixture. The evaluation of column bleed as part of the column performance standard operating procedure should be performed whenever running the Phillips mix, however.

4. Conclusions

In this preliminary work, we have introduced the fundamentals of GC × GC column characterization. The Phillips mix is proposed as a characterization mixture that will facilitate the evaluation of GC × GC column-set performance as well as the monitoring of the effects of various operational parameters of the resolution response of the instrument. It is therefore a valuable test mixture for beginning GC × GC practitioners and expert users alike. A standardization methodology based on this mixture would help normalize many chromatographic parameters or processes conceptually and experimentally. Validation of this mixture will be undertaken through the investigation of an exhaustive set of column stationary phase combinations. Finally, it is worth noting that while the Phillips mix, like the Grob mix, is an important general purpose test mixture it will be necessary to develop other mixtures better suited for use in specific areas. For example, the use of a test mixture for use in GC × GC/ECD systems will most likely be based on the selection of organohalogens, and a test mixture relevant for the flavor and fragrance industry will contain compounds most relevant to common use in that particular field.

Acknowledgements

This investigation was supported by a Research Infrastructure in Minority Institutions Award from the National Center for Research Resources with funding from the Office of Research on Minority Health (Grant No.RR11598). GCC, IC and JFF also wish to thank the Oak Ridge Institute for Science and Education (ORISE) for post-graduate research fellowship support.

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