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1   **Ionic liquid stationary phases for multidimensional gas chromatography**

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4   **Abstract**

5   Ionic liquids (ILs) are a class of organic salts that meet many of the requirements of GC

6   stationary phases including high thermal stability, high viscosity, and tunable selectivity through

7   the modification of the chemical structure. IL-based columns, when incorporated either in the

8   first or second dimension, can offer unique selectivity compared to polydimethyl(siloxane) and

9   poly(ethyleneglycol) derived GC stationary phases for the separation of complex samples by

10   multidimensional gas chromatography. In addition, IL-based columns are emerging as superior

11   choices for applications requiring high polarity as well as high thermal stability. The present

12   contribution provides an overview on IL-based stationary phases for multidimensional gas

13   chromatography with an emphasis on developments in the period from 2012 to early 2018. The

14   analysis of various analytes (e.g., fatty acids, polycyclic aromatic sulfur heterocycles, and

15   biodiesels) in complex matrices as well as the developments of new IL-based stationary phases

16   for multidimensional gas chromatography are described.

17   **Keywords:** Comprehensive two-dimensional gas chromatography; Ionic liquids;

18   Multidimensional gas chromatography

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27 **1.   Introduction**

28   Multidimensional gas chromatography (MDGC) is one of the most useful tools available

29 for the analysis of volatile and semi-volatile analytes in complex mixtures. MDGC typically

30 combines two or more independent separation mechanisms to increase the peak capacity and

31 improve the resolution of unresolved regions within the 1D chromatographic separation. Heart

32 cutting multidimensional gas chromatography (H/C MDGC) typically connects two columns

33 using a flow-switching device which directs a specific segment of the primary column effluent

34 into the secondary column to improve the separation of the heart-cut region. In comparison,

35 comprehensive two-dimensional gas chromatography (GC × GC) connects two columns

36 possessing different selectivities (i.e., nonpolar × polar or polar × nonpolar column configuration)

37 to maximize peak capacity. All eluted compounds from the first column are transferred as a pulse

38 into a second column. For more information regarding the fundamentals of instrumental

39 principles for GC × GC and H/C MDGC, readers are encouraged to consult a number of

40 excellent review articles [1-4].

41   The analysis of complex samples such as petrochemicals, food additives, forensic

42 samples, fragrances, and pharmaceutical compounds requires more and more powerful analytical

43 tools due to the increasing demand for high resolution, high sensitivity, and information rich

44 analysis. The improvement of analyte detection limits, peak resolution, and peak capacity

45 requires the constant development of detectors, modulators, data analysis software, and GC

46 stationary phases that exhibit unique selectivity in MDGC. Recent developments of

47 instrumentation and data analysis methods in MDGC have been reviewed by Synovec and co-

48 workers [5]. Although advanced instrumentation and methods can improve separation results, the

2

49   selectivity, thermal stability, and inertness of the GC stationary phase always plays an important

50   role in the resolution, retention order, and analyte distribution in MDGC.

51   Ionic liquids (ILs) are salts that possess melting points at or below 100 °C [6]. A number

52   of IL-based stationary phases have been commercialized and have received increasing attention

53   due to their high thermal stability, low vapor pressure, and unique separation selectivities [7].

54   The chemical structure of ILs can be tailored to undergo various solvation interactions and

55   ultimately provide unique chromatographic selectivities. In addition, the chemical structures of

56   ILs can be modified to produce highly viscous products possessing high thermal stability. It is of

57   continued interest to design new IL-based stationary phases that can be coated to possess high

58   separation efficiencies as well as provide enhanced maximum allowable operating temperatures

59   (MAOT) that rival other commercially available stationary phases. Compared to more

60   conventional stationary phases based on polydimethyl(siloxane) (PDMS) and

61   poly(ethyleneglycol) (PEG), IL-based stationary phases are commonly considered as highly

62   polar phases based on the overall polarities derived from their McReynolds constants [8]. A

63   polarity scale system referred to as polarity number (PN) was introduced by Mondello and co-

64   workers and is used in the naming of commercialized Supelco IL GC columns, such as SLB-

65   IL59, SLB-IL100, and SLB-IL111 [8]. As shown in Figure 1, the IL-based GC columns

66   generally possess much higher overall polarity and PN values than PDMS- and PEG-based

67   columns, while providing similar or even higher MAOT than commercial PEG-based GC

68   columns (e.g., MAOT of 290 °C and polarity of 2705 for SLB-IL61; MAOT of 280 °C and

69   polarity of 2324 for the SUPELCOWAX10 column).

70   The first application of an IL-based column for MDGC was reported in 2006 [9]. A dual-

71   column setup consisting of an immobilized IL column (equivalent to commercially-available

3

72   SLB-IL100) was used to exploit stop-flow conditions at specific analysis times. Since this report,

73   a number of publications have demonstrated the use of IL-based columns in MDGC to provide

74   unique selectivities for target analytes. This review focuses on the recent applications of

75   commercial IL-based GC columns and the development of new IL-based stationary phases in GC

76   × GC and other selected types of MDGC, with an emphasis on developments made between

77   2012 to early 2018.

78

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

80   Table 1 lists seven of the most widely used commercially available IL-based GC columns.

81   For an overview of the early developments and applications of IL-based stationary phases in

82   MDGC, readers are encouraged to consult an excellent review article published by Mondello and

83   co-workers in 2012 [10]. Over the past few years as more IL columns with unique selectivity and

84   improved inertness as well as more sensitive and selective detectors were introduced, great

85   improvements have been made in detection, analyte identification, and applications using

86   MDGC. IL-based columns have been successfully used in the MDGC to improve the separation

87   and detection of analytes from complex matrices including food samples, agricultural products,

88   petrochemicals, environmental samples, and pharmaceutical compounds. Due to their high

89   overall polarity, IL-based columns have been widely applied for the analysis of highly polar

90   compounds in complex matrices (e.g., free and methylated fatty acids, fragrances, essential oils,

91   and pesticides). Selected applications of IL-based stationary phases in MDGC separations and

92   analysis are described below and are also summarized in Table 2.

93

94   *2.1 Fatty acid methyl esters*

95   By far, the majority of MDGC separations employing IL-based GC columns have been

96   applied for the analysis of fatty acid methyl esters (FAMEs). Recently, a review article was

97   published focusing on IL-based stationary phases for 1D-GC as well as MDGC separation of

98   FAMEs [11].

99   Delmonte et al. investigated the GC × GC separation of FAMEs using a SLB-IL111 (200

100   m × 0.25 mm × 0.20 µm) × SLB-IL111 (2.5 m × 0.10 mm × 0.08 µm) column set [12].

101   Compared to a previous study employing a single 200 m SLB-IL111 column, most of the

102   FAMEs were resolved through an addition of a second dimension of separation. The FAMEs

103   could be easily identified using a simple interpretation model based on the degree of saturation

104   and the carbon skeleton numbers.

105   To test the chromatographic conditions for the separation of the FAMEs from complex

106   samples, Delmonte et al. used GC × GC to analyze FAMEs prepared from menhaden oil [13].

107   The results showed the potential of resolving nearly all of the FAMEs prepared from complex

108   fats and oils in a single analysis. Figure 2 compares a 1D-GC chromatogram and GC × GC

109   contour plot for the separation of FAMEs from C20:0 to C22:6. Multiple co-eluted peaks of

110   FAMEs were observed using the 1D-GC separation. In comparison, the GC × GC separation

111   using the SLB-IL111 columns resolved most of the analytes within the separation space. These

112   results highlight the separation power of GC × GC when coupled with highly polar IL-based GC

113   stationary phases.

114   Delmonte also compared the performance of highly polar stationary phases consisting of

115   SP2560 (poly(90% biscyanopropyl/10% cyanopropylphenylsiloxane)) and the SLB-IL111 IL

116   (1,9-Di(3-vinylimidazolium)nonane bis[(trifluoromethyl)sulfonyl]imide) for the resolution of

117   geometric and positional isomers of the unsaturated fatty acids (FAs) occurring in dairy products

5

118   and partially hydrogenated vegetable oils [14]. The cyanopropyl modified PDMS-based

119   stationary phases (CP-Sil 88 and SP-2560) were used in the approved American Oil Chemists'

120   Society (AOCS) official methods for the separation of cis-, trans-, saturated, and unsaturated

121   fatty acids [15-17]. GC × GC employing a SP2560 × SLB-IL111 column set operated at 180 °C

122   was shown to separate C18:1 *trans* FAs (*t*FAs) and C18:2 *t*FAs from other FAMEs contained in

123   a hydrogenated soybean oil sample. However, the 18:3 *t*FAs partially co-eluted with C20:1

124   FAMEs. In comparison, GC × GC with the SLB-IL111 × SLB-IL111 column set operated at

125   160 °C separated 18:1 *t*FAs and 18:3 *t*FAs from other FAMEs, but was not able to separate 18:2

126   *t*FAs. Neither of the two column sets provided the separation of all C18:1, C18:2, and C18:3

127   *t*FAs from other FAMEs in the hydrogenated soybean oil sample.

128   Zeng et al. used an integrated GC × GC/MDGC system in the analysis of FAMEs

129   employing SLB-IL76, SLB-IL100, and SLB-IL111 columns [18]. This system possessed two

130   functional analysis pathways. The GC×GC mode provided the high resolution separation with

131   identification capability of different FAME isomers according to their 2D pattern, while the H/C

132   MDGC mode with a long ^{2}D IL-based column provided improved separation of the target region

133   under optimized conditions. This study used different IL columns as the second dimension

134   column to study retention behavior of FAMEs in MDGC separation. The estimated peak capacity

135   for the C18 FAMEs (C18:0 to c9, c12, c15-C18:3) increased from 10 (1D DB-5ms) to 30, 34, 41,

136   and 42 on FFAP, SLB-IL76, SLB-IL100, and SLB-IL111, respectively. This expanded

137   separation space on the IL column was found to be superior to PDMS or PEG-based phases

138   while offering better separation for complex FA samples.

139   Nosheen et al. used GC × GC employing a range of IL-based column sets (SLB-IL59,

140   SLB-IL61, SLB-IL76, SLB-IL82, SLB-IL100, SLB-IL111) to analyze safflower oil containing a

141   complex mixture of C18 saturated and unsaturated FAs amongst other FAs [19]. Compared to

142   other tested column sets, safflower oil FAMEs were well separated in less than 16 min using GC

143   × GC employing a SLB-IL111/IL59 column set. In addition, detection of less abundant FAs (e.g.,

144   myristic acid (C14:0) and palmitoleic acid (C16:1)) was determined and two new FAMEs

145   (pentadecanoic acid (C15:0) and heptadecanoic acid (C17:0)) were reported for the first time in

146   safflower oil.

147   To further understand and predict the retention behavior of FAMEs on IL-based columns

148   in GC × GC separations, Kulsing and co-workers developed a method using the molecular

149   structure of the stationary phases and target analytes to predict the separation results [20]. Using

150   correlations between molecular simulation and linear solvation energy relationships, a reliable

151   prediction of the equivalent chain length of FAMEs on each IL column (e.g., SLB-IL59, SLB-

152   IL61, SLB-IL76, SLB-IL82, SLB-IL100, SLB-IL111) was established for GC × GC. An

153   effective IL column selection method and a guide for the rational design of novel IL stationary

154   phases for the separation of FAMEs in GC × GC was achieved with reliable predicted separation

155   results.

156   Nolvachai et al. developed a theoretical concept and method to achieve a degree of

157   orthogonality in GC × GC for the separation of FAMEs using a single IL stationary phase [21].

158   The SLB-IL111 column was selected due to its great thermal sensitivity, which resulted in

159   significant differences between 1D temperature-programmed and 2D isothermal separations. The

160   switchable separation result, which inverts the retention of saturated and unsaturated FAME on

161   the 2D column, was achieved by varying the column diameters and surface thicknesses of the IL-

162   coated layers. The thermal and surface sensitivity of the IL stationary phase demonstrated in this

7

163 study revealed a complementary separation mechanism and a valid approach for selecting a

164 column set with the best orthogonality employed in GC × GC.

165   Nolvachai and co-workers subsequently developed a theoretical model to simplify the

166 process in selecting the best column sets including a number of IL-based columns for GC × GC

167 [22]. They demonstrated analyte/stationary phase dependent selection approaches based on the

168 linear solvation energy relationship. The best column sets for each separation of a sample could

169 be determined according to the orthogonality, which indicates the quality of GC × GC separation

170 results.

171   Webster et al. developed a method to identify and quantify trace-level contamination of

172 FAMEs in diesel fuel using H/C MDGC with electron and chemical ionization MS [23]. A

173 unique column set (100 m HP-1 PONA × 30 m SLB-IL60) was used for the identification of

174 individual FAMEs at the low mg/L level. This system achieved detection limits for individual

175 FAMEs ranging from 0.5 to 5.0 mg/L, which is two orders of magnitude lower than any

176 previously reported analysis incorporating FAME speciation. The IL-based column provided

177 unique selectivity as well as high thermal stability (up to 300 °C). This study demonstrated that

178 the selection of a unique column set was critical in achieving sufficient resolution and high

179 maximum allowable operating temperatures for complete elution of the analytes.

180   Wong et al. used GC × GC with a polar × apolar column set to study *Copaifera* oleoresin

181 [24]. Elution temperatures (Te) of diterpenic acid methyl esters (DAME) increased as the overall

182 polarity value of the first dimension stationary phase (Rxi-17Sil, SUPELCOWAX10, SLB-IL59,

183 and SLB-IL111) decreased. Since the Te of sesquiterpene hydrocarbons decreased with

184 increased polarity, the SLB-IL111 first dimension stationary phase lead to excessive peak

185 broadening in the second dimension apolar phase (Rxi-5Sil MS and BPX5) due to increased

186   second dimension retention. Compared to other columns sets, GC × GC separation with the

187   combination of SLB-IL59 and a nonpolar column (either Rxi-5Sil MS or BPX5) provided the

188   optimal use of the separation space and low Te for sesquiterpenes and DAME, without excessive

189   peak broadening in the second dimension.

190   In 2016, a new class of inert IL stationary phases, namely SLB-IL60i, SLBIL76i, and

191   SLB-IL111i were introduced to the market. Pojjanapornpun et al. examined the performance of

192   these new inert IL-based columns as well as conventional IL-based columns for the separation of

193   FAMEs in GC × GC [25]. The inert and conventional IL columns showed comparable retention

194   times and distribution patterns indicating nearly equivalent selectivity for FAME compounds.

195   However, the inert IL columns exhibited reduced peak widths, reduced peak tailing, and lower

196   column bleed. This study proved that the SLB-IL111i × SLB-IL59 column set is a good choice

197   for the GC × GC analysis of FAMEs.

198

199   *2.2   Polychlorinated biphenyls*

200   Polychlorinated biphenyls (PCBs) were once widely used in coolant fluids, carbonless

201   copy paper, and as heat transfer fluids. According to the US Environmental Protection Agency,

202   PCBs are considered as probable human carcinogens. Due to the complexity of mixtures of

203   isomers with different degrees of chlorination, no single column can separate all 209 congeners.

204   Ros and co-workers investigated the use of different GC columns including HT-8,

205   SUPELCOWAX10, SLB-IL59, SLB-IL61, SLB-IL76, SLB-IL82, SLB-IL100, and SLB-IL111

206   for the separation of PCBs using conventional 1D-GC [26]. The SLB-IL76 and SLB-IL59

207   stationary phases allowed the unambiguous determination of 47 and 51 of the evaluated

208   congeners, respectively. In addition, the SLB-IL59 phase was the only one capable of providing

209 complete resolution of the most toxic non-ortho congeners # 77, 126 and 169 from other PCBs in

210 the test mixture. However, co-elution of PCB congeners was still observed including 3 (101/74,

211 118/110/175 and118/110/175) and 2 (52/47 and 118/110/136) on the SLB-IL 59 and SLB-IL76

212 phases, respectively. GC × GC employing apolar × IL-based column sets was investigated as a

213 possible solution to this challenge.

214   Zapadlo et al. investigated the use of GC × GC with highly polar IL-based columns for

215 the analysis of PCBs [27]. As shown in Figure 3(A-D), distinct retention behavior was observed

216 for the PDMS and IL-based stationary phases in the GC × GC separation of 209 PCBs. GC × GC

217 separations employing the DB-5 × SLB-IL36 (commercially available as SLB-IL59) column set

218 exhibited a wider distribution pattern of the PCBs congeners and PCB isomers. Figure 3(E-H)

219 showed the GC × GC separation of toxic PCBs 81 and 105 from other PCBs. The DB-5 × SLB-

220 IL36 column set exhibited wider distribution of PCBs and separated PCBs 105 and 127, which

221 co-eluted on the DB-5 × BPX-70 column set. In a subsequent study, the same authors used a

222 SPB-Octyl column possessing a poly(50%-n-octyl-50%-methyl)siloxane) stationary phase and

223 the same IL column to further increase the orthogonality of the column set and improve the

224 separation [28]. As a result, a total of 196 out of 209 PCB congeners were resolved and

225 identified using GC×GC coupled with a time-of-flight MS (TOFMS) detector.

226

227 *2.3   Polycyclic aromatic sulfur heterocycles*

228   Mahé et al. studied the optimization of experimental conditions for the high temperature

229 GC × GC analysis of polycyclic aromatic sulfur heterocycles (PASHs) [29]. GC × GC coupled

230 with a sulfur chemiluminescence detector (SCD) was used to obtain a quantitative distribution of

231 heavy sulfur species contained in vacuum gas oils. The SLB-IL59 column was found to be much

10

232   more selective towards highly aromatic sulfur-containing compounds compared to the BPX-50,

233   DB1-HT and DB5-HT stationary phases. GC × GC separation using SLB-IL59 and an apolar

234   column (e.g., DB-1HT, DB-5HT, and BPX-50) provided an innovative sulfur group-type

235   separation, especially for the naphthenoaromatic sulfur-containing compound family. In this

236   study, the sensitivity of the chromatographic system was evaluated via calculation of the

237   detection limit, which was found to be lower than 0.5 pg/s (minimum detectable level of the SCD

238   detector as specified by Agilent Technologies). The limit of quantification was lower than 0.8

239   ppb w/w of sulfur.

240   Antle et al. examined the retention behavior of 119 PASHs and their alkylated

241   homologues on four commercially-available IL stationary phases [30]. As shown in Figure 4, IL-

242   based stationary phases provided better separation of polar compounds than non-polar columns,

243   while withstanding higher temperatures than typical polar columns. Additionally, the utility of IL

244   columns in GC × GC/MS analyses of PASH-containing coal tar samples was examined and it

245   was found that the use of an IL column lead to improvements in the separation. For example,

246   improved separation was observed using GC × GC employing the SLB-IL60 column for several

247   homologous series of PAHs (e.g., alkylphenanthrene/anthracenes and chrysenes) and PASHs.

248

249   *2.4   Fragrances, essential oils, and food samples*

250   MDGC analysis has been widely applied for the analysis of fragrances, essential oils, and

251   food samples. Recent review articles regarding MDGC analysis of food and essential oils have

252   been published [31, 32]. GC × GC employing IL-based columns can provide unique separation

253   selectivities to further advance these applications.

11

254   Purcaro et al. evaluated the use of a rapid-scanning quadrupole MS detector for GC × GC

255 employing an IL-based column as the ^{2}D column [33]. The performance of GC × GC/QMS

256 system was evaluated by analyzing mixtures of 24 allergens and a commercial perfume sample.

257 Under the developed conditions, more than 15 data points per peak were obtained using the GC

258 × GC/QMS system, meeting the requirements for reliable peak reconstruction. This study

259 demonstrated the possibility to use a quadrupole MS instrument for quantification in the GC ×

260 GC separation. The IL-based stationary phase employed in the second dimension provided a

261 comparable polarity to that of a commercial PEG-based stationary phase (most commonly used

262 for fragrance analysis) while providing higher thermal stability. Twelve allergens, all declared on

263 the label, were identified in the commercial perfume sample with the concentration higher than

264 the legal limit.

265   Tranchida et al. tested a GC × GC system coupled with a high-speed triple quadrupole

266 MS for the analysis of mandarin essential oil contaminated with preservatives as well as

267 phytosanitary compound spiked spearmint essential oil [34]. This study proved that high speed

268 MS was able to match the high speed requirements of GC × GC (mass range: 40–360 m/z; scan

269 speed: 20,000 amu/s). A polar × apolar column set (SLB-5ms × SLB-IL60) was employed in this

270 study. For the phytosanitary product (e.g., terbufos, fenchlorphos, fenthion, bupiramate, and

271 resmethrin (I/II)) spiked essential oil sample, resmethrin I/II were successfully separated from

272 interfering substances with the aid of a second dimension separation on the IL-based column.

273 The selectivity contributed from the second dimension also provided additional separation power,

274 while the targeted analyte (e.g., terbufos) co-eluted with unknown interferences on the first

275 dimension column.

276   Chin et al. used an integrated H/C MDGC and GC × GC system with FID, MS, and

277   olfactometric detectors to resolve the component co-elutions in the analysis and identification of

278   odor-active volatile molecules in coffee and wine samples [35]. A column set consisting of SLB-

279   IL59 and a mid-polar VF-200ms phase was tested for headspace analysis of ground coffee

280   volatiles. A majority of the extracted volatile compounds eluted after 10 min on the 1D SLB-

281   IL59 column. The long retention of the extracted volatile compounds on the SLB-IL59 column is

282   advantageous to modulate most of the compounds using a cryogenic modulator in GC × GC.

283   Strong retention for coffee volatiles lead to a higher elution temperature and resulted in shorter

284   ^{2}D retention times. Compared with the use of a 15 m FFAP column (acid modified PEG phase)

285   in one dimensional separation, the SLB-IL59 × VF-200ms column set reduced the possibility of

286   compound wrap-around during GC × GC analysis.

287   Sciarrone et al. reported a multidimensional GC-GC-GC preparative system coupled to

288   online normal phase LC for the separation and collection of low-amount constituents from

289   essential oils [36]. This four-dimensional LC-GC-GC-GC system utilized a SUPELCOSIL LC-

290   Si column with Equity-5, SLB-IL59, and SUPELCOWAX10 GC columns. This online four-

291   dimensional system is an effective tool to collect target compounds at low concentration (less

292   than 5%) from essential oil at milligram level amounts in a short period of time. For a specific

293   constituent contained at the 4% level, only two LC-GC-GC-GC runs were required to isolate 1

294   mg (108 min per run). In another study by Pantò et. al., LC-GC-GC-prep and GC-GC-GC-prep

295   configurations of the system were used to collect important sesquiterpene alcohols from

296   sandalwood essential oil (see Table 2 for detailed column configurations) [37]. The SLB-IL59

297   column exhibited different selectivity compared to PDMS and PEG-based columns and was

298   effectively used in the third GC dimension for the final purification step. Seven of the most

299 important sesquiterpene components were collected from sandalwood essential oil. High

300 amounts of sesquiterpene components (190-1730 µg) were collected in a short time without any

301 sample preparation step (about 1 hr per run for the GC-GC-GC-prep configuration; about 90 min

302 per run for the LC-GC-GC-prep configuration). The system can be a valuable alternative to the

303 standard fractional distillation method for the purification of essential oil components.

304

305 *2.5   Petrochemicals and fuels*

306   Mogollon et al. investigated the use of the SLB-IL61 column as the second dimension in

307 the GC × GC separation of biodiesel [38]. It was observed that nonpolar analytes such as

308 aliphatic hydrocarbons were not well resolved in the second dimension, while polar analytes

309 such as FAMEs were successfully identified.

310   Diesel and naphtha samples were analyzed by Cappelli Fontanive et al. using GC ×

311 GC/TOFMS employing IL-based columns for the analysis of organic sulfur compounds and

312 nitrogen-containing compounds [39]. After investigating a series of column sets with different

313 stationary phase chemistries, namely DB-5MS × DB-17, DB-17 × DB-5MS, DB-5MS × SLB-

314 IL59, and SLB-IL59 × DB-5MS, the DB-5MS × SLB-IL59 column set was chosen for organic

315 sulfur compounds analysis, while the SLB-IL59 × DB-5MS column set was chosen for nitrogen

316 compounds. Each stationary phase column set was observed to provide the best chromatographic

317 efficiency resulting in a higher number of resolved peaks for these two classes of compounds.

318   Manzano et al. used GC × GC coupled to TOFMS detector to analyze thia-arenes and

319 aza-arenes in standard mixtures containing 45 polycyclic aromatic compounds (PACs) [40]. The

320 SLB-IL60 × Rxi-17 column configuration favored molecular similarity grouping over isomer

321 separation. This column configuration was used to increase the selectivity towards relatively

14

322   more polar and less abundant aza-arenes to fully resolve them from complex matrices. The risk

323   of false positives and overestimations in the analysis of thia-arenes, aza-arenes, and alkylated

324   PACs was further reduced by using GC × GC/TOFMS with the SLB-IL60 × Rxi-17 column set,

325   compared to 1D-GC/MS analysis. This is important for aza-arenes analysis due to their relatively

326   low abundance compared to other PACs.

327

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

329   Petrochemicals consisting of mostly aliphatic hydrocarbons and monoterpene

330   hydrocarbons are generally not well retained by IL-based columns such as SLB-IL59, SLB-IL61,

331   SLB-IL100, and SLB-IL111 [38-44]. The conventional categorizing system of GC stationary

332   phases is based on the polarity calculated from McReynolds constants. This method is generally

333   widely accepted by the chromatography community and is recommended as a guideline for the

334   column selection process by various major companies. However, the solvation properties of the

335   IL-based stationary phases can be structurally-tuned and designed to improve the separation

336   performance toward target classes of analytes. Table 1 lists the chemical names and structures of

337   new IL-based stationary phases used in MDGC.

338   To overcome the shortcomings of commercial IL stationary phases in the separation of

339   nonpolar analytes, new IL stationary phases capable of expanding the range of analytes that can

340   be efficiently separated by GC × GC have been developed by Hantao et al. [45]. As shown in

341   Figure 5, these new IL-based stationary phases, namely trihexyl(tetradecyl)phosphonium

342   tetrachloroferrate ($[P_{66614}][FeCl_4]$) and trihexyl(tetradecyl)phosphonium

343   tris(pentafluoroethyl)trifluorophosphate ($[P_{66614}][FAP]$), provided improved separation of

344   nonpolar analytes (aliphatic hydrocarbons) in complex samples compared to the commercial IL-

345　based columns. This study demonstrated that IL stationary phases possessing long alkyl chains as

346　substituent groups on the cationic moiety are less cohesive and capable of improved nonspecific

347　dispersive interactions with nonpolar analytes. In addition, the $[P_{66614}][FeCl_4]$ IL stationary phase

348　exhibited a MAOT of 320 °C, which was 40 °C higher than that of the SUPELCOWAX10

349　stationary phase. This study demonstrated that IL-based stationary phases can be structurally

350　tuned to provide better thermal stabilities and greater selectivities for the targeted analytes.

351　　　Zhang et al. investigated the role that structural features of ILs play on the enhanced

352　selectivity of nonpolar analytes [46]. To evaluate functionalized ILs with varied cation/anion

353　composition, a total of twelve imidazolium-based dicationic ILs with various anions were

354　examined as second dimension stationary phases in GC × GC separations. This study showed

355　that dispersive interactions play a key role for the separation of nonpolar aliphatic hydrocarbons

356　by IL-based stationary phases. Zhang et al. further developed crosslinked polymeric ILs as

357　stationary phases possessing high thermal stability (MAOT of 325 °C) as well as enhanced

358　selectivity toward nonpolar analytes [47].

359　　　Nan et al. used lipid-inspired ILs as a class of low melting imidazolium-based ILs with

360　long alkyl side-chain substituents to further improve the separation of nonpolar aliphatic

361　hydrocarbons [48]. Lipidic ILs were designed to be less cohesive through the addition of

362　symmetry breaking moieties (e.g., double bonds, thioether chains, and cyclopropanyl groups)

363　within long alkyl side chains to produce ILs with low melting points. The palmitoleyl IL ((Z)-1-

364　(9-hexadecenyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide) provided the highest

365　selectivity compared to other lipidic ILs as well as a commercial SUPELCOWAX10 column.

366　The 2D resolution values of selected analytes increased from 2.20, 2.05, and 7.23 for the

367　SUPELCOWAX10 column to 2.81, 2.49, and 7.32 for the palmitoleyl lipidic IL. Moreover, a

16

368 few groups of analytes that could not be separated on the Rtx-5 × SUPELCOWAX10 column set

369 were fully resolved on the Rtx-5 × palmitoleyl lipidic IL column set. This study demonstrates the

370 highly diverse approaches that can be undertaken to modify the structural features of ILs in an

371 effort to tune solvation properties as well as thermal stabilities of the IL-based stationary phase

372 for improved GC × GC separation of targeted analytes in complex samples. Recently, Talebi et

373 al. evaluated twelve branched-chain dicationic ILs for 1D-GC separation of FAMEs [49]. The

374 polarity as well as selectivity of IL-based stationary phases were found to be strongly influenced

375 by the structural modification on the alkyl linkage chain. The expansive 100 m SP-2560 column

376 used in official American Oil Chemists Society method can be replaced by a selected 30 m IL-

377 based column in many applications (e.g., *cis-trans* FAME isomers). These structurally-tuned ILs

378 can be certainly expected to provide more opportunities for various applications in MDGC

379 analysis.

380

381 **4.   Advances and future trends**

382   New generations of IL-based stationary phases with improved selectivity, thermal

383 stability, surface wetting ability, and inertness are needed for the further development and

384 application in MDGC analysis. It was reported that the DB-Wax column was considered as a

385 preferred choice for the analysis of coffee volatiles due to its superior inertness, despite the IL-

386 based column also exhibiting excellent resolution and efficiency [50]. SLB-IL61 and SLB-IL60

387 columns with improved inertness were first introduced to replace the SLB-IL59 column

388 possessing similar chemical structures. The number of adsorbed peaks and the relative

389 adsorption values (calculated by dividing the absolute peak area of compounds determined on IL

390 column by that obtained on OV-1701, a highly inert column) of the SLB-IL60 and SLB-IL61

17

391 columns are much smaller than that of SLB-IL59 column [51]. Subsequently, a new generation

392 of inert columns including SLB-IL60i, SLB-IL76i, and SLB-IL111i was introduced in 2016. The

393 performance of these new inert IL columns were evaluated and the results show that these

394 stationary phases are competitive in all respect with other commonly used PDMS or PEG-based

395 columns (e.g. SE-52, OV-1, OV-1701, and PEG-20 M) for qualitative and quantitative analysis

396 of fragrance and essential oils [52]. These new IL-based columns have been successfully applied

397 for the GC × GC analysis of FAMEs with improved peak shape and inertness [25]. More

398 applications using these inert columns in MDGC are certainly to be expected.

399   Column bleed at high oven temperatures is a factor that should continue to be improved

400 for IL-based GC columns. Recently, Patil et al. investigated the thermal decomposition

401 mechanisms of dicationic imidazolium, pyrrolidinium, and phosphonium-based ILs [53]. The

402 heteroatom-carbon bonds (e.g., C-O, C-N, and C-P) as well as position and number of

403 substituents on the linkage chain was found to strongly affect the thermal stability of these ILs.

404 For example, dicationic ILs with a PEG linker were much more prone to thermal decomposition

405 due to the prolific breaking of C-O bonds. The thermal stability of IL-based stationary phases

406 can hinder applications requiring higher operating temperature. It has been reported that column

407 bleeding occurs at lower temperature for the SLB-IL59 × DB5-HT column set compared to the

408 DB5-HT × BPX50 column set. This resulted in a loss of elution for highly aromatic compounds

409 and prevented an accurate quantification of the dinaphthodibenzothiophenes family of solutes,

410 despite the SLB-IL59 × DB5-HT column set providing a better separation of naphtheno-aromatic

411 sulfur compounds [29]. In addition, more sensitive and selective detectors (e.g., TOFMS, sulfur

412 chemiluminescence detector (SCD), electron capture detector (ECD), and nitrogen phosphorus

413 detector (NPD)) have been or are in the progress of being coupled with MDGC using IL-based

414 columns to improve the detection and identification of analytes in complex matrices. Therefore,

415 continued developments in enhancing the polarity, inertness, and thermal stability are needed.

416 New IL stationary phase chemistries that provide unique selectivity towards target

417 analytes are needed to improve the separation performance and versatility of MDGC. Since the

418 solvation properties of ILs can be modified by incorporating desirable structural features, IL-

419 based stationary phases possess great potential to tune separation selectivity and overall

420 performance in MDGC. Recently, new types of ILs with unique solvation properties have been

421 explored, such as ILs with triflate anions, glucaminium-based ILs, and metal-containing ILs [54-

422 56]. Cagliero et al. investigated the use of water-compatible IL-based stationary phases to

423 circumvent common problems in direct GC analysis of aqueous samples such as poor peak

424 asymmetry, poor sensitivity and efficiency, strong adsorption, and stationary phase degradation

425 [57]. This study showed that these IL-based columns can be routinely used for the direct analysis

426 of samples with water as the main solvent. ILs possess unique selectivity towards water, acids,

427 amines, alcohols, and unsaturated hydrocarbons and have great potential to further expand the

428 use of IL-based GC columns in MDGC separations.

429

432

433 *The authors have declared no conflicts of interest*

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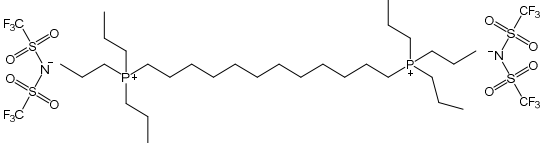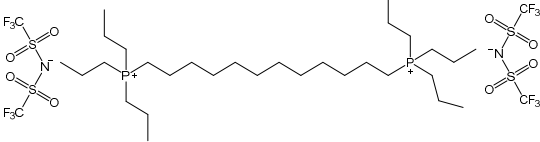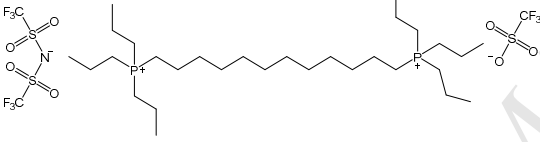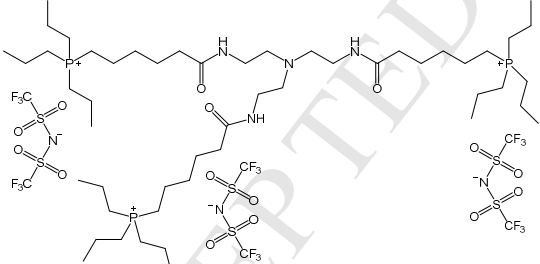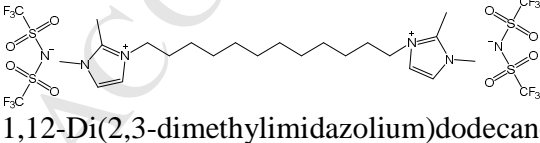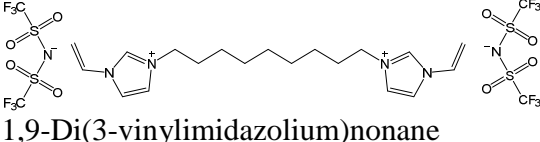
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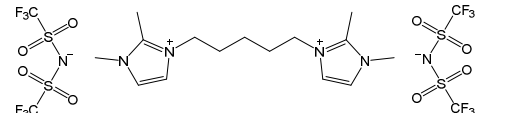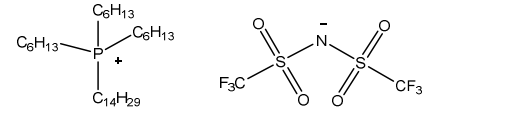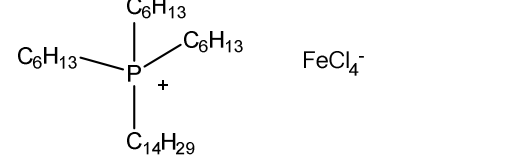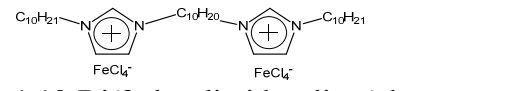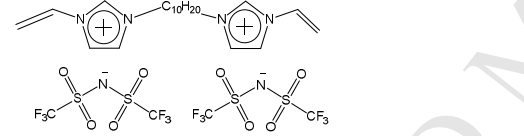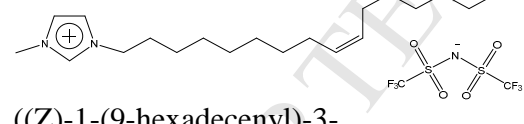613 quadrupole mass spectrometry for quantitative analysis, J. Chromatogr. A, 1255 (2012) 177-183.

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632

633

634 **Table 1** Chemical name and structure of selected IL-based stationary phases and their
635 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]

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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]
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]

636   [a]Overall polarity values derived from McReynolds constants were obtained from reference [8,
637   10].
638   [b]ILs do not possess commercial brand names.
639   [c]The polarity values have not been reported.

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

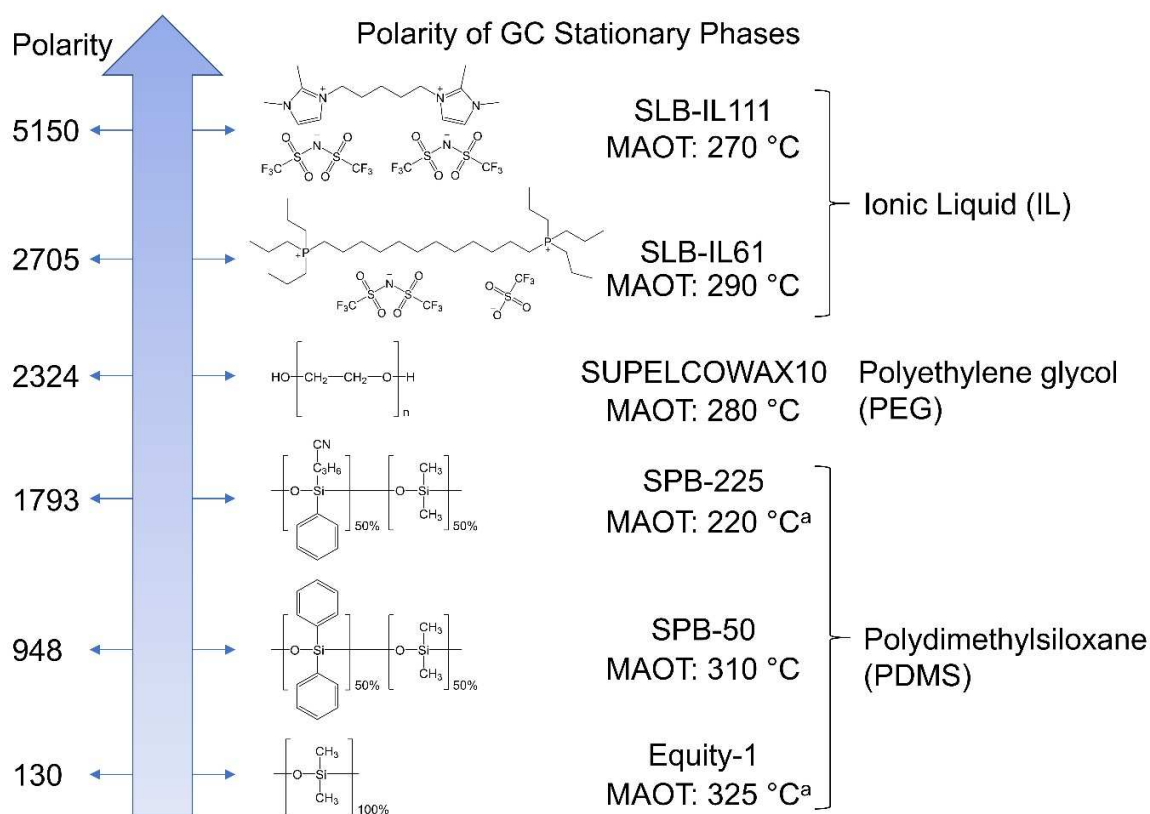| Year	Sample	Column Set[a]	Instrumentation	Reference
2018	FAMEs	[1]D: SLB-IL59i, SLB-IL60i, SLB-IL76i, and SLBIL111i (30 m × 0.25 mm × 0.25 µm) [2]D: SLB-IL59, SLB-IL60, SLB-IL76, and SLBIL111 (0.825 m × 0.10 mm × 0.08 µm)	GC × GC-MS (Thermal modulation)	Pojjanaporrnpun et al. [25]
2018	Mixtures of 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	[1]D: SLB-IL60 (20 m × 0.18 mm ×	GC × GC-	Manzano

	(Diesel)	$0.07\ \mu m$) [2]D: Rxi-17 ($1.0\ m \times 0.10\ mm \times 0.10\ \mu m$)	TOFMS (Thermal modulation)	et al. [40]
2016	Petrochemicals	[1]D: Rtx-5 ($30\ m \times 0.25\ mm \times 0.25\ \mu m$) [2]D: Immobilized imidazolium IL-based columns ($1.2\ m \times 0.25\ mm \times 0.28\ \mu m$)	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 ($30\ m \times 0.25\ mm \times 0.20\ \mu m$) and SLB-IL111 ($4\ m \times 0.10\ mm \times 0.08\ \mu m$) [2]D: SLB-IL111 ($0.825\ m \times 0.10\ mm \times 0.08\ \mu m$)	GC × GC-FID (Thermal modulation)	Nolvachai et al. [21]
2015	Coffee and wine aroma	[1]D: SLB-IL59 ($30\ m \times 0.25\ mm \times 0.20\ \mu m$) [2]D: VF-200 MS ($30\ m \times 0.25\ mm \times 0.25\ \mu m$), microbore VF-200 MS ($1.0\ m \times 0.10\ mm \times 0.10\ \mu m$)	Integrated GC × GC and H/C MDGC with MS or olfactory detector (Thermal modulation)	Chin et al. [35]
2015	Petrochemicals	[1]D: Rtx-5 ($30\ m \times 0.25\ mm \times 0.25\ \mu m$) [2]D: Imidazolium IL-based columns ($1.2\ m \times 0.25\ mm \times 0.28\ \mu m$)	GC × GC-FID (Thermal modulation)	Zhang et al. [46]
2015	Essential oils	LC: LC-Si column ($250\ mm \times 4.6\ mm\ ID \times 5\ \mu m\ d_p$) GC1: SUPELCOWAX10 ($30\ m \times 0.53\ mm \times 2.0\ \mu m$) GC2: Equity-5 ($30\ m \times 0.53\ mm \times 5.0\ \mu m$) GC3: SLB-IL59 ($30\ m \times 0.53\ mm \times 0.85\ \mu m$)	LC-GC-GC-GC (Valve-based modulation)	Pantò et al. [37]
2014	FAMEs in menhaden oil	[1]D: SLB-IL111 ($100\ m \times 0.25\ mm \times 0.20\ \mu m$) [2]D: SLB-IL111 ($2\ m \times 0.10\ mm \times 0.08\ \mu m$)	GC × GC-FID (Thermal modulation)	Delmonte et al. [13]
2014	PASH	[1]D: RXI-5MS ($30\ m \times 0.25\ mm \times 0.25\ \mu m$) [2]D: SLB-IL60 ($1\ m \times 0.1\ mm \times 0.08\ \mu m$)	GC × GC-MS (Thermal modulation)	Antle et al. [30]
2014	Petrochemicals	[1]D: Rtx-5 ($30\ m \times 0.25\ mm \times 0.25\ \mu m$) [2]D: Phosphonium IL-based columns ($1.2\ m \times 0.25\ mm \times 0.28\ \mu m$)	GC × GC-FID (Thermal modulation)	Hantao et al. [45]

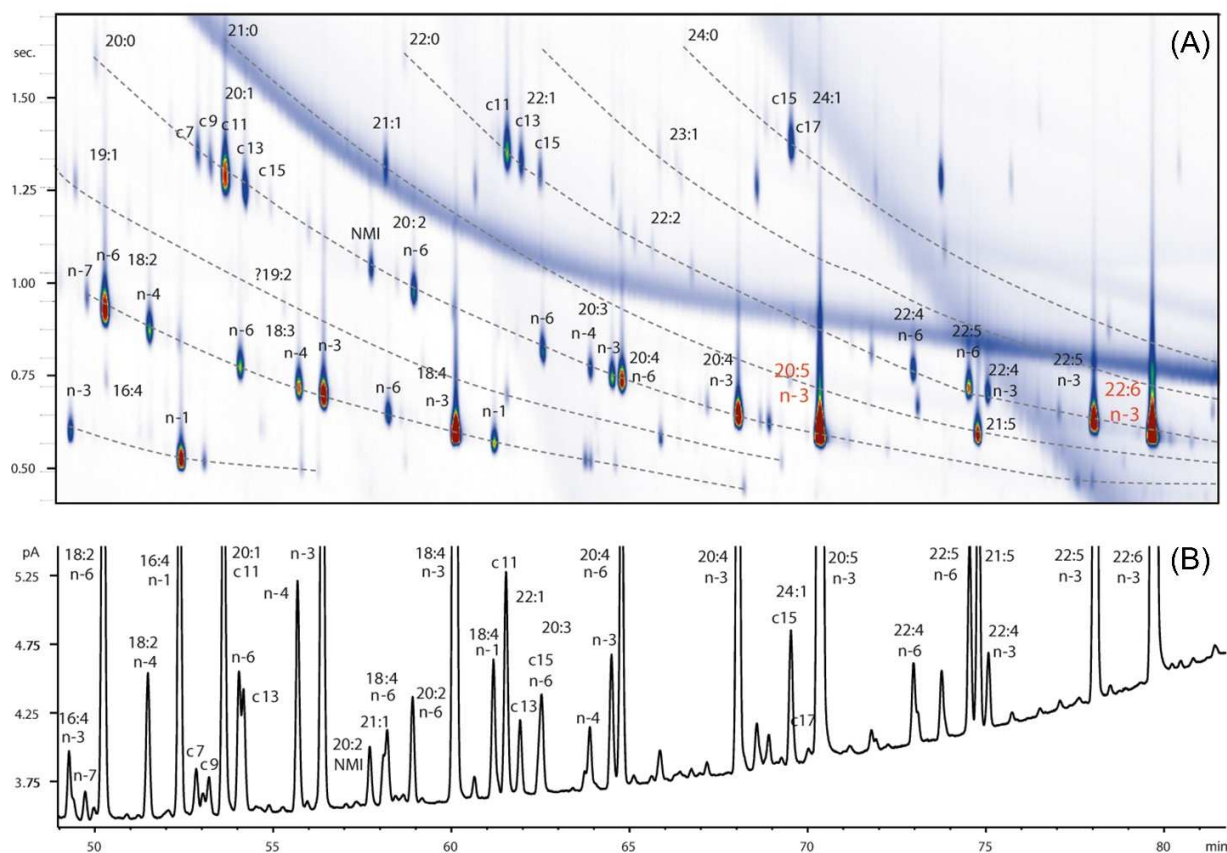| 2014	Petrochemicals	^{1}D: SLB-IL100 (25 m × 0.25 mm × 0.20 µm) ^{2}D: HP-5MS (5 m × 0.25 mm × 0.25 µm)	GC × GC-FID (Flow modulation)	Májek et al. [64]
2014	Essential oils	LC: LC-Si column (250 mm × 4.6 mm ID × 5 µm d_p) GC1: Equity-5 (30 m × 0.53 mm × 5.0 µm) GC2: SLB-IL59 (30 m × 0.53 mm × 0.85 µm) 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]
2011	PCBs	^{1}D: SPB-Octyl (30 m × 0.25 mm × 0.25 µm)	GC × GC-TOFMS	Zapadlo et al. [28]

33

		[2]D: SLB-IL59 (1.8 m × 0.10 mm × 0.24 µm)	(Thermal modulation)	
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]

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

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Polarity of GC Stationary Phases
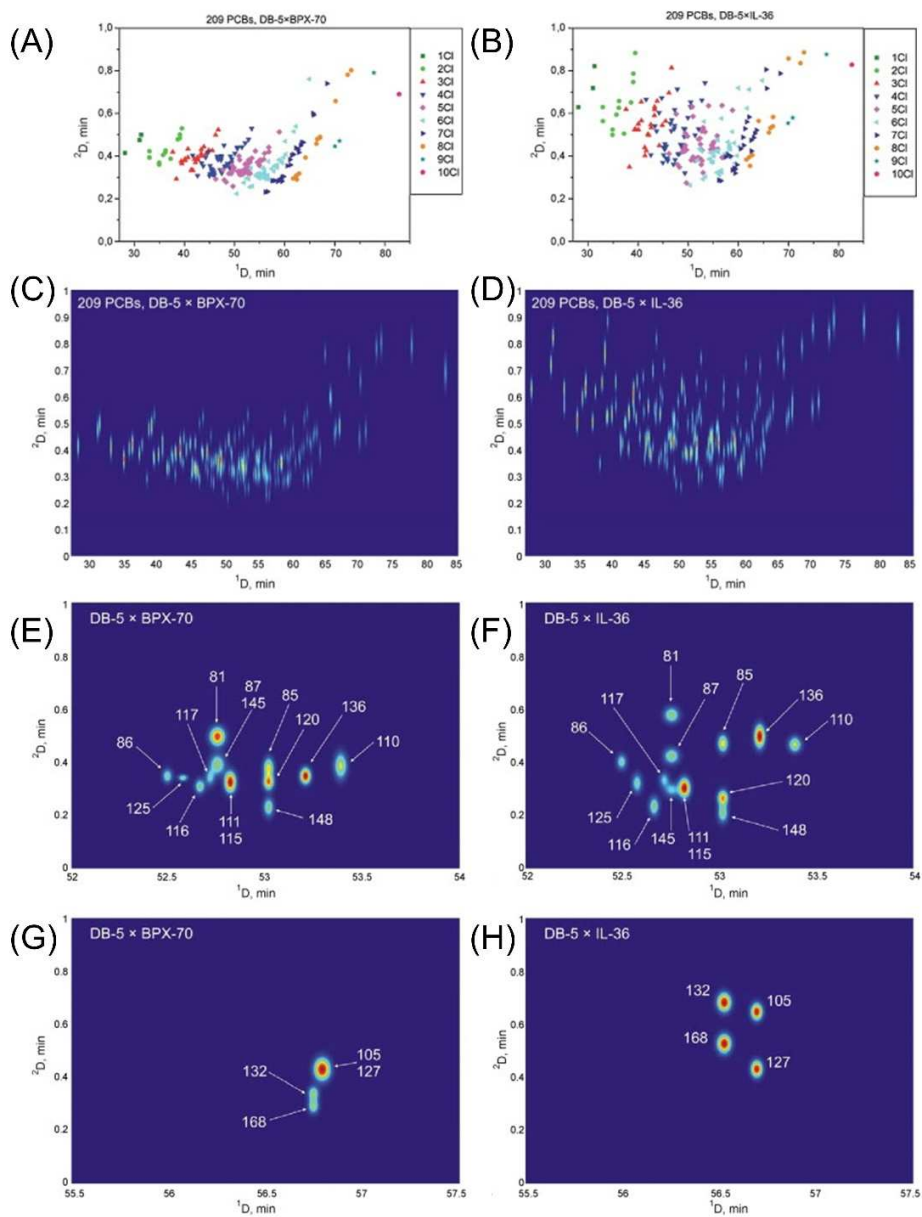
Figure 1 Chemical structure and overall polarity values of selected commercially-available GC

stationary phases. The overall polarity values are obtained from the references [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.
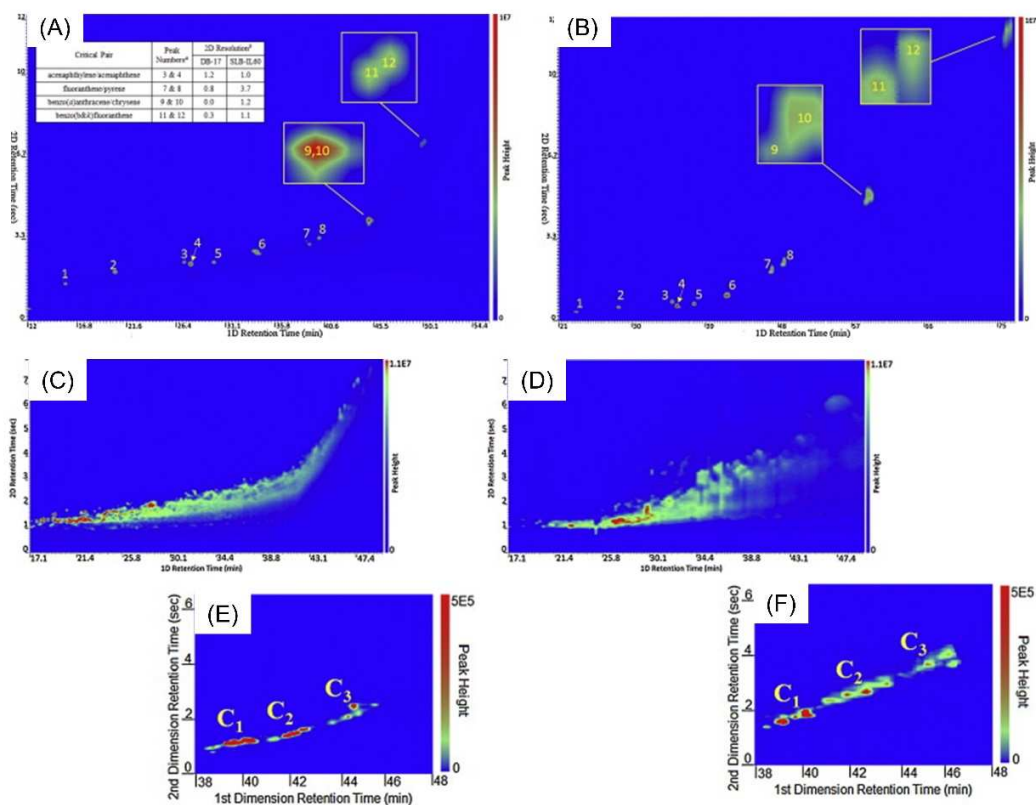
652
653 **Figure 2** Partial GC × GC (A) and 1D-GC separation (B) of FAMEs prepared from menhaden

654 oil eluting from 20:0 to 22:6. A SLB-IL111 (100 m × 0.25 mm × 0.20 µm) × SLB-IL111 (2 m ×

655 0.10 mm × 0.08 µm) column set was used. The 1D-GC separation was achieved by disabling the

656 modulator. The figure is adapted with permission from reference [13].

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658
659 **Figure 3** GC × GC chromatograms illustrating the distribution of 209 PCBs (A-D) and toxic,

660 dioxin-like PCBs 81 and 105 (E-H) employing DB-5 × BPX-70 and DB-5 × IL-36 column sets.

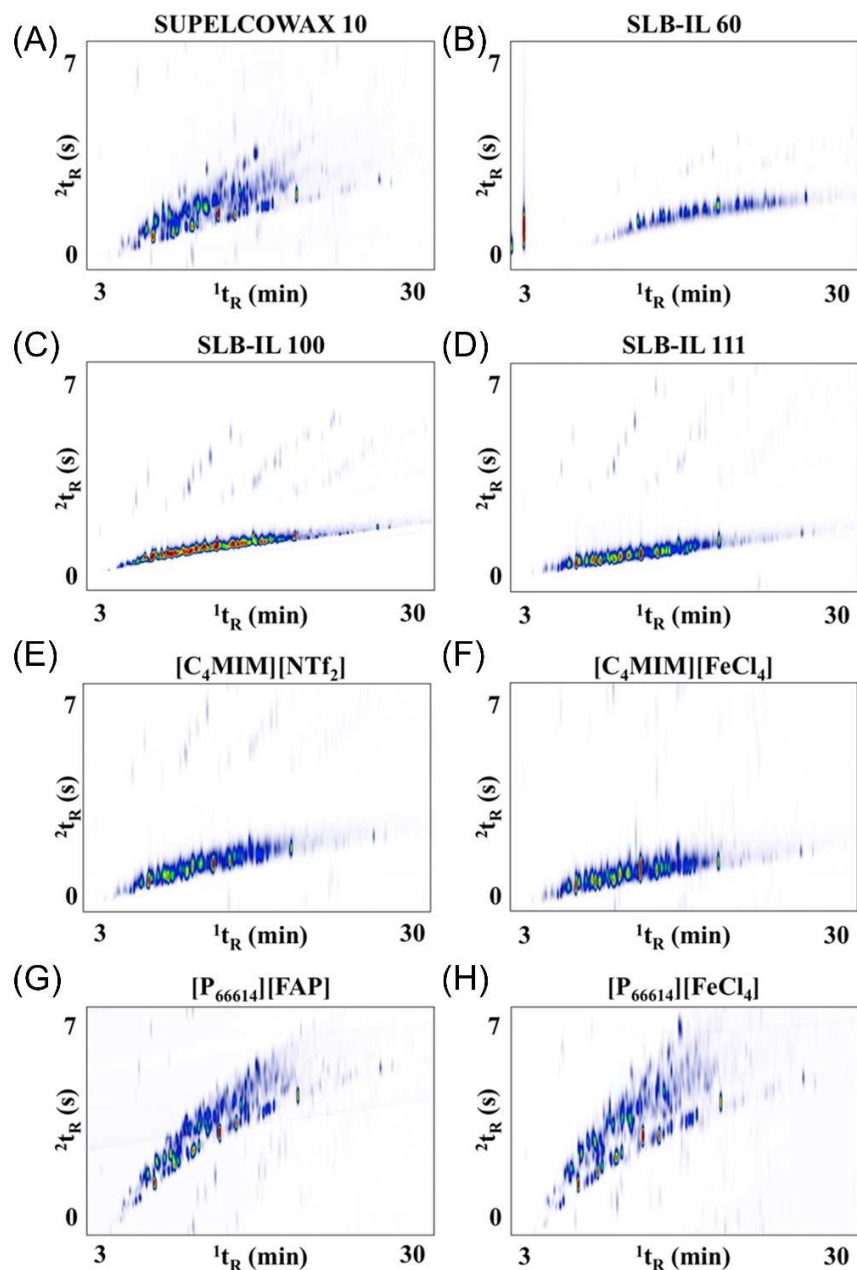661 The figure is adapted with permission from reference [27].

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664

665 **Figure 4** GC × GC/MS analysis of PAH standards (A and B) and PASH in coal tar (C and D)

666 using DB-5/DB-17 (A and C) and DB-5/SLB-IL60 (B and D). Peaks: 1,4-dichlorobenzene-d_4 (1);

667 naphthalene (2); acenaphthylene (3); acenaphthene (4); fluorene (5); phenanthrene/anthracene

668 (6); fluoranthene (7); pyrene (8); benzo(a)anthracene (9); chrysene (10); benzo(b)fluoranthene

669 (11); benzo(k)fluoranthene (12). (E) and (F) are expanded region of (C) and (D). The figure is

670 adapted with permission from reference [30].

671

Figure 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$_4$MIM][NTf$_2$] IL, (F) [C$_4$MIM][FeCl$_4$] IL, (G) [P$_{66614}$][FAP] IL, and (H) [P$_{66614}$][FeCl$_4$] IL.

The figure is adapted with permission from reference [45].

Highlights

• Overview of ionic liquid stationary phases for multidimensional gas chromatography

• Applications of different ionic liquid stationary phases are reviewed

• Polarity, inertness, and thermal stability of IL stationary phases are discussed

• Recent advances including new IL-based stationary phases are highlighted