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Ionic liquid stationary phases for multidimensional gas chromatography

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ABSTRACT

Ionic liquids (ILs) are a class of organic salts that meet many of the requirements of GC stationary phases including high thermal stability, high viscosity, and tunable selectivity through the modification of the chemical structure. IL-based columns, when incorporated either in the first or second dimension, can offer unique selectivity compared to polydimethyl(siloxane) and poly(ethyleneglycol) derived GC stationary phases for the separation of complex samples by multidimensional gas chromatography. In addition, IL-based columns are emerging as superior choices for applications requiring high polarity as well as high thermal stability. The present contribution provides an overview on IL-based stationary phases for multidimensional gas chromatography with an emphasis on developments in the period from 2012 to early 2018. The analysis of various analytes (e.g., fatty acids, polycyclic aromatic sulfur heterocycles, and biodiesels) in complex matrices as well as the developments of new IL-based stationary phases for multidimensional gas chromatography are described.

1. Introduction

Multidimensional gas chromatography (MDGC) is one of the most useful tools available for the analysis of volatile and semi-volatile analytes in complex mixtures. MDGC typically combines two or more independent separation mechanisms to increase the peak capacity and improve the resolution of unresolved regions within the 1D chromatographic separation. Heart cutting multidimensional gas chromatography (H/C MDGC) typically connects two columns using a flow-switching device which directs a specific segment of the primary column effluent into the secondary column to improve the separation of the heart-cut region. In comparison, comprehensive two-dimensional gas chromatography (GC × GC) connects two columns possessing different selectivities (i.e., nonpolar × polar or polar × nonpolar column configuration) to maximize peak capacity. All eluted compounds from the first column are transferred as a pulse into a second column. For more information regarding the fundamentals of instrumental principles for GC × GC and H/C MDGC, readers are encouraged to consult a number of excellent review articles [1–4].

The analysis of complex samples such as petrochemicals, food additives, forensic samples, fragrances, and pharmaceutical compounds requires more and more powerful analytical tools due to the increasing demand for high resolution, high sensitivity, and information rich analysis. The improvement of analyte detection limits, peak resolution, and peak capacity requires the constant development of detectors, modulators, data analysis software, and GC stationary phases that exhibit unique selectivity in MDGC. Recent developments of instrumentation and data analysis methods in MDGC have been reviewed by Synovec and coworkers [5]. Although advanced instrumentation and methods can improve separation results, the selectivity, thermal stability, and inertness of the GC stationary phase always plays an important role in the resolution, retention order, and analyte distribution in MDGC.

Ionic liquids (ILs) are salts that possess melting points at or below 100 °C [6]. A number of IL-based stationary phases have been commercialized and have received increasing attention due to their high thermal stability, low vapor pressure, and unique separation selectivities [7]. The chemical structure of ILs can be tailored to undergo various solvation interactions and ultimately provide unique chromatographic selectivities. In addition, the chemical structures of ILs can be modified to produce highly viscous products possessing high thermal stability. It is of continued interest to design new IL-based stationary phases that can be coated to

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possess high separation efficiencies as well as provide enhanced maximum allowable operating temperatures (MAOT) that rival other commercially available stationary phases. Compared to more conventional stationary phases based on polydimethyl(siloxane) (PDMS) and poly(ethyleneglycol) (PEG), IL-based stationary phases are commonly considered as highly polar phases based on the overall polarities derived from their McReynolds constants [8]. A polarity scale system referred to as polarity number (PN) was introduced by Mondello and co-workers and is used in the naming of commercialized Supelco IL GC columns, such as SLB-IL59, SLB-IL100, and SLB-IL111 [8]. As shown in Fig. 1, the IL-based GC columns generally possess much higher overall polarity and PN values than PDMS- and PEG-based columns, while providing similar or even higher MAOT than commercial PEG-based GC columns (e.g., MAOT of 290 °C and polarity of 2705 for SLB-IL61; MAOT of 280 °C and polarity of 2324 for the SUPELCOWAX10 column).

The first application of an IL-based column for MDGC was reported in 2006 [9]. A dual-column setup consisting of an immobilized IL column (equivalent to commercially-available SLB-IL100) was used to exploit stop-flow conditions at specific analysis times. Since this report, a number of publications have demonstrated the use of IL-based columns in MDGC to provide unique selectivities for target analytes. This review focuses on the recent applications of commercial IL-based GC columns and the development of new IL-based stationary phases in GC × GC and other selected types of MDGC, with an emphasis on developments made between 2012 to early 2018.

2. Recent applications of commercial IL-based stationary phases in MDGC

Table 1 lists seven of the most widely used commercially available IL-based GC columns. For an overview of the early developments and applications of IL-based stationary phases in MDGC, readers are encouraged to consult an excellent review article published by Mondello and co-workers in 2012 [10]. Over the past few years as more IL columns with unique selectivity and improved inertness as well as more sensitive and selective detectors were introduced, great improvements have been made in detection, analyte identification, and applications using MDGC. IL-based columns have been successfully used in MDGC to improve the separation and detection of analytes from complex matrices including food samples, agricultural products, petrochemicals, environmental samples, and pharmaceutical compounds. Due to their high overall polarity, IL-based columns have been widely applied for the analysis of highly polar compounds in complex matrices (e.g., free and methylated fatty acids, fragrances, essential oils, and pesticides). Selected applications of IL-based stationary phases in MDGC separations and analysis are described below and are also summarized in Table 2.

2.1. Fatty acid methyl esters

By far, the majority of MDGC separations employing IL-based GC columns have been applied for the analysis of fatty acid methyl esters (FAMEs). Recently, a review article was published focusing on IL-based stationary phases for 1D-GC as well as MDGC separation of FAMEs [11].

Delmonte et al. investigated the GC × GC separation of FAMEs using a SLB-IL111 (200 m × 0.25 mm × 0.20 μm) × SLB-IL111 (2.5 m × 0.10 mm × 0.08 μm) column set [12]. Compared to a previous study employing a single 200 m SLB-IL111 column, most of the FAMEs were resolved through an addition of a second dimension of separation. The FAMEs could be easily identified using a simple interpretation model based on the degree of saturation and the carbon skeleton numbers.

To test the chromatographic conditions for the separation of the FAMEs from complex samples, Delmonte et al. used GC × GC to analyze FAMEs prepared from menhaden oil [13]. The results showed the potential of resolving nearly all of the FAMEs prepared from complex fats and oils in a single analysis. Fig. 2 compares a 1D-GC chromatogram and GC × GC contour plot for the separation of FAMEs from C20:0 to C22:6. Multiple co-eluted peaks of FAMEs were observed using the 1D-GC separation. In comparison, the GC × GC separation using the SLB-IL111 columns resolved most of the analytes within the separation space. These results highlight

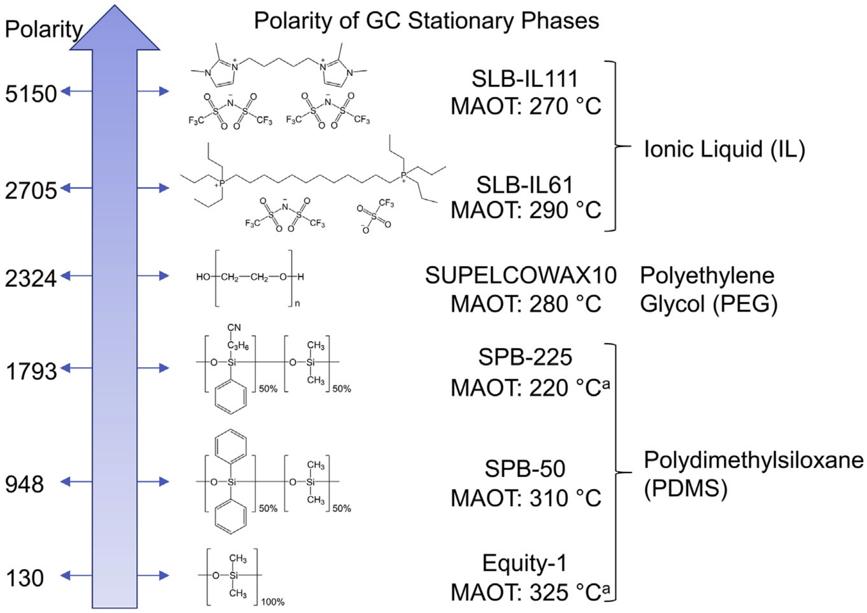
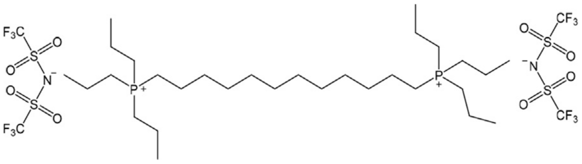
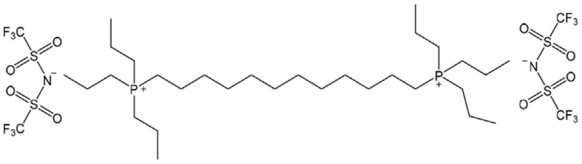
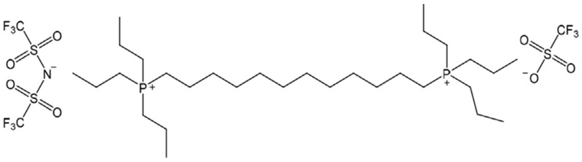
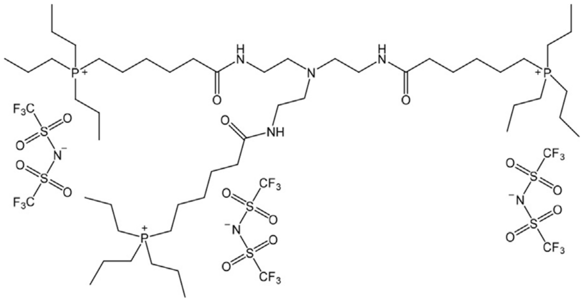
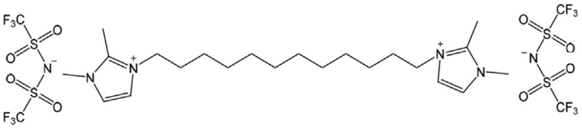
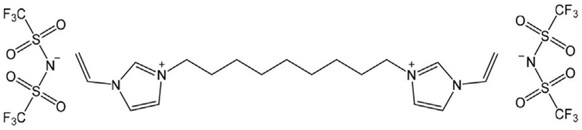
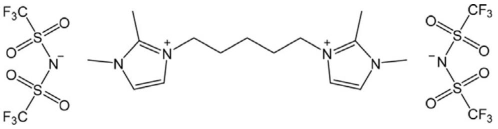
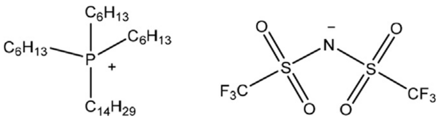


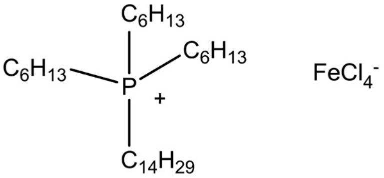
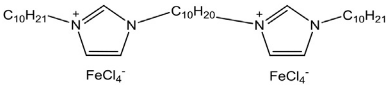
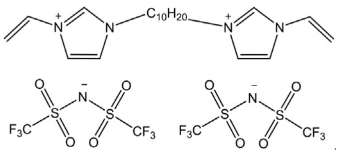
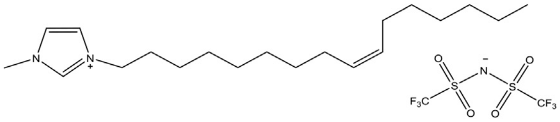
Fig. 1. Chemical structures and overall polarity values of selected commercially-available GC stationary phases. The overall polarity values are obtained from Refs. [8,10]. The numbers 61 and 111 for SLB-IL61 and SLB-IL111, respectively, indicate the PN values of the stationary phases. The PN values were calculated based on the overall polarity values. Note: [a]The MAOT values of SPB-225 and Equity-1 columns are under isothermal conditions.

Table 1
Chemical names and structures of selected IL-based stationary phases and their applications in multidimensional gas chromatography.

GC column	Chemical name and structure	Overall polarity[a]	Applications
SLB IL-59	 1,12-Di(tripropylphosphonium)dodecane bis[(trifluoromethyl)sulfonyl]imide	2624	FAMEs [19–21,24,25] PCB [27,28] PASH [29] Petrochemicals [39] Food aroma [35] Perfume [33] Pesticides [58] Essential oil [36,37]
SLB IL-60	 1,12-Di(tripropylphosphonium)dodecane bis[(trifluoromethyl)sulfonyl]imide	2666	FAMEs [23,25] PASH [30] Petrochemicals [38,40,59,60] Essential oil [34]
SLB IL-61	 1,12-Di(tripropylphosphonium)dodecane bis[(trifluoromethyl)sulfonyl]imide trifluoromethylsulfonate	2705	FAMEs [19,21] PASH [30] Petrochemicals [61]
SLB IL-76	 Tri(tripropylphosphoniumhexanamido)triethylamine bis[(trifluoromethyl)sulfonyl]imide	3379	FAMEs [18,19,21,25] PCBs [28] PASH [30]
SLB IL-82	 1,12-Di(2,3-dimethylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide	3681	FAMEs [19,21]
SLB IL-100	 1,9-Di(3-vinylimidazolium)nonane bis[(trifluoromethyl)sulfonyl]imide	4437	FAMEs [18,19,21,62,63] Petrochemical [64]
SLB IL-111	 1,5-Di(2,3-dimethylimidazolium)pentane bis[(trifluoromethyl)sulfonyl]imide	5150	FAMEs [12–14,18–21,24,25] PASH [30]
NA[b]	 trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide	–[c]	Petrochemicals [44]

(continued on next page)

Table 1 (*continued*)

GC column	Chemical name and structure	Overall polarity[a]	Applications
NA[b]	 trihexyl(tetradecyl)phosphonium tetrachloroferrate	–[c]	Petrochemicals [45]
NA[b]	 1,10-Di(3-decylimidazolium)decane tetrachloroferrate	–[c]	Petrochemicals [46]
NA[b]	 1,10-Di(3-vinylimidazolium)decane bis[(trifluoromethyl)sulfonyl]imide	–[c]	Petrochemicals [47]
NA[b]	 (Z)-1-(9-hexadecenyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	–[c]	Petrochemicals [48]

[a] Overall polarity values derived from McReynolds constants were obtained from Refs. [8,10].

[b] ILs do not possess commercial brand names.

[c] The polarity values have not been reported.

the separation power of GC × GC when coupled with highly polar IL-based GC stationary phases.

Delmonte also compared the performance of highly polar stationary phases consisting of SP2560 (poly(90% biscyanopropyl/10% cyanopropylphenylsiloxane)) and the SLB-IL111 IL (1,9-Di(3-vinylimidazolium)nonane bis[(trifluoromethyl)sulfonyl]imide) for the resolution of geometric and positional isomers of the unsaturated fatty acids (FAs) occurring in dairy products and partially hydrogenated vegetable oils [14]. The cyanopropyl modified PDMS-based stationary phases (CP-Sil 88 and SP-2560) were used in the approved American Oil Chemists' Society (AOCS) official methods for the separation of *cis*-, *trans*-, saturated, and unsaturated fatty acids [15–17]. GC × GC employing a SP2560 × SLB-IL111 column set operated at 180 °C was shown to separate C18:1 *trans* FAs (*t*FAs) and C18:2 tFAs from other FAMEs contained in a hydrogenated soybean oil sample. However, the 18:3 tFAs partially co-eluted with C20:1 FAMEs. In comparison, GC × GC with the SLB-IL111 × SLB-IL111 column set operated at 160 °C separated 18:1 tFAs and 18:3 tFAs from other FAMEs, but was not able to separate 18:2 tFAs. Neither of the two column sets provided the separation of all C18:1, C18:2, and C18:3 tFAs from other FAMEs in the hydrogenated soybean oil sample.

Zeng et al. used an integrated GC × GC/MDGC system in the analysis of FAMEs employing SLB-IL76, SLB-IL100, and SLB-IL111 columns [18]. This system possessed two functional analysis pathways. The GC × GC mode provided the high resolution separation with identification capability of different FAME isomers according to their 2D pattern, while the H/C MDGC mode with a long ^{2}D IL-based column provided improved separation of the target region under optimized conditions. This study used different IL columns as the second dimension column to study retention behavior of FAMEs in MDGC separation. The estimated peak capacity for the C18 FAMEs (C18:0 to c9, c12, c15-C18:3) increased from 10 (1D DB-5ms) to 30, 34, 41, and 42 on FFAP, SLB-IL76, SLB-IL100, and SLB-IL111, respectively. This expanded separation space on the IL column was found to be superior to PDMS or PEG-based phases while offering better separation for complex FA samples.

Nosheen et al. used GC × GC employing a range of IL-based column sets (SLB-IL59, SLB-IL61, SLB-IL76, SLB-IL82, SLB-IL100, SLB-IL111) to analyze safflower oil containing a complex mixture of C18 saturated and unsaturated FAs amongst other FAs [19]. Compared to other tested column sets, safflower oil FAMEs were well separated in less than 16 min using GC × GC employing a SLB-IL111/IL59 column set. In addition, detection of less abundant FAs (e.g., myristic acid (C14:0) and palmitoleic acid (C16:1)) was determined and two new FAMEs (pentadecanoic acid (C15:0) and heptadecanoic acid (C17:0)) were reported for the first time in safflower oil.

To further understand and predict the retention behavior of FAMEs on IL-based columns in GC × GC separations, Kulsing and co-workers developed a method using the molecular structure of the stationary phases and target analytes to predict the separation results [20]. Using correlations between molecular simulation and linear solvation energy relationships, a reliable prediction of the equivalent chain length of FAMEs on each IL column (e.g., SLB-IL59, SLB-IL61, SLB-IL76, SLB-IL82, SLB-IL100, SLB-IL111) was established for GC × GC. An effective IL column selection method and a guide for the rational design of novel IL stationary phases for the separation of FAMEs in GC × GC was achieved with reliable predicted separation results.

Nolvachai et al. developed a theoretical concept and method to achieve a degree of orthogonality in GC × GC for the separation of FAMEs using a single IL stationary phase [21]. The SLB-IL111 column was selected due to its great thermal sensitivity, which resulted in significant differences between 1D temperature-programmed and 2D isothermal separations. The switchable separation result, which inverts the retention of saturated and unsaturated FAME on the 2D column, was achieved by varying the column diameters and surface

Table 2
Selected recent applications of IL-based columns for MDGC.

Year	Sample	Column set[a]	Instrumentation	Reference
2018	FAMEs	^{1}D: SLB-IL59i, SLB-IL60i, SLB-IL76i, and SLBIL111i (30 m × 0.25 mm × 0.25 μm) ^{2}D: SLB-IL59, SLB-IL60, SLB-IL76, and SLBIL111 (0.825 m × 0.10 mm × 0.08 μm)	GC × GC-MS (Thermal modulation)	Pojjanapornpun et al. [25]
2018	Mixtures of alkanes and alcohols	^{1}D: SLB-5MS (30 m × 0.25 mm × 0.25 μm) ^{2}D$_1$: SLB-IL60, SUPELCOWAX10 (1 m × 0.10 mm × 0.08 μm) ^{2}D$_2$: SUPELCOWAX10, BPX5 (1 m × 0.10 mm × 0.10 μm)	GC × GC-MS (Flow modulation)	Sharif et al. [60]
2017	Petrochemicals (Biodiesel)	^{1}D: HP-5 (30 m × 0.25 mm × 0.25 μm) ^{2}D: SLB-IL61 (1 m × 0.10 mm × 0.08 μm)	GC × GC-FID/MS (Thermal modulation)	Mogollón et al. [61]
2017	Petrochemicals	^{1}D: Rtx-5 (30 m × 0.25 mm × 0.25 μm) ^{2}D: Lipidic IL-based columns (1.2 m × 0.25 mm × 0.28 μm)	GC × GC-FID (Thermal modulation)	Nan et al. [48]
2016	FAMEs in vegetable oils	^{1}D: SLB-IL111 (100 m × 0.25 mm × 0.20 μm) or SP2560 (100 m × 0.25 mm × 0.20 μm) ^{2}D: SLB-IL111 (2 m × 0.10 mm × 0.08 μm)	GC × GC-FID (Thermal modulation)	Delmonte [14]
2016	Mixtures of alkanes and alcohols	^{1}D: SLB-5ms (30 m × 0.25 mm × 0.25 μm) or SLB-IL60 (30 m × 0.25 mm × 0.20 μm) ^{2}D: SUPELCOWAX10 (2 m × 0.10 mm × 0.10 μm)	GC × GC-MS (Flow modulation)	Sharif et al. [59]
2016	FAMEs in Biodiesel fuels	^{1}D: HP-1 PONA (100 m × 0.25 mm × 0.5 μm) ^{2}D: SLB-IL60 (30 m × 0.25 mm × 0.20 μm)	H/C MDGC/MS (Flow modulation)	Webster et al. [23]
2016	*Copaifera* oleoresin	^{1}D: SLB-IL111 (30 m × 0.25 mm × 0.20 μm), SLB-IL59 (30 m × 0.25 mm × 0.20 μm) ^{2}D: Rxi-5Sil MS, BPX5 (1 m × 0.10 mm × 0.10 μm)	GC × GC-TOFMS (Thermal modulation)	Wong et al. [24]
2016	Petrochemicals	^{1}D: DB-17 (30 m × 0.25 mm × 0.25 μm) ^{2}D: SLB-IL59 (2.0 m × 0.10 mm × 0.08 μm)	GC × GC-MS (Thermal modulation)	Cappelli Fontanive et al. [39]
2016	Petrochemicals (Diesel)	^{1}D: SLB-IL60 (20 m × 0.18 mm × 0.07 μm) ^{2}D: Rxi-17 (1.0 m × 0.10 mm × 0.10 μm)	GC × GC-TOFMS (Thermal modulation)	Manzano et al. [40]
2016	Petrochemicals	^{1}D: Rtx-5 (30 m × 0.25 mm × 0.25 μm) ^{2}D: Immobilized imidazolium IL-based columns (1.2 m × 0.25 mm × 0.28 μm)	GC × GC-FID (Thermal modulation)	Zhang et al. [47]
2015	FAMEs	^{1}D: SLB-IL111, SLB-IL100, SLB-IL82, SLB-IL76, SLB-IL61, SLB-IL59 (30 m × 0.25 mm × 0.20 μm) and SLB-IL111 (4 m × 0.10 mm × 0.08 μm) ^{2}D: SLB-IL111 (0.825 m × 0.10 mm × 0.08 μm)	GC × GC-FID (Thermal modulation)	Nolvachai et al. [21]
2015	Coffee and wine aroma	^{1}D: SLB-IL59 (30 m × 0.25 mm × 0.20 μm) ^{2}D: VF-200 MS (30 m × 0.25 mm × 0.25 μm), microbore VF-200 MS (1.0 m × 0.10 mm × 0.10 μm)	Integrated GC × GC and H/C MDGC with MS or olfactory detector (Thermal modulation)	Chin et al. [35]
2015	Petrochemicals	^{1}D: Rtx-5 (30 m × 0.25 mm × 0.25 μm) ^{2}D: Imidazolium IL-based columns (1.2 m × 0.25 mm × 0.28 μm)	GC × GC-FID (Thermal modulation)	Zhang et al. [46]
2015	Essential oils	LC: LC-Si column (250 mm × 4.6 mm ID × 5 μm d_p) GC1: SUPELCOWAX10 (30 m × 0.53 mm × 2.0 μm) GC2: Equity-5 (30 m × 0.53 mm × 5.0 μm) GC3: SLB-IL59 (30 m × 0.53 mm × 0.85 μm)	LC-GC-GC-GC (Valve-based modulation)	Pantò et al. [37]
2014	FAMEs in menhaden oil	^{1}D: SLB-IL111 (100 m × 0.25 mm × 0.20 μm) ^{2}D: SLB-IL111 (2 m × 0.10 mm × 0.08 μm)	GC × GC-FID (Thermal modulation)	Delmonte et al. [13]
2014	PASH	^{1}D: RXI-5MS (30 m × 0.25 mm × 0.25 μm) ^{2}D: SLB-IL60 (1 m × 0.1 mm × 0.08 μm)	GC × GC-MS (Thermal modulation)	Antle et al. [30]
2014	Petrochemicals	^{1}D: Rtx-5 (30 m × 0.25 mm × 0.25 μm) ^{2}D: Phosphonium IL-based columns (1.2 m × 0.25 mm × 0.28 μm)	GC × GC-FID (Thermal modulation)	Hantao et al. [45]
2014	Petrochemicals	^{1}D: SLB-IL100 (25 m × 0.25 mm × 0.20 μm) ^{2}D: HP-5MS (5 m × 0.25 mm × 0.25 μm)	GC × GC-FID (Flow modulation)	Májek et al. [64]
2014	Essential oils	LC: LC-Si column (250 mm × 4.6 mm ID × 5 μm d_p) GC1: Equity-5 (30 m × 0.53 mm × 5.0 μm) GC2: SLB-IL59 (30 m × 0.53 mm × 0.85 μm) GC3: SUPELCOWAX10 (30 m × 0.53 mm × 2 μm)	LC-GC-GC-GC (Valve-based modulation)	Sciarrone et al. [36]
2013	FAMEs	^{1}D: SLB-IL111 (200 m × 0.25 mm × 0.20 μm) ^{2}D: SLB-IL111 (2.5 m × 0.10 mm × 0.08 μm)	GC × GC-FID (Thermal modulation)	Delmonte et al. [12]
2013	FAMEs	^{1}D: DB-5MS (30 m × 0.25 mm × 0.25 μm) ^{2}D: SLB-IL111 (30 m × 0.25 mm × 0.2 μm), SLB-IL100 (30 m × 0.25 mm × 0.2 μm), or SLB-IL76 (30 m × 0.25 mm × 0.2 μm)	Integrated GC × GC-FID and H/C MDGC-FID (Thermal modulation)	Zeng et al. [18]
2013	FAMEs	^{1}D: SLB-IL111 (30 m × 0.25 mm × 0.20 μm) ^{2}D: SLB-IL111, SLB-IL100, SLB-IL82, SLB-IL76, SLB-IL61, SLB-IL59 (1 m × 0.25 mm × 0.08 μm)	GC × GC-FID (Thermal modulation)	Nosheen et al. [19]
2013	Essential oil	^{1}D: SLB-5MS (11.75 m × 0.10 mm × 0.10 μm) ^{2}D: SLB-IL60 (5.0 m × 0.25 mm × 0.25 μm)	GC × GC-QqQMS (Flow modulation)	Tranchida et al. [34]
2013	Biodiesel	^{1}D: HP-5 (30 m × 0.25 mm × 0.25 μm) ^{2}D: SLB-IL60 (1.0 m × 0.10 mm × 0.08 μm)	GC × GC-FID or MS (Thermal modulation)	Mogollon et al. [38]
2012	Pesticides	^{1}D: SLB-5MS (30 m × 0.25 mm × 0.25 μm) ^{2}D: SLB-IL59 (1.0 m × 0.10 mm × 0.08 μm)	GC × GC-MS (Thermal modulation)	Silva et al. [58]
2011	FAMEs	^{1}D: DB-1MS (10 m × 0.10 mm × 0.10 μm) ^{2}D: SLB-IL100 (4 m × 0.25 mm × 0.2 μm) or SLB-IL82 (4 m × 0.25 mm × 0.2 μm)	GC × GC-FID (Flow modulation)	Gu et al. [62]

(*continued on next page*)

Table 2 (*continued*)

Year	Sample	Column set[a]	Instrumentation	Reference
2011	PCBs	^{1}D: SPB-Octyl (30 m × 0.25 mm × 0.25 μm) ^{2}D: SLB-IL59 (1.8 m × 0.10 mm × 0.24 μm)	GC × GC-TOFMS (Thermal modulation)	Zapadlo et al. [28]
2011	PASH	^{1}D: DB5-HT (30 m × 0.32 mm × 0.10 μm) or BPX50 (30 m × 0.25 mm × 0.10 μm) ^{2}D: SLB-IL59 (1 m × 0.10 mm × 0.10 μm)	GC × GC-TOFMS or SCD (Thermal modulation)	Mahé et al. [29]
2010	PCBs	^{1}D: DB-5 (40 m × 0.10 mm × 0.10 μm) ^{2}D: SLB-IL36 (3 m × 0.10 mm × 0.24 μm) (Commercially SLB-IL59)	GC × GC-FID (Flow modulation)	Zapadlo et al. [27]
2010	Perfume	^{1}D: SLB-5MS (30 m × 0.25 mm × 0.25 μm) ^{2}D: SLB-IL59 (1.0 m × 0.10 mm × 0.08 μm)	GC × GC-MS (Thermal modulation)	Purcaro et al. [33]
2010	FAMEs in milk and beef fat	^{1}D: SLB-IL100 (60 m × 0.20 mm × 0.20 μm) ^{2}D: BPX-50 (3.0 m × 0.10 mm × 0.10 μm)	GC × GC-FID (Thermal modulation)	Villegas et al. [63]
2010	Diesel	^{1}D: DB-5 (30 m × 0.10 mm × 0.50 μm) ^{2}D: Imidazolium IL-based column (4 m × 0.10 mm × 0.08 μm) ^{3}D: DB-Wax (1 m × 0.10 mm × 0.10 μm)	GC^3-FID (Valve-based modulation)	Siegler et al. [42]

[a] Selected column sets employing IL-based columns as ^{1}D or ^{2}D columns were demonstrated.

thicknesses of the IL-coated layers. The thermal and surface sensitivity of the IL stationary phase demonstrated in this study revealed a complementary separation mechanism and a valid approach for selecting a column set with the best orthogonality employed in GC × GC.

Nolvachai and co-workers subsequently developed a theoretical model to simplify the process in selecting the best column sets including a number of IL-based columns for GC × GC [22]. They demonstrated analyte/stationary phase dependent selection approaches based on the linear solvation energy relationship. The best column sets for each separation of a sample could be determined according to the orthogonality, which indicates the quality of GC × GC separation results.

Webster et al. developed a method to identify and quantify trace-level contamination of FAMEs in diesel fuel using H/C MDGC with electron and chemical ionization MS [23]. A unique column set (100 m HP-1 PONA × 30 m SLB-IL60) was used for the identification of individual FAMEs at the low mg/L level. This system achieved detection limits for individual FAMEs ranging from 0.5 to 5.0 mg/L, which is two orders of magnitude lower than any previously reported analysis incorporating FAME speciation. The IL-based column provided unique selectivity as well as high thermal stability (up to 300 °C). This study demonstrated that the selection of a unique column set was critical in achieving sufficient resolution and high maximum allowable operating temperatures for complete elution of the analytes.

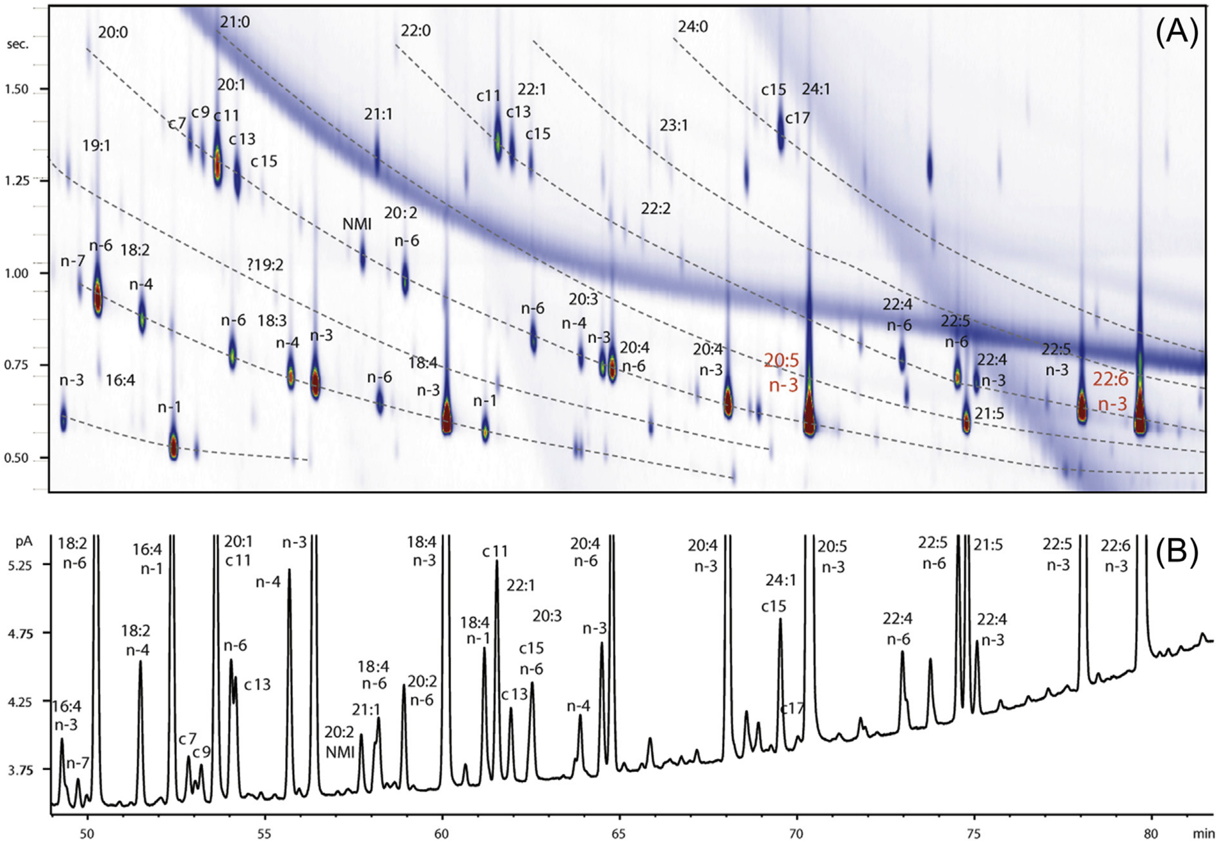


Fig. 2. Partial GC × GC (A) and 1D-GC separation (B) of FAMEs prepared from menhaden oil eluting from 20:0 to 22:6. A SLB-IL111 (100 m × 0.25 mm × 0.20 μm) × SLB-IL111 (2 m × 0.10 mm × 0.08 μm) column set was used. The 1D-GC separation was achieved by disabling the modulator. The figure is adapted with permission from Ref. [13].

Wong et al. used GC × GC with a polar × apolar column set to study *Copaifera* oleoresin [24]. Elution temperatures (Te) of diterpenic acid methyl esters (DAME) increased as the overall polarity value of the first dimension stationary phase (Rxi-17Sil, SUPELCOWAX10, SLB-IL59, and SLB-IL111) decreased. Since the Te of sesquiterpene hydrocarbons decreased with increased polarity, the SLB-IL111 first dimension stationary phase lead to excessive peak broadening in the second dimension apolar phase (Rxi-5Sil MS and BPX5) due to increased second dimension retention. Compared to other columns sets, GC × GC separation with the combination of SLB-IL59 and a nonpolar column (either Rxi-5Sil MS or BPX5) provided the optimal use of the separation space and low Te for sesquiterpenes and DAME, without excessive peak broadening in the second dimension.

In 2016, a new class of inert IL stationary phases, namely SLB-IL60i, SLBIL76i, and SLB-IL111i were introduced to the market. Pojjanapornpun et al. examined the performance of these new inert IL-based columns as well as conventional IL-based columns for the separation of FAMEs in GC × GC [25]. The inert and conventional IL columns showed comparable retention times and distribution patterns indicating nearly equivalent selectivity for FAME compounds. However, the inert IL columns exhibited reduced peak widths, reduced peak tailing, and lower column bleed. This study proved that the SLB-IL111i × SLB-IL59 column set is a good choice for the GC × GC analysis of FAMEs.

2.2. *Polychlorinated biphenyls*

Polychlorinated biphenyls (PCBs) were once widely used in coolant fluids, carbonless copy paper, and as heat transfer fluids. According to the US Environmental Protection Agency, PCBs are considered as probable human carcinogens. Due to the complexity of mixtures of isomers with different degrees of chlorination, no single column can separate all 209 congeners. Ros and co-workers investigated the use of different GC columns including HT-8, SUPELCOWAX10, SLB-IL59, SLB-IL61, SLB-IL76, SLB-IL82, SLB-IL100, and SLB-IL111 for the separation of PCBs using conventional 1D-GC [26]. The SLB-IL76 and SLB-IL59 stationary phases allowed the unambiguous determination of 47 and 51 of the evaluated congeners, respectively. In addition, the SLB-IL59 phase was the only one capable of providing complete resolution of the most toxic non-ortho congeners # 77, 126 and 169 from other PCBs in the test mixture. However, co-elution of PCB congeners was still observed including 3 (101/74, 118/110/175 and118/110/175) and 2 (52/47 and 118/110/136) on the SLB-IL59 and SLB-IL76 phases, respectively. GC × GC employing apolar × IL-based column sets was investigated as a possible solution to this challenge.

Zapadlo et al. investigated the use of GC × GC with highly polar IL-based columns for the analysis of PCBs [27]. As shown in Fig. 3(A–D), distinct retention behavior was observed for the PDMS and IL-based stationary phases in the GC × GC separation of 209 PCBs. GC × GC separations employing the DB-5 × SLB-IL36 (commercially available as SLB-IL59) column set exhibited a wider distribution pattern of the PCBs congeners and PCB isomers. Fig. 3(E–H) shows the GC × GC separation of toxic PCBs 81 and 105 from other PCBs. The DB-5 × SLB-IL36 column set exhibited wider distribution of PCBs and separated PCBs 105 and 127, which co-eluted on the DB-5 × BPX-70 column set. In a subsequent study, the same authors used a SPB-Octyl column possessing a poly(50%-*n*-octyl–50%-methyl)siloxane stationary phase and the same IL column to further increase the orthogonality of the column set and improve the separation [28]. As a result, a total of 196 out of 209 PCB congeners were resolved and identified using GC × GC coupled with a time-of-flight MS (TOFMS) detector.

2.3. *Polycyclic aromatic sulfur heterocycles*

Mahé et al. studied the optimization of experimental conditions for the high temperature GC × GC analysis of polycyclic aromatic sulfur heterocycles (PASHs) [29]. GC × GC coupled with a sulfur chemiluminescence detector (SCD) was used to obtain a quantitative distribution of heavy sulfur species contained in vacuum gas oils. The SLB-IL59 column was found to be much more selective towards highly aromatic sulfur-containing compounds compared to the BPX-50, DB1-HT and DB5-HT stationary phases. GC × GC separation using SLB-IL59 and an apolar column (e.g., DB-1HT, DB-5HT, and BPX-50) provided an innovative sulfur group-type separation, especially for the naphthenoaromatic sulfur-containing compound family. In this study, the sensitivity of the chromatographic system was evaluated via calculation of the detection limit, which was found to be lower than 0.5 pg/s (minimum detectable level of the SCD detector as specified by Agilent Technologies). The limit of quantification was lower than 0.8 ppb w/w of sulfur.

Antle et al. examined the retention behavior of 119 PASHs and their alkylated homologues on four commercially-available IL stationary phases [30]. As shown in Fig. 4, IL-based stationary phases provided better separation of polar compounds than non-polar columns, while withstanding higher temperatures than typical polar columns. Additionally, the utility of IL columns in GC × GC/MS analyses of PASH-containing coal tar samples was examined and it was found that the use of an IL column lead to improvements in the separation. For example, improved separation was observed using GC × GC employing the SLB-IL60 column for several homologous series of PAHs (e.g., alkylphenanthrene/anthracenes and chrysenes) and PASHs.

2.4. *Fragrances, essential oils, and food samples*

MDGC analysis has been widely applied for the analysis of fragrances, essential oils, and food samples. Recent review articles regarding MDGC analysis of food and essential oils have been published [31,32]. GC × GC employing IL-based columns can provide unique separation selectivities to further advance these applications.

Purcaro et al. evaluated the use of a rapid-scanning quadrupole MS detector for GC × GC employing an IL-based column as the ^{2}D column [33]. The performance of GC × GC/QMS system was evaluated by analyzing mixtures of 24 allergens and a commercial perfume sample. Under the developed conditions, more than 15 data points per peak were obtained using the GC × GC/QMS system, meeting the requirements for reliable peak reconstruction. This study demonstrated the possibility to use a quadrupole MS instrument for quantification in the GC × GC separation. The IL-based stationary phase employed in the second dimension provided a comparable polarity to that of a commercial PEG-based stationary phase (most commonly used for fragrance analysis) while providing higher thermal stability. Twelve allergens, all declared on the label, were identified in the commercial perfume sample with the concentration higher than the legal limit.

Tranchida et al. tested a GC × GC system coupled with a high-speed triple quadrupole MS for the analysis of mandarin essential oil contaminated with preservatives as well as phytosanitary compound spiked spearmint essential oil [34]. This study proved that high speed MS was able to match the high speed requirements of GC × GC (mass range: 40–360 m/z; scan speed: 20,000 amu/s). A polar × apolar column set (SLB-5ms × SLB-IL60) was employed in this study. For the phytosanitary product (e.g., terbufos, fenchlorphos, fenthion, bupiramate, and resmethrin (I/II)) spiked essential oil sample, resmethrin I/II were successfully separated from interfering substances with the aid of a second dimension

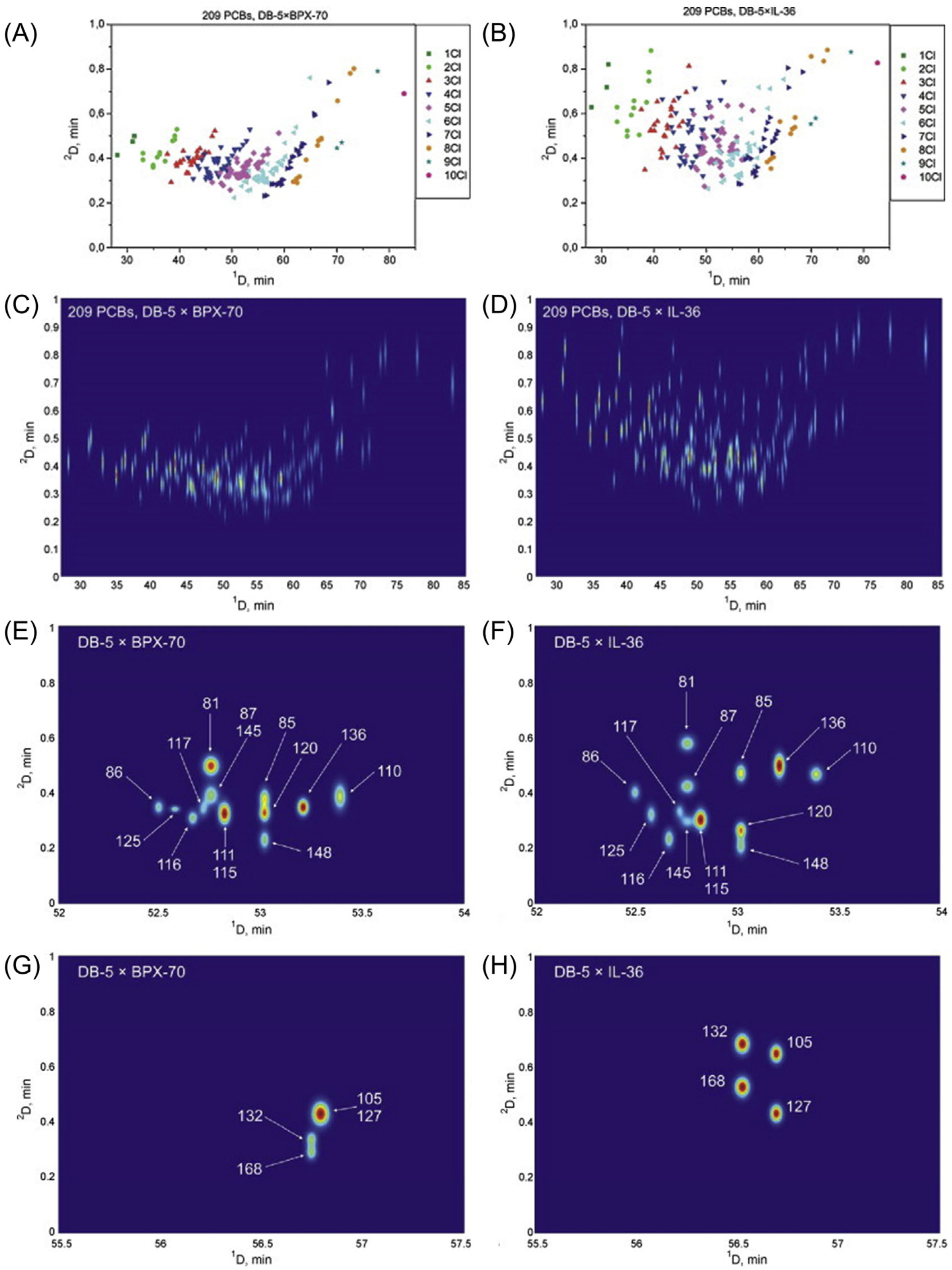
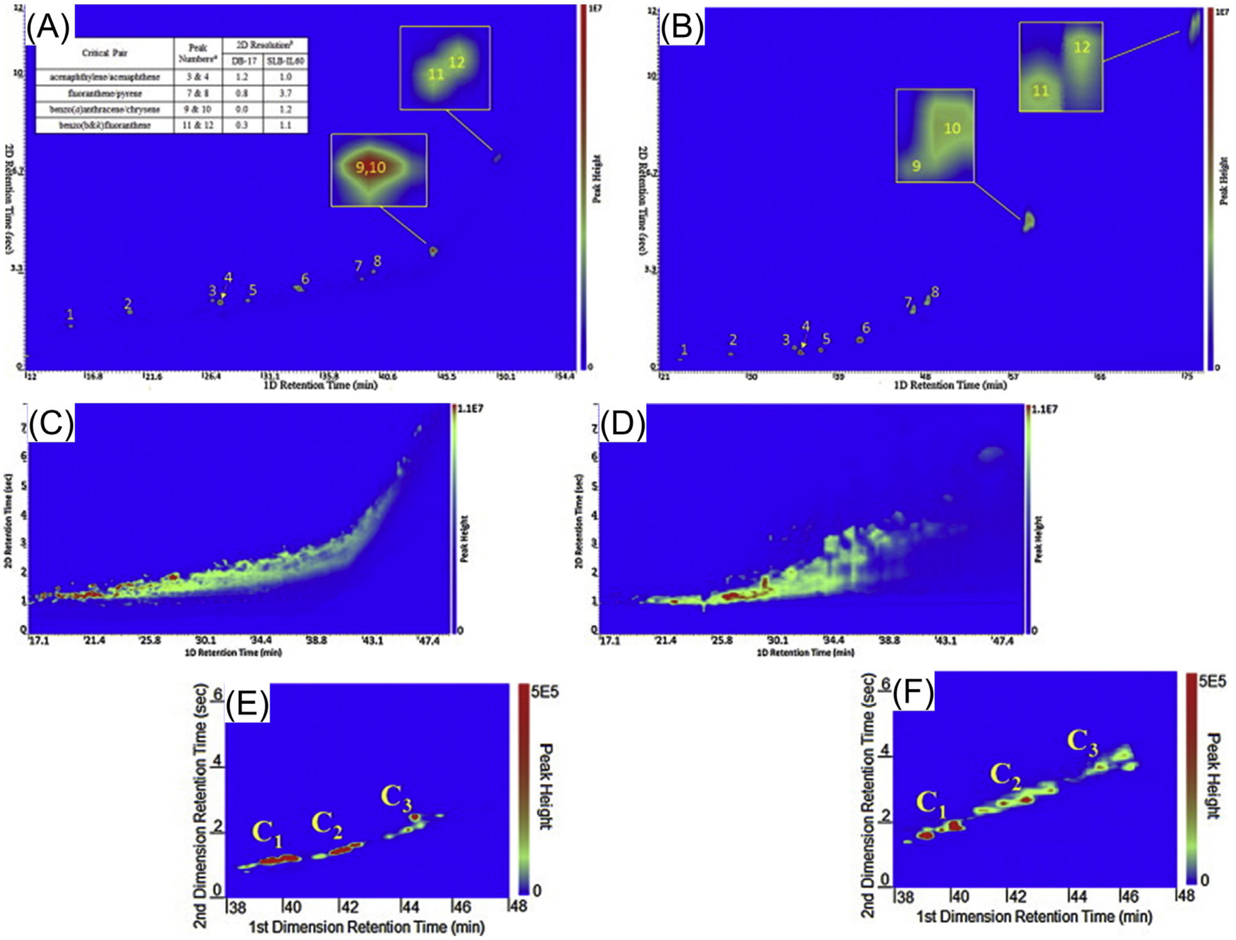


Fig. 3. GC × GC chromatograms illustrating the distribution of 209 PCBs (A–D) and toxic, dioxin-like PCBs 81 and 105 (E–H) employing DB-5 × BPX-70 and DB-5 × IL-36 column sets. The figure is adapted with permission from Ref. [27].

separation on the IL-based column. The selectivity contributed from the second dimension also provided additional separation power, while the targeted analyte (e.g., terbufos) co-eluted with unknown interferences on the first dimension column.

Chin et al. used an integrated H/C MDGC and GC × GC system with FID, MS, and olfactometric detectors to resolve the component co-elutions in the analysis and identification of odor-active volatile molecules in coffee and wine samples [35]. A column set consisting of SLB-IL59 and a mid-polar VF-200 ms phase was tested for headspace analysis of ground coffee volatiles. A majority of the extracted volatile compounds eluted after 10 min on the 1D SLB-IL59 column. The long retention of the extracted volatile compounds on the SLB-IL59 column is advantageous to modulate most of the compounds using a cryogenic modulator in GC × GC. Strong retention for coffee volatiles lead to a higher elution temperature and resulted in shorter ^{2}D retention times. Compared with the use of a 15 m FFAP column (acid modified PEG phase) in one dimensional separation, the SLB-IL59 × VF-200 ms column set reduced the possibility of compound wrap-around during GC × GC analysis.



Critical Pair	Peak Numbers[a]	2D Resolution[b]	
		DB-17	SLB-IL60
acenaphthylene/acenaphthene	3 & 4	1.2	1.0
fluoranthene/pyrene	7 & 8	0.8	3.7
benzo(*a*)anthracene/chrysene	9 & 10	0.0	1.2
benzo(b&k)fluoranthene	11 & 12	0.3	1.1

Fig. 4. GC × GC/MS analysis of PAH standards (A and B) and PASH in coal tar (C and D) using DB-5/DB-17 (A and C) and DB-5/SLB-IL60 (B and D). Peaks: 1,4-dichlorobenzene-d_4 (1); naphthalene (2); acenaphthylene (3); acenaphthene (4); fluorene (5); phenanthrene/anthracene (6); fluoranthene (7); pyrene (8); benzo(*a*)anthracene (9); chrysene (10); benzo(*b*) fluoranthene (11); benzo(k)fluoranthene (12). (E) and (F) are expanded region of (C) and (D). The figure is adapted with permission from Ref. [30].

Sciarrone et al. reported a multidimensional GC–GC–GC preparative system coupled to online normal phase LC for the separation and collection of low-amount constituents from essential oils [36]. This four-dimensional LC–GC–GC–GC system utilized a SUPELCOSIL LC-Si column with Equity-5, SLB-IL59, and SUPELCOWAX10 GC columns. This online four-dimensional system is an effective tool to collect target compounds at low concentration (less than 5%) from essential oil at milligram level amounts in a short period of time. For a specific constituent contained at the 4% level, only two LC–GC–GC–GC runs were required to isolate 1 mg (108 min per run). In another study by Pantò et al., LC–GC–GC-prep and GC–GC–GC-prep configurations of the system were used to collect important sesquiterpene alcohols from sandalwood essential oil (see Table 2 for detailed column configurations) [37]. The SLB-IL59 column exhibited different selectivity compared to PDMS and PEG-based columns and was effectively used in the third GC dimension for the final purification step. Seven of the most important sesquiterpene components were collected from sandalwood essential oil. High amounts of sesquiterpene components (190–1730 μg) were collected in a short time without any sample preparation step (about 1 h per run for the GC–GC–GC-prep configuration; about 90 min per run for the LC–GC–GC-prep configuration). The system can be a valuable alternative to the standard fractional distillation method for the purification of essential oil components.

2.5. Petrochemicals and fuels

Mogollon et al. investigated the use of the SLB-IL61 column as the second dimension in the GC × GC separation of biodiesel [38]. It was observed that nonpolar analytes such as aliphatic hydrocarbons were not well resolved in the second dimension, while polar analytes such as FAMEs were successfully identified.

Diesel and naphtha samples were analyzed by Cappelli Fontanive et al. using GC × GC/TOFMS employing IL-based columns for the analysis of organic sulfur compounds and nitrogen-containing compounds [39]. After investigating a series of column sets with different stationary phase chemistries, namely DB-5MS × DB-17, DB-17 × DB-5MS, DB-5MS × SLB-IL59, and SLB-IL59 × DB-5MS, the DB-5MS × SLB-IL59 column set was chosen for organic sulfur compounds analysis, while the SLB-IL59 × DB-5MS column set was chosen for nitrogen compounds. Each stationary phase column set was observed to provide the best chromatographic efficiency resulting in a higher number of resolved peaks for these two classes of compounds.

Manzano et al. used GC × GC coupled to TOFMS detector to analyze thia-arenes and aza-arenes in standard mixtures containing 45 polycyclic aromatic compounds (PACs) [40]. The SLB-IL60 × Rxi-17 column configuration favored molecular similarity grouping over isomer separation. This column configuration was used to increase the selectivity towards relatively more polar and less abundant aza-arenes to fully resolve them from complex matrices. The risk of false positives and overestimations in the analysis of thia-arenes, aza-arenes, and alkylated PACs was further reduced by using GC × GC/TOFMS with the SLB-IL60 × Rxi-17 column set, compared to 1D-GC/MS analysis. This is important for aza-arenes analysis due to their relatively low abundance compared to other PACs.

3. Tuning the selectivity of IL-based stationary phases for MDGC

Petrochemicals consisting of mostly aliphatic hydrocarbons and monoterpene hydrocarbons are generally not well retained by IL-based columns such as SLB-IL59, SLB-IL61, SLB-IL100, and SLB-IL111 [38–44]. The conventional categorizing system of GC stationary phases is based on the polarity calculated from McReynolds constants. This method is generally widely accepted by the chromatography community and is recommended as a guideline for the column selection process by various major companies. However, the solvation properties of the IL-based stationary phases can be structurally-tuned and designed to improve the separation performance toward target classes of analytes. Table 1 lists the chemical names and structures of new IL-based stationary phases used in MDGC.

To overcome the shortcomings of commercial IL stationary phases in the separation of nonpolar analytes, new IL stationary phases capable of expanding the range of analytes that can be efficiently separated by GC × GC have been developed by Hantao et al. [45]. As shown in Fig. 5, these new IL-based stationary phases, namely trihexyl(tetradecyl)phosphonium tetrachloroferrate ($[P_{66614}][FeCl_4]$) and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate ($[P_{66614}]$[FAP]), provided improved separation of nonpolar analytes (aliphatic hydrocarbons) in complex samples compared to the commercial IL-based columns. This study demonstrated that IL stationary phases possessing long alkyl chains as substituent groups on the cationic moiety are less cohesive and capable of improved nonspecific dispersive interactions with nonpolar analytes. In addition, the $[P_{66614}][FeCl_4]$ IL stationary phase exhibited a MAOT of 320 °C, which was 40 °C higher than that of the SUPELCOWAX10 stationary phase. This study demonstrated that IL-based stationary phases can be structurally tuned to provide better thermal stabilities and greater selectivities for the targeted analytes.

Zhang et al. investigated the role that structural features of ILs play on the enhanced selectivity of nonpolar analytes [46]. To evaluate functionalized ILs with varied cation/anion composition, a total of twelve imidazolium-based dicationic ILs with various anions were examined as second dimension stationary phases in GC × GC separations. This study showed that dispersive interactions play a key role for the separation of nonpolar aliphatic hydrocarbons by IL-based stationary phases. Zhang et al. further developed crosslinked polymeric ILs as stationary phases possessing high thermal stability (MAOT of 325 °C) as well as enhanced selectivity toward nonpolar analytes [47].

Nan et al. used lipid-inspired ILs as a class of low melting imidazolium-based ILs with long alkyl side-chain substituents to further improve the separation of nonpolar aliphatic hydrocarbons [48]. Lipidic ILs were designed to be less cohesive through the addition of symmetry breaking moieties (e.g., double bonds, thioether chains, and cyclopropanyl groups) within long alkyl side chains to produce ILs with low melting points. The palmitoleyl IL ((Z)-1-(9-hexadecenyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide) provided the highest selectivity compared to other lipidic ILs as well as a commercial SUPELCOWAX10 column. The 2D resolution values of selected analytes increased from 2.20, 2.05, and 7.23 for the SUPELCOWAX10 column to 2.81, 2.49, and 7.32 for the palmitoleyl lipidic IL. Moreover, a few groups of analytes that could not be separated on the Rtx-5 × SUPELCOWAX10 column set were fully resolved on the Rtx-5 × palmitoleyl lipidic IL column set. This study demonstrates the highly diverse approaches that can be undertaken to modify the structural features of ILs in an effort to tune solvation properties as well as thermal stabilities of the IL-based stationary phase for improved GC × GC separation of targeted analytes in complex samples. Recently, Talebi et al. evaluated twelve branched-chain dicationic ILs for 1D-GC separation of FAMEs [49]. The polarity as well as selectivity of IL-based stationary phases were found to be strongly influenced by the structural modification on the alkyl linkage chain. The expansive 100 m SP-2560 column used in official American Oil Chemists Society method can be replaced by a selected 30 m IL-based column in many applications (e.g., *cis–trans* FAME isomers). These structurally-tuned ILs can be certainly expected to provide more opportunities for various applications in MDGC analysis.

4. Advances and future trends

New generations of IL-based stationary phases with improved selectivity, thermal stability, surface wetting ability, and inertness are needed for the further development and application in MDGC analysis. It was reported that the DB-Wax column was considered as a preferred choice for the analysis of coffee volatiles due to its superior inertness, despite the IL-based column also exhibiting excellent resolution and efficiency [50]. SLB-IL61 and SLB-IL60 columns with improved inertness were first introduced to replace the SLB-IL59 column possessing similar chemical structures. The number of adsorbed peaks and the relative adsorption values (calculated by dividing the absolute peak area of compounds determined on IL column by that obtained on OV-1701, a highly inert column) of the SLB-IL60 and SLB-IL61 columns are much smaller than that of SLB-IL59 column [51]. Subsequently, a new generation of inert columns including SLB-IL60i, SLB-IL76i, and SLB-IL111i was introduced in 2016. The performance of these new inert IL columns were evaluated and the results show that these stationary phases are competitive in all respect with other commonly used PDMS or PEG-based columns (e.g. SE-52, OV-1, OV-1701, and PEG-20 M) for qualitative and quantitative analysis of fragrance and essential oils [52]. These new IL-based columns have been successfully applied for the GC × GC analysis of FAMEs with improved peak shape and inertness [25]. More applications using these inert columns in MDGC are certainly to be expected.

Column bleed at high oven temperatures is a factor that should continue to be improved for IL-based GC columns. Recently, Patil et al. investigated the thermal decomposition mechanisms of dicationic imidazolium, pyrrolidinium, and phosphonium-based ILs [53]. The heteroatom-carbon bonds (e.g., CO, CN, and CP) as well as position and number of substituents on the linkage chain was found to strongly affect the thermal stability of these ILs. For example, dicationic ILs with a PEG linker were much more prone to thermal decomposition due to the prolific breaking of CO bonds. The thermal stability of IL-based stationary phases can hinder applications requiring higher operating temperature. It has been reported that column bleeding occurs at lower temperature for the SLB-IL59 × DB5-HT column set compared to the DB5-HT × BPX50 column set. This resulted in a loss of elution for highly aromatic compounds and prevented an accurate quantification of the dinaphthodibenzothiophenes family of solutes, despite the SLB-IL59 × DB5-HT column set providing a better separation of naphtheno-aromatic sulfur compounds [29]. In addition, more sensitive and selective detectors (e.g., TOFMS, sulfur chemiluminescence detector (SCD), electron capture detector (ECD), and

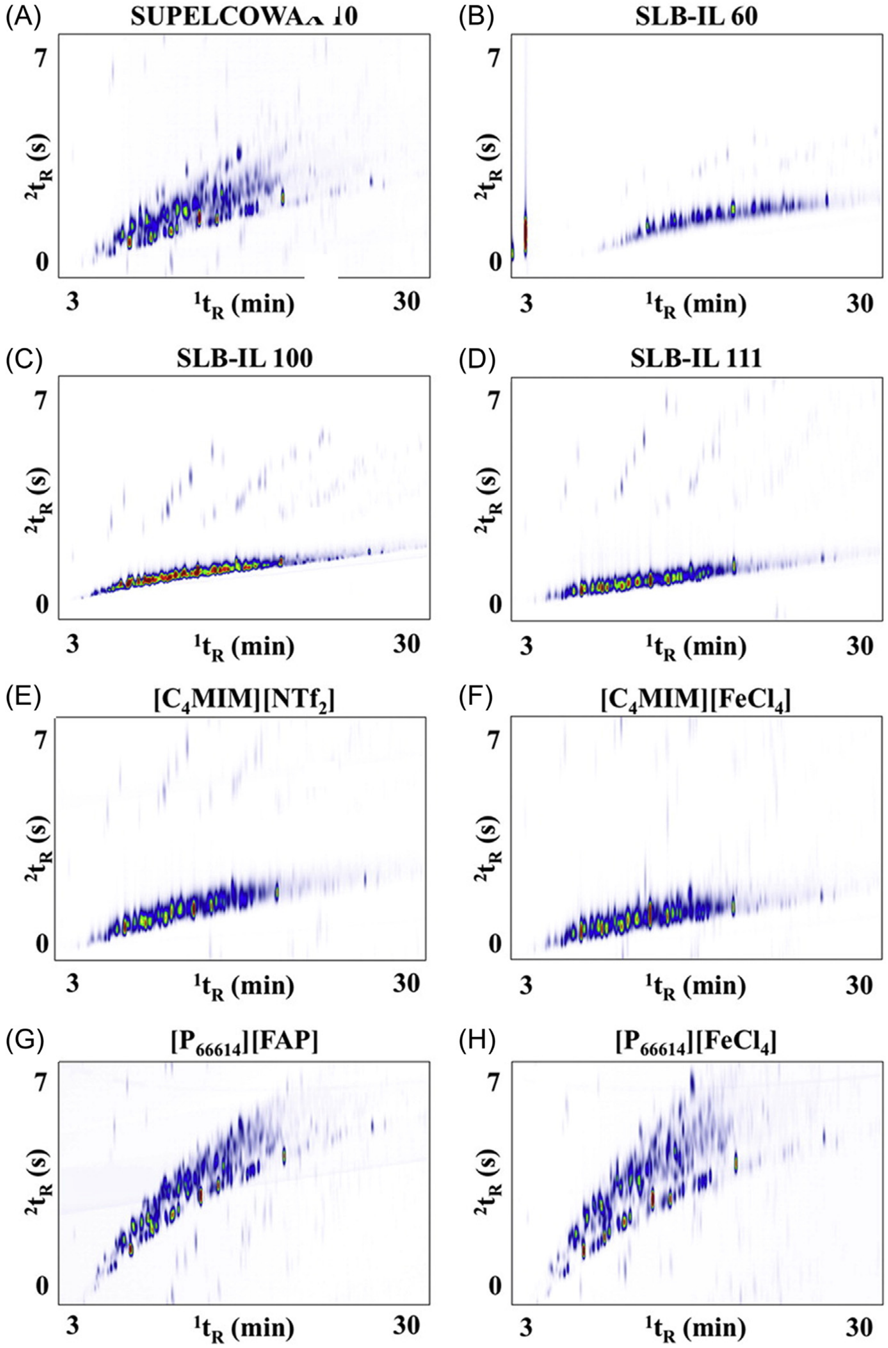


Fig. 5. GC × GC-FID chromatograms of kerosene employing several Rtx-5 × polar column sets: (A) SUPELCOWAX10, (B) SLB-IL60, (C) SLB-IL100, (D) SLB-IL111, (E) $[C_4MIM][NTf_2]$ IL, (F) $[C_4MIM][FeCl_4]$ IL, (G) $[P_{66614}][FAP]$ IL, and (H) $[P_{66614}][FeCl_4]$ IL. The figure is adapted with permission from Ref. [45].

nitrogen phosphorus detector (NPD)) have been or are in the progress of being coupled with MDGC using IL-based columns to improve the detection and identification of analytes in complex matrices. Therefore, continued developments in enhancing the polarity, inertness, and thermal stability are needed.

New IL stationary phase chemistries that provide unique selectivity towards target analytes are needed to improve the separation performance and versatility of MDGC. Since the solvation properties of ILs can be modified by incorporating desirable structural features, IL-based stationary phases possess great potential to tune separation selectivity and overall performance in MDGC. Recently, new types of ILs with unique solvation properties have been explored, such as ILs with triflate anions, glucaminium-based ILs, and metal-containing ILs [54–56]. Cagliero et al. investigated the use of water-compatible IL-based stationary phases to circumvent common problems in direct GC analysis of aqueous samples such as poor peak asymmetry, poor sensitivity and efficiency, strong adsorption, and stationary phase degradation [57]. This study showed that these IL-based columns can be routinely used for the direct analysis of samples with water as the main solvent. ILs possess unique selectivity towards water, acids, amines, alcohols, and unsaturated hydrocarbons and have great potential to further expand the use of IL-based GC columns in MDGC separations.

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