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**Ionic liquids as stationary phases for gas chromatography—Unusual selectivity of ionic liquids with a phosphonium cation and different anions in the flavor, fragrance and essential oil analyses**

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(Article begins on next page)

1 *Ionic liquids as stationary phases for gas chromatography – Unusual*  
2 *selectivity of ionic liquids with a phosphonium cation and different anions in*  
3 *the flavor, fragrance and essential oil analyses*

4

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17

18 **Abstract**

19 Room-temperature ionic liquids (ILs) have been shown to be successful as stationary phases (SPs) for gas  
20 chromatography in several fields of applications because of their unique and tunable selectivity, low vapor  
21 pressure and volatility, high thermal stability (over 300°C), and good chromatographic properties. This study has  
22 been focused on two ILs based on a phosphonium cation (trihexyl(tetradecyl)phosphonium, P<sub>66614</sub>) combined  
23 with different anions, previously shown to be suitable as gas chromatography (GC) SPs. In particular,  
24 trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide ([P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]) and  
25 trihexyl(tetradecyl)phosphonium chloride ([P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>]) were investigated, as the Abraham linear solvation  
26 energy relationship has shown their ability to interact with the solute(s) when tested with a set of 26 to 34 probe  
27 analytes. The chromatographic performance were investigated on narrow bore and conventional test columns  
28 using the following: i) Grob test, ii) a group of model mixtures of compounds characteristic of the flavor, fragrance  
29 and essential oil fields (FFMix), iii) a standard mixture of 29 volatile allergens (AIMix), and iv) two essential oils  
30 of different complexity (sage and vetiver essential oils). The columns coated with the investigated IL SPs were  
31 characterized by similar polarity (Polarity Number (PN): 37 for [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] and 33 for [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]), high  
32 efficiency and highly satisfactory inertness. The two IL SPs also exhibited a completely different separation  
33 performance, with [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] test columns mainly characterized by high retention and selectivity based on the  
34 analyte functional groups, and [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>] test columns featured by short retention and selectivity mainly  
35 related to the analyte volatility and polarity. These results were also confirmed with the analysis of sage and  
36 vetiver essential oils.

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42 **Keywords:** ionic liquid stationary phases; gas chromatography, phosphonium-based ionic liquids; selectivity;  
43 chromatographic properties; flavours, fragrances and essential oils

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## 45 1. Introduction

46 The interest of room-temperature ionic liquids (ILs) as stationary phases (SPs) for gas chromatography is  
47 constantly increasing not only because of their unique and tunable selectivity but also for their low vapor pressure  
48 and volatility, thermal stability (over 300°C), and compatibility with modern column technology (viscosity and  
49 wetting properties). The use of ILs in analytical chemistry (from sample preparation to analysis including GC),  
50 was exhaustively reviewed by Ho et al. in 2014 [1] and recently updated by Berthod et al. [2]. These articles also  
51 list a number of other reviews published over the past decade describing developments, chromatographic  
52 properties, and applications to specific fields of several ILs and polymeric ILs (PILs) in GC and MDGC. Other  
53 reviews by Hantao et al. [3], Kulsing et al. [4], Sun et al. [5], and Nan and Anderson [6] have since addressed IL  
54 applications in GC.

55 The popularity of IL coated GC columns was strongly influenced by their commercial introduction by Supelco in  
56 2008. The first one of them, know with the acronym SLB-IL100, was followed by a group of others, including  
57 SLB-IL59, SLB-IL60, SLB-IL61, SLB-IL76, SLB-IL82, SLB-IL111, characterized by different polarities mainly  
58 based on nitrogen and phosphorus cations. The number distinguishing each column is the Polarity Number  
59 defined through their Mc Reynolds constants [7]. The performance and selectivity of these IL columns were of  
60 high interest for several fields, but further efforts had to be made in column manufacturing to reduce their activity,  
61 particularly towards polar or active analytes. The goal of inertness comparable to that of conventional columns,  
62 in particular for routine quantitative analysis, was achieved in 2016 by Sidisky and the Supelco group that  
63 developed a new generation of highly-inert columns coated with three of the most applied ionic liquids (i.e. SLB-  
64 IL60i, SLB-IL76i and SLB-IL111i) by carefully tuning the surface treatment of the fused silica during column  
65 preparation [8-12].

66 The peculiar selectivity of ILs made them of great interest, also for the flavor, fragrance and essential oil (EO)  
67 fields whose analysts are constantly looking for new stationary phases with unconventional selectivities  
68 compared to those currently-used based on polysiloxane and polyethylene glycol derivatives, while always  
69 maintaining good chromatographic properties in terms of efficiency and inertness [9, 13, 14]. This need is  
70 necessitated because samples of these fields are often complex mixtures of isomeric and/or homologous  
71 components with similar structural and physical characteristics (e.g. mono- and sesquiterpenoids in EOs) whose  
72 correct identification requires a decisive contribution of diagnostic chromatographic data (e.g. retention indices)  
73 to be combined with their mass spectra [15]. A number of applications of IL columns have already been reported  
74 in these fields, including the analysis of flavor and fragrance mixtures [16, 17], allergens [9, 13, 14, 18], coffee  
75 aroma [19] and several EOs (i.e. peppermint essential oil [20], lemon essential oil [7], fennel, cinnamon and  
76 nutmeg essential oils [21], chamomile and sandalwood essential oils [9], and cornmint and vetiver essential oils  
77 [14]). Because of their peculiar selectivity, IL stationary phases were also successfully and widely applied in  
78 multidimensional GC systems; Nan and Anderson [6] have recently exhaustively reviewed this topic. Three quite

79 recent applications among others: i) Sciarrone et al. applied HS-SPME-Heart/Cut (H/C)-C-IRMS with  
80 simultaneous quadrupole MS detection using SLB-IL59 in the second GC dimension to authenticate and monitor  
81 the traceability of truffles (*Tuber magnatum* Pico) by measuring  $\delta^{13}\text{C}$  of its odorous principle  
82 (bis(methylthio)methane) [22], ii) Wong et al. used IL columns in the second dimension in enantioselective-  
83 GC $\times$ GC-ToF-MS analysis to determine adulteration, or to detect additives affecting the enantiomeric ratios, in  
84 commercial Australian tea tree oils [8], iii) Yan et al. used a novel sequential three-dimensional gas  
85 chromatography-high-resolution time-of-flight mass spectrometry (3D GC-accTOFMS) system where a first  
86 non-polar column is on-line combined through a microfluidic heart-cutting (H/C) with a GC $\times$ GC system using an  
87 ionic liquid column as 3<sup>rd</sup> dimension (GC<sub>np</sub>-GC<sub>PEG</sub> $\times$ GC<sub>IL</sub>) to analyze oxygenated sesquiterpenes in hop  
88 (*Humulus lupulus* L.) essential oil and agarwood (*Aquilaria malaccensis*) oleoresin [23]. ILs as GC stationary  
89 phases were also used for micropreparative systems, in particular Mondello's group isolated pure components  
90 from very complex essential oils through a sophisticated multidimensional system consisting of four dimensions  
91 (LC-GC-GC-GC) including an SLB-IL59 column in one of them [24, 25].

92 The search for new IL stationary phases with uncommon selectivity to be applied to GC separation in the flavor,  
93 fragrance and essential oil fields is therefore of high interest. The possibilities of the anion-cation combinations  
94 to obtain ILs are unlimited. Therefore, this study has been focused on ILs based on phosphonium cations  
95 combined with different anions whose fundamental characteristics (or better chromatographic properties) were  
96 already studied by Breitbach and Armstrong in 2008 [26]. They reported the results of an in-depth and  
97 comprehensive study into the solvation properties for eight monocationic and three newly synthesized dicationic  
98 phosphonium-based versus those of analogous imidazolium-based ILs by inverse GC using the Abraham linear  
99 solvation energy relationship applied to a set of 26-34 probe analytes. The Abraham linear solvation energy  
100 relationship [27] is described by the following equation:  $\log k = c + eE + sS + aA + bB + lL$  where  $E$ ,  $S$ ,  $A$ ,  $B$ , and  
101  $L$  are solutes (analytes) descriptors representing their excess molar refraction, dipolarity, H-bond acidity, H-bond  
102 basicity, and gas-hexadecane partition coefficient, respectively. Whereas,  $e$ ,  $s$ ,  $a$ ,  $b$ , and  $l$  are a measure of the  
103 ability for the solvent (stationary phase) to interact with the solute through  $\pi$ /nonbonding electrons, dipole-dipole  
104 interactions, H-bond basicity, H-bond acidity, or dispersion forces, respectively. With all investigated ILs,  
105 Breitbach and Armstrong found that the hydrogen bond basicity ( $a$  coefficient in the Abraham relationship)  
106 prevailed as a system constant while the others (i.e.,  $e$ ,  $s$ ,  $b$ , and  $l$ ) were by far less relevant [26]. The hydrogen  
107 bond basicity interaction parameter ranged from 1.55 for trihexyl(tetradecyl)phosphonium  
108 bis[(trifluoromethyl)sulfonyl]imide ([P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]), to 6.94 for tributyl(ethyl)phosphonium diethyl phosphate  
109 ([P<sub>4442</sub><sup>+</sup>] [DEP]). They also measured the physico-chemical properties and studied the thermal stabilities for all  
110 of the investigated phosphonium-based ILs.

111 These results and in particular the difference in the value of the  $a$  coefficient in the Abraham relationship [26]  
112 were the basis for the choice of the two ILs investigated in this study. In particular, they consisted of the same

113 cation associated with different counter-anions, i.e., trihexyl(tetradecyl)phosphonium chloride [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>], (a  
114 term: 6.60) and [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>], (a term: 1.55) (Figure 1a). Moreover, both ILs have viscosities and densities  
115 suitable for capillary column coating, solid/liquid transformation temperature by far below 0°C affording very low  
116 minimum operative temperatures and good thermal stability ranging from 335°C for [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] to 380°C for  
117 [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] with zero column bleeding until 280°C and 300°C, respectively [26].

118 This study examines the chromatographic properties and selectivity of columns coated with the above ILs and  
119 the influence of their different chemical composition on separation, as well as the maximization of their  
120 performance in terms of efficiency and inertness in view of possible applications in the flavor, fragrance and  
121 essential oil fields. The results were compared to those of conventional and commercially-available IL columns.  
122

## 123 2. Experimental

### 124 2.1 Samples and chemicals

125 The Grob test mixture [28], consisting of a mixture of **1**: decane , **2**: dodecane , **3**: 1-octanol , **4**: 2,3-butanediol,  
126 **5**: methyl decanoate, **6**: methyl undecanoate , **7**: methyl dodecanoate, **8**: 2,6-dimethylphenol, **9**: 2,6-  
127 dimethylaniline, **10**: dicyclohexylamine, and **11**: 2-ethylhexanoic acid in hexane and trichloromethane, was  
128 purchased from Merck (Milan, Italy) and analyzed as received.

129 The Polarity Number of IL SPs was calculated on a mixture (PN mixture) of pure benzene, *n*-butanol, 2-  
130 pentanone, nitropropane and pyridine (100 µL each); a mixture of pure light hydrocarbons, C5-C14 (100 µL  
131 each) was also prepared. All standards were from Merck (Milan, Italy)

132 The mixture of menthol isomers and derivatives contained 7 compounds: menthol, *iso*-menthol, *neo*-menthol,  
133 *neo-i*-menthol, menthone, *i*-menthone and menthyl acetate (Figure 1b). Phenylpropenoids standard mixture  
134 consisted of 4 compounds: anethole, estragole, eugenol, *i*-eugenol (Figure 1c). Both mixtures were prepared at  
135 a concentration of 200 mg/L in cyclohexane and all standards were from Merck (Milan, Italy) or from the author's  
136 standard collection.

137 The flavour and fragrance standard mixture (FFMix) consisted of 38 compounds: **1**., β-pinene, **2**: limonene, **3**:  
138 nonane (ISTD), **4**: undecane (ISTD), **5**: tridecane (ISTD), **6**: 1,8-cineole, **7**: camphor, **8**: menthone, **9**: *i*-  
139 menthone, **10**: pulegone, **11**: linalyl acetate, **12**: bornyl acetate, **13**: menthyl acetate, **14**: lavandulyl acetate, **15**:  
140 terpinyl acetate, **16**: ethyl 2-methylbutanoate, **17**: caryophyllene, **18**: estragole, **19**: anethole, **20**: γ-hexalactone,  
141 **21**: γ-heptalactone, **22**: γ-octalactone, **23**: 2-methylbutanol, **24**: 1-octanol, **25**: terpinen-4-ol, **26**: linalool, **27**: α-  
142 terpineol, **28**: *neo*-menthol, **29**: *neo-i*-menthol, **30**: menthol, **31**: *i*-menthol, **32**: lavandulol, **33**: borneol, **34**:  
143 viridiflorol, **35**: eugenol, **36**: *i*-eugenol, **37**: thymol, **38**: carvacrol. All compounds were from Merck (Milan, Italy)  
144 or from author's standard collection and were solubilized at a concentration of 100 mg/L in cyclohexane.

145 The suspected allergens standard mixture (AlMix) consisted of 29 compounds: 1: limonene, 2: linalool, 3:  
146 estragole, 4: phenylacetaldehyde, 5: methyl 2-octynoate, 6: citronellol, 7: geraniol, 8: benzyl alcohol, 9: neral,  
147 10: geranial, 11:  $\alpha$ -isomethyl ionone, 12: methyl eugenol, 13: hydroxycitronellal, 14:  $\alpha$ -ionone, 15: eugenol, 16:  
148 lillial, 17: cinnamaldehyde, 18: anisyl alcohol, 19: farnesol isomers, 20: cinnamyl alcohol, 21: amyl  
149 cinnamaldehyde, 22: hexyl cinnamaldehyde, 23:  $\alpha$ -pentylcinnamyl alcohol, 24: vanillin, 25: lylal isomers, 26:  
150 coumarin, 27: benzyl benzoate, 28: benzyl salicylate, 29: benzyl cinnamate. They were solubilized at a  
151 concentration of 500 mg/L in cyclohexane.

152 The essential oil (EO) of sage (*Salvia officinalis* L.) was obtained by hydrodistillation following the procedure of  
153 the European Pharmacopoeia [4] while the vetiver EO (*Chrysopogon zizanioides* (L.) Roberty) was kindly  
154 provided by Robertet (Grasse, France); they were solubilized in cyclohexane at a concentration of 1 mg/ml  
155 before analysis.

156 All solvents were all HPLC grade from Merck (Milan, Italy).

157

## 158 2.2 Analysis conditions

### 159 2.2.1. Instrumental set-up

160 Analyses were carried out on a Shimadzu GC-FID 2010 unit equipped with Shimadzu GC Solution 2.53U  
161 software and a Shimadzu GC 2010 – Shimadzu QP2010-PLUS GC-MS system equipped with GCMS 2.51  
162 software (Shimadzu, Milan, Italy). FID was used to determine chromatographic parameters, while MS was used  
163 for identification purposes.

### 164 2.2.2. Columns

165 The investigated IL SPs were  $[P_{66614}^+][NTf_2^-]$ , and  $[P_{66614}^+][Cl^-]$  (Figure 1a). Trihexyl(tetradecyl)phosphonium  
166 chloride (~97%) was purchased from Strem Chemicals (Newburyport, MA, USA). The IL was purified using  
167 liquid-liquid extraction with acetonitrile and hexane. Following purification, the IL was dried under vacuum until  
168 dry.  $[P_{66614}^+][NTf_2^-]$  was prepared by dissolving purified  $[P_{66614}^+][Cl^-]$  in acetone followed by the dropwise addition  
169 of a 2 molar excess of  $[Li^+][NTf_2^-]$  in an aqueous solution. The crude product was dried under rotary evaporation  
170 until dry and then further purified by dissolving in diethyl ether and washing several times with water. The final  
171 product was then dried under rotary evaporation followed by extensive drying in a vacuum oven to afford the dry  
172 product.

173 Columns with different characteristic coatings of both IL SPs were prepared by Mega (Legnano (MI), Italy) using  
174 the static coating procedure after a proprietary deactivation process. In particular, the determination of polarity  
175 number and menthol mixture analyses were carried out with 30 m, 0.25 mm  $d_c \times 0.25 \mu m d_f$  columns covered

176 with the investigated SPs, while all other samples were analyzed with a test [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] NB column (l: 5 m, d<sub>c</sub>:  
177 0.1 mm, d<sub>f</sub>: 0.1 μm) and a test [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] NB column (l: 5 m, d<sub>c</sub>: 0.1 mm, d<sub>f</sub>: 0.15 μm)  
178 Commercial SLB-IL60i, SLB-IL76i and SLB-IL111i (30 m, 0.25 mm d<sub>c</sub> × 0.20 μm d<sub>f</sub>) from Merck (Milan, Italy) and  
179 OV1701 (30 m, 0.25 mm d<sub>c</sub> × 0.25 μm d<sub>f</sub>) from Mega (Legnano (MI), Italy) were used for comparative studies.

### 180 2.2.3. GC-MS conditions

181 GC-MS analyses were carried out under the following conditions: temperatures: injector: 240°C; transfer line:  
182 240°C, ion source: 200°C; carrier gas: He, flow control mode: constant linear velocity, flow rate for conventional  
183 columns: 1 mL/min, for 5 m narrow bore (NB) test column 0.4 mL/min. The linear velocity for PN calculation was  
184 set at 40 cm/s as recommended by Mondello et al. [7]. Injection conditions were: mode: split; split ratio: 1:50,  
185 volume: Grob test: 2 μL, all other samples 1 μL. Oven temperatures were programmed as follows: i) for PN  
186 determination: isothermal 120°C (15 min); ii) for analysis of menthol model mixture: 50°C // 2 °C/min // 220°C  
187 (2 min); iii) for all samples analysed with NB test column: 40°C // 2 °C/min // 220°C (2 min). The MS operated  
188 in electron impact ionization mode (EI) at 70 eV, scan rate 1250 u/s, mass range: 35-350 m/z.

189 *Analyte identification:* when necessary, analytes were identified through their mass spectra and/or linear  
190 retention indices. Mass spectra were compared to those of authentic standards or to those of commercial or in-  
191 house libraries, or literature data. Retention indices of the available standards were calculated *versus* a C9-C25  
192 hydrocarbon solution analyzed under the conditions reported above.

### 193 2.2.4. GC-FID conditions

194 GC-FID analyses were carried out under the following conditions: temperatures: injector: 240°C; detector:  
195 240°C; carrier gas: H<sub>2</sub>. All other analysis conditions were the same as those reported in the previous GC-MS  
196 paragraph. FID sampling rate: 40 ms.

### 197 2.2.5. Polarity Number (PN) mixture sampling conditions

198 A 1 μl volume of the PN and of the light hydrocarbons mixtures were sampled by headspace-solid-phase  
199 microextraction (HS-SPME) with a divinylbenzene/carboxen/poly dimethylsiloxane fiber (Merck, Milan, Italy) at  
200 30°C for 1 min. The sampled analytes were then recovered by thermal desorption in the GC inlet for 2 min.

201 PN was calculated according to the following equation:  $PN_x = (P_x / P_{SLB-IL100}) \times 100$  where P (Polarity) = sum of  
202 the first five McReynolds Constants and PN= polarity (P) normalized to SLB-IL100 (set at P=100) [7].

203

### 204 2.2.6. Calculation of relative area % ratios

205 The relative area % ratio was calculated by normalizing the analytes peak areas to those of decane for the Grob  
206 test and limonene for AlMix, and then by comparing the normalized areas to those obtained with the reference



207 columns (i.e. SLB-IL60i for the Grob test and MEGA-1701 for the AIMix). The data processed are the mean  
208 calculated over three injections; RSD for each component never exceeded 3%.

209

### 210 **3 Results and discussion**

211 This section consists of three parts: the first one reporting the chromatographic performance of the columns  
212 prepared with the investigated ILs, the second one discussing their selectivity and the third one showing two  
213 applications to real world samples. A set of 5 meter narrow bore (NB) test columns with film thickness of 0.1  $\mu\text{m}$   
214 for [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] and of 0.15  $\mu\text{m}$  for [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] were used. Some experiments were also carried out with 30  
215 m, 0.25 mm  $d_c$ , 0.25  $\mu\text{m}$   $d_f$  conventional columns. The chromatographic performance was first investigated with  
216 the Grob test together with four standard solutions consisting of i) a model mixture of menthol isomers and  
217 derivatives (Figure 1b), ii) a model mixture of differently substituted phenylpropenoids (figure 1c), iii) a standard  
218 mixture of 38 volatiles characteristic in the flavor, fragrance and essential oil fields (FFMix), and iv) a standard  
219 mixture of 29 allergens (AIMix); the test NB columns were also applied to the analysis of two essential oils of  
220 different complexity (sage and vetiver essential oils) as examples of real world samples. Unless specified  
221 otherwise, all analyses are carried out under the same chromatographic conditions to facilitate comparisons.

222

#### 223 *3.1 IL gas chromatographic performance*

224 The ILs were evaluated in terms of chromatographic properties to validate them as new stationary phases for  
225 routine gas chromatography. The Grob test was here used as a diagnostic mixture to study the GC performance  
226 of the investigated ILs.

227 Figure 2 shows the GC patterns of the Grob test obtained with a) OV-1701 (reference), b) SLB-IL60i (reference),  
228 c) [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] and d) [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] SPs. Column efficiency and inertness were first investigated. Table 1  
229 summarizes the chromatographic data of [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] and [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] test columns obtained with the Grob  
230 test. The efficiency was first measured: the [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] column showed a number of theoretical plates per meter  
231 (N/m), calculated by the isothermal separation of 1-octanol (**3**) at 80°C, of 9817 N/m, while that coated with  
232 [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] of 9619 N/m. The separation power of the two columns was measured over the total Grob test  
233 pattern through the separation measure  $\Delta s$ , i.e. the number of consecutive non-overlapping  $\sigma$ -intervals within  
234 an arbitrary time interval ( $t_b - t_a$ ), calculated through the following equation:  $\Delta s = (t_b - t_a) / [(\sigma_a + \sigma_b) / 2]$ , where  $t_a$  and  
235  $t_b$  are the retention times of the first and last eluting peaks and  $\sigma_a$  and  $\sigma_b$  are their peak widths. [29]. Its value  
236 was similar for both ILs and worth highlighting, i.e., 1352 for [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] calculated between the first (*n*-C<sub>10</sub> (**1**))  
237 and the last (ethylhexanoic acid (**11**)) eluting peaks and 1299 for [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] measured between *n*-C<sub>10</sub> (**1**)  
238 and *n*-C<sub>12</sub> methyl ester (**5**).

239 The two columns showed very similar efficiency, but considerable difference in retention. Under the same  
240 analysis conditions, retention is drastically higher for [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>], with the last peak (ethylhexanoic acid (**11**))

241 eluting with a retention time ( $t_R$ ) of about 62 minutes, compared to that of [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>], where the last peak (*n*-  
242 C<sub>12</sub> methyl ester (5)) elutes in 37.3 min. The difference of retention of the two investigated IL SPs is discussed  
243 in Section 3.2.

244 The peak width ( $\sigma$ ), column activity, and inertness (tailing factor and relative adsorption) were then measured  
245 with the Grob test components because of their different chemical structures. In general, the average peak  
246 widths ( $\sigma$ ) of [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>] and [P<sub>66614</sub><sup>+</sup>] [Cl], are rather similar, varying from 0.039 min to 0.045 min  
247 respectively. With single compounds,  $\sigma$  ranges from 0.010 min for *n*-C<sub>10</sub> (1) to 0.052 min for ethylhexanoic acid  
248 (11) with [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>], and from 0.011 for *n*-C<sub>10</sub> (1) to 0.078 min for ethylhexanoic acid (11) with [P<sub>66614</sub><sup>+</sup>] [Cl-  
249 ]. The analytes 2,6-dimethylaniline (9) and dicyclohexylamine (10) were not considered in the average  $\sigma$  and  
250 tailing factor determination because their peaks were too severely distorted on both columns; the only exception  
251 was 2,6-dimethylaniline (9) with [P<sub>66614</sub><sup>+</sup>] [Cl] that had a  $\sigma$  of 0.042. The peak symmetry was evaluated through  
252 the tailing factors calculated at 5% of peak height. With [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>], the nine peaks considered in the Grob  
253 test were inside the selected window (i.e., between 0.8 and 1.2), and with [P<sub>66614</sub><sup>+</sup>] [Cl] only four peaks were  
254 outside the window; these results are highly satisfactory and compatible with those of OV-1701 and SLB-IL60i  
255 taken as reference columns [9]. Here too, 2,6-dimethylaniline (9) showed good peak symmetry with [P<sub>66614</sub><sup>+</sup>] [Cl-  
256 ] (tailing factor: 1.041).

257 Another important representative parameter of column inertness is the relative area % ratio. Figure 3 shows the  
258 recovery of the Grob test components relative to SLB-IL60i taken as reference because of its high inertness [9].  
259 OV-1701 was also included for comparison purposes. With [P<sub>66614</sub><sup>+</sup>] [Cl], most components presented relative  
260 areas vs. SLB-IL60i of at least 80 %; and only the three linear methyl esters were below, although all were  
261 always above 70%. Some components appear to be less adsorbed compared to SLB-IL60i, in particular those  
262 with a free hydroxyl or a carboxyl group in their structure. Remarkable are the cases of i) 2,3-butanediol (4) that  
263 is not included in the diagram of Figure 2 because it was fully adsorbed with the SLB-IL-60i column, and ii)  
264 ethylhexanoic acid (11) that is completely adsorbed with OV-1701 and highly distorted with SLB-IL60i, while it  
265 seems not to be adsorbed at all with both of the investigated IL SPs. With [P<sub>66614</sub><sup>+</sup>] [Cl], the ethylhexanoic acid  
266 (11) relative area % ratio vs SLB-IL60i was 530% with a peak width ( $\sigma$ ) of 0.078 min and a tailing factor of 1.465,  
267 while the P<sub>66614</sub> NTf<sub>2</sub>, possessed an area ratio of 476% with a  $\sigma$  of 0.052 min and a tailing factor of 1.171. On the  
268 other hand, with this stationary phase dicyclohexylamine (10) was completely adsorbed and 2,6-dimethylaniline  
269 (9) showed a relative area ratio of about 5%.

270 The column temperature stability was also investigated by evaluating a 5 m NB column for each IL SP and  
271 submitting it to step conditioning by increasing the temperature by 20°C for each step and controlling its  
272 performance with the Grob test. The two columns did not present bleeding and gave perfectly superimposable  
273 Grob test patterns up to 280°C for [P<sub>66614</sub><sup>+</sup>] [Cl] and 240°C for [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]. These results are in good

274 agreement with those reported by Breitbach and Armstrong [230] for [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>], but significantly lower for  
275 [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] (240 vs. 300°C).

276

### 277 3.2 Polarity and selectivity

278 In general, commercially-available room temperature IL SPs exhibit medium high to high polarities and peculiar  
279 selectivity [1, 7] and these characteristics were also studied for the IL SPs investigated in this study.

280 Analogous to the commercial columns, the Polarity Number (PN) of these IL SPs was first determined by  
281 rigorously applying the methods and conditions described by Mondello et al [7]. Under these conditions, [P<sub>66614</sub><sup>+</sup>]  
282 [Cl<sup>-</sup>] gave a PN of 37 and [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>], of 33. The reliability of the measured PNs was confirmed by measuring  
283 the PNs values of three commercial IL columns (SLB-IL60i, SLB-IL76i and SLB-IL111i), which provided numbers  
284 in perfect agreement with those of the column labels. The two new IL SPs showed a similar polarity, but  
285 remarkably lower than that of IL columns that are currently commercially-available (33 or 37 vs. a minimum of  
286 59).

287 In spite of this similarity, the chromatographic behavior of these columns was completely different in terms of  
288 retention and selectivity. These properties were investigated in depth with the aforementioned standard solutions  
289 of i) menthol isomers and derivatives, ii) phenylpropenoids, iii) FFMix, and iv) AIMix. Samples iii and iv were  
290 used because they consist of compounds with different polarity, structure and functionality. The model mixture  
291 of the menthol derivatives analyzed with the 5 m NB test [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] column under the adopted conditions  
292 resulted in coelutions of *n-i*-menthol and *n*-menthol and *i*-menthone and *i*-menthol. The coelutions were probably  
293 due to a lack of efficiency of the test NB column (N: ~ 48,000): the test column was successfully replaced with  
294 a conventional 0.25 mm *d<sub>c</sub>*, 30 m column (N: ~ 180,000) that provided a baseline separation of all analytes. A  
295 conventional [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] column (l: 30 m, *d<sub>c</sub>*: 0.25 mm, *d<sub>f</sub>*: 0.25 μm) was used also to analyze this model mixture  
296 to enable comparisons, although its seven components were baseline with the test NB column.

297 3.2.1. - [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] column – Figure 4a shows the GC patterns of menthol and phenylpropenoid standard  
298 mixtures analyzed with the investigated IL SP. The GC pattern of the menthol model mixture shows that this IL  
299 SP drastically discriminates the analytes depending on their organic functional groups, i.e., first ketones  
300 (menthone isomers), then esters (menthyl acetate) and alcohols (menthol isomers) (Figure 1b). The analyte  
301 elution temperatures with this column are very different ranging from 102°C for menthone (i.e., the first eluting  
302 carbonyl derivative) to 163°C for *n*-menthol (i.e., the first eluting hydroxyl derivative) resulting in a marked  
303 difference in retention (from about 26 minutes for menthone to above 56 minutes for *neo-i*-menthol) with a  
304 separation of more than 26 minutes between the clusters of carbonyl and hydroxyl-containing compounds. This  
305 pattern is completely different not only from that obtained with conventional stationary phases but also from that

306 obtained with other IL columns [20]. The phenylpropenoid standard mixture contains phenolic ethers (estragole  
307 and anethole) and phenols (eugenol and *i*-eugenol) were each isomers differing in the position of the double  
308 bond in the C<sub>3</sub> side chain (i.e. propenyl or allyl groups) (Figure 1c). The results of phenylpropenoids analysis  
309 with the test NB column confirmed those of menthol derivatives, the phenolic ethers elute far before phenols,  
310 with the elution temperature of estragole and eugenol at 62°C and 155°C, respectively. In this case, two groups  
311 are also clearly separated, with the *t<sub>R</sub>* of estragole at about 11 min and that of eugenol at about 57 min with a  
312 difference between phenolic ether and phenol clusters of about 39 min. Within the two groups, the propenyl  
313 isomers elute before allyl isomers likely because the formers can extend their aromaticity with the double bond  
314 of the side chain. This behavior where analytes are separated mainly because of nature of the functional group  
315 is in agreement with the results of the Abraham model [26] according to which the [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] SP is  
316 characterized by a high hydrogen bond basicity interaction (*a* coefficient of 6.60).

317 After analysis of the Grob test, menthol and phenylpropenoid model mixtures, other more complex standard  
318 mixtures were tested. This included the FFMix (38 components) consisting of compounds with similar structures  
319 but different organic functional groups, and the AIMix (29 components) containing compounds with randomly  
320 different structures and volatility.

321 Figure 5a shows the GC pattern of the FFMix analyzed with the [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] test column. These results confirm  
322 those reported above with the early elution of hydrocarbons followed by carbonyl derivatives (i.e., ketones, esters  
323 and lactones in sequence), followed by alcohols. For the latter group, a clear discrimination between aliphatic  
324 alcohols and phenols is also observed. The elution order is obviously also influenced by other analyte  
325 characteristics such as volatility as indicated by the C<sub>6</sub>-C<sub>8</sub> homologous series of  $\gamma$ -lactones (20-22),  
326 caryophyllene (17) (a C<sub>15</sub> sesquiterpene hydrocarbon) and viridiflorol (34) (a C<sub>15</sub> sesquiterpene alcohol).

327 The AIMix exhibits a similar behavior, although the discrimination is less clear-cut because several components  
328 are multifunctional. Figure 6a shows the GC pattern of the AIMix analyzed with the [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] test column.  
329 Three main groups can be identified: hydrocarbons, ethers and carbonyl containing derivatives, and hydroxyl  
330 derivatives. Even here, the elution order also depends on other analyte characteristics besides their organic  
331 functional groups, such as molecular weight and volatility. Clear examples are i) the three benzyl esters  
332 (benzoate (27), cinnamate (28) and salicylate (29) in order of elution) where the salicylate derivative elute later  
333 likely because of the free hydroxyl moiety on the aromatic ring, ii) the hydroxyaldehydes (hydroxycitronellal (13),  
334 and lylal a and b (25a, 25b)) that elute with the hydroxyl derivatives, probably due to the prevalent interaction of  
335 the hydroxy group with the IL SP, and iii) homologs with longer side chains (amylcinnamaldehyde (21) and  
336 hexylcinnamaldehyde (22)) eluting with hydroxyl compounds because of their long retention due to high  
337 molecular weight.

338 3.2.2. - [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup> column – Figure 4b shows the GC patterns of menthol and phenylpropenoid model  
339 mixtures with this column. This IL SP shows immediately a different behavior from [P<sub>66614</sub><sup>+</sup>] [Cl]<sup>-</sup>, mainly  
340 highlighted by a very low retention and a selectivity not depending on the organic functional group of the analytes  
341 investigated. After the preliminary experiments, the film thickness of the [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup> test NB column was  
342 increased to 0.15 μm, while keeping constant the column length and inner diameter; the conventional column  
343 used with the menthol model mixture was not modified. For instance, *i*-menthol (the last peak eluting of menthol  
344 model mixture) elutes at 67°C (about 9 min) on the [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup> IL and at 166°C (about 58 min) on the [P<sub>66614</sub><sup>+</sup>]  
345 [Cl]<sup>-</sup> IL, and *i*-eugenol in the phenylpropenoid mixture elutes at 113°C (about 36 min) with [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup> and at  
346 about 169°C (65 min) with [P<sub>66614</sub><sup>+</sup>] [Cl]<sup>-</sup>. Moreover, all menthol derivatives elute in a time range of about 3 min  
347 with [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup> and in 33 min with [P<sub>66614</sub><sup>+</sup>] [Cl]<sup>-</sup>. The selectivity within the phenolic ether and phenol groups  
348 is maintained. In the case of the [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup> IL, the separation between allyl and propenyl derivatives almost  
349 doubles in terms of elution temperature and retention times.

350 On the contrary, the elution order of menthol derivatives cannot reliably be explained although all components  
351 are baseline separated. The [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup> behaviour is in line with the fact that any of the Abraham model  
352 coefficients (*e*, *s*, *a*, *b* and *l*) [26] remarkably prevails on the others.

353 These results are also confirmed with FFMix and AIMix. Figure 5b shows the GC pattern of the FFMix analyzed  
354 with the [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup> column. As already observed with the Grob test, hydrocarbons are also well separated  
355 from the oxygenated compounds, and within the latter group, an analogous elution sequence begins with non-  
356 aromatic hydroxyl compounds followed by esters, phenols and lactones. Figure 6b shows the GC pattern of the  
357 AIMix analyzed with the [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup> column. As already observed for [P<sub>66614</sub><sup>+</sup>] [Cl]<sup>-</sup>, the chemical complexity  
358 of the components of this mixture makes its selectivity more difficult to rationalize. The analysis of AIMix with  
359 this IL SP confirms the results of FFMix indicating, in addition, that aldehydes elute in proximity to the  
360 corresponding alcohol, i.e., the organic functional group does not play a prevalent role in selectivity as it does  
361 with the [P<sub>66614</sub><sup>+</sup>] [Cl]<sup>-</sup> IL. In general, the selectivity of this IL SP seems to be more conventional and is mainly  
362 driven by analyte volatility: this consideration is also in agreement with its polarity number (33), which is far lower  
363 than those of the IL columns currently commercially available.

364 These results are also substantiated when the separation measures ( $\Delta s$ ) of the two test columns were calculated  
365 on both FFMix and AIMix. The FFMix values of  $\Delta s$  are significantly different (i.e., 1860 for [P<sub>66614</sub><sup>+</sup>] [Cl]<sup>-</sup> and 1138  
366 for [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup>). The explanation is that, under the adopted analytical conditions, the peculiar selectivity of  
367 [P<sub>66614</sub><sup>+</sup>] [Cl]<sup>-</sup> on different functional groups dramatically influences the retention time of the last eluting peak, i.e.  
368 thymol (**37**) accounting for about 73 min, while the limited retention power of [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub>]<sup>-</sup> gives an elution  
369 time for the last eluting peak ( $\gamma$ -octalactone (**22**)) of about 38 min.

370 On the other hand, the AIMix values of  $\Delta s$  are closer (i.e., 2632 for [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] and 2125 for [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>]).  
371 This result was expected because of the significant structural heterogeneity of its components that limits the  
372 influence of the specific selectivity of [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] towards the organic functional groups and increases the role  
373 of polarity, which is similar for the two investigated IL SPs (PN being 37 and 33, respectively). This makes the  
374 difference of the total analysis time on the last eluted peak to be less pronounced under the adopted conditions.  
375 For example, benzyl salicylate (**28**) on the [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] IL eluted at about 87 min and benzyl cinnamate (**29**)  
376 eluted at about 60 on the [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] IL.

377 Finally, the inertness of the two new IL SP columns was evaluated *versus* the allergen standard mixture because  
378 of the widely different chemical nature of its components. Figure 7 shows the relative area % ratios of the  
379 components within the allergen model mixture calculated vs. those obtained with OV-1701 taken as reference.  
380 SLB-IL60i values are also included for comparison. The results showed that most components were recovered  
381 above 80% and some of them above 60% for both columns. The exceptions are: a) for [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>], benzyl  
382 salicylate (**29**) (almost fully adsorbed) and vanillin (**24**) (recovered at 20%), and b) for [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>], farnesol 1  
383 (**19a**) (fully adsorbed), farnesol 2 (**19b**) (recovered at 20%), anisyl alcohol (**18**) (40%), vanillin (**24**) (42%), and  
384 hydroxyl citronellal (**13**) (42%).

### 385 3.3 Analysis of real world samples

386 The two proposed IL SPs have then been tested with real world samples to verify their ability in routine analysis.  
387 Two essential oils of highly different complexity were therefore chosen because these matrices mainly consist  
388 of components where a number of skeletons is substituted with different functional groups, i.e., these are  
389 samples where selectivity plays a fundamental role in the separation.

390 Sage (*Salvia officinalis* L.) essential oil consists of about 40 components, mainly well-known monoterpenoids  
391 (and to a lesser extent sesquiterpenoids), belonging to hydrocarbons, ketones, esters, and alcohols. Figure 8  
392 shows GC-MS data analyzed with [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] and [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] 5 m NB test columns. The [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>]  
393 pattern shows a very clear separation between the components as a function of their organic functional groups  
394 and number of carbon atoms, for example, (in order of elution) monoterpenoids (C<sub>10</sub>) including hydrocarbons  
395 and 1,8-cineole, ketones, esters, sesquiterpene (C<sub>15</sub>) hydrocarbons, and monoterpene alcohols. On the other  
396 hand, the [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] pattern clearly discriminates between hydrocarbons and oxygenated monoterpenoids  
397 and also incorporates sesquiterpene hydrocarbons, with the retention of this IL SP also significantly conditioned  
398 by analyte volatility and polarity.

399 Vetiver (*Chrysopogon zizanioides* (L.) Roberty) essential oil is very complex and mainly consists of hydrocarbon  
400 and oxygenated sesquiterpenoids. Filippi et al. separated more than 250 sesquiterpenoids by GCxGC-MS and  
401 identified 216 of them with 122 being sesquiterpene hydrocarbons and 94 sesquiterpenoids (acids, alcohols,  
402 aldehydes, esters, ethers, ketones), 49 of them being sesquiterpene alcohols [30]. Belhassen et al. recently

403 reviewed vetiver essential oil composition and discussed its variation depending on origin and quality [31]. This  
404 essential oil was used as a representative test of the selectivity of the two investigated IL SPs mainly consisting  
405 of a highly complex mixture of C<sub>15</sub> based skeleton components, although with different functional groups. The  
406 investigated essential oil was first submitted to a preliminary flash chromatography separation on a silica gel  
407 column with solvents of increasing polarity to separate hydrocarbons from oxygenated components in different  
408 fractions. The two fractions were then analyzed with the two IL coated NB columns under the same GC  
409 conditions. Figure 9 shows the GC-MS patterns of the hydrocarbon and oxygenated fractions of the investigated  
410 vetiver essential oil analyzed with [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] (a) and [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] (b) 5 m NB columns. The unique selectivity  
411 on the organic functional groups of [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] SP was kept also on this very complex essential oil. This is  
412 clearly shown when the patterns of the two fractions are compared (Figure 9a) where the hydrocarbon fraction  
413 does not overlap at all with the components of the oxygenated fraction; moreover, within the oxygenated fraction,  
414 the ketone group elutes separately from esters, and, in their turn, the latter are clearly separated from alcohols.  
415 Further studies are under way with longer columns that provide efficiency suitable for the complexity of the  
416 mixtures under investigation. The GC-MS analysis of the above fractions of this essential oil using the [P<sub>66614</sub><sup>+</sup>]  
417 [NTf<sub>2</sub><sup>-</sup>] as IL SP also confirm its properties in that hydrocarbons are well separated from oxygenated fraction  
418 components but the latter without discrimination of the analytes with different functional groups (Figure 9b) .

419

#### 420 **4. Conclusions**

421 The reported results show that the two investigated ILs with phosphonium cation are highly useful and of high  
422 interest as SPs for gas chromatography because of their thermal stability, chromatographic properties and  
423 uncommon but complementary selectivity. In particular, the [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] SP has been shown to be able to  
424 discriminate analytes through their functional groups, while the [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] SP separates them as a function  
425 of their polarity and volatility. Further studies have still to be performed to make these columns suitable for  
426 routine use by: i) extending the investigated ILs to routine analysis of complex real-world samples and combining  
427 their selectivity with suitable column efficiency and characteristics (including length, inner diameter and film  
428 thickness) that have obviously limited the test columns investigated in this study, and ii) evaluating their  
429 applicability in not only 1D but also to 2D separations, planar columns and micropreparative GC.

430 These results are part of a wide study aiming to introduce new stationary phases for GC that exhibit uncommon  
431 analyte selectivity complementary to conventional and commercially-available IL SPs that should be highly  
432 useful in flavor (aroma), fragrance and essential oil analyses, where the analytical procedures (and analysis  
433 conditions) are well established and highly consolidated. The introduction of additional tools capable of providing  
434 different patterns of separation will extend the use of metabolomics approaches (mainly fingerprinting and

435 profiling) to other fields. This will enable the characterization of samples with the maximum number of diagnostic  
436 representative data to achieve the searched level of information.

437

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442



443 **References**

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525 **Captions to figures**

526 Figure 1: Structure of a) investigated ILs, b) menthol isomers and derivatives, c) phenylpropenoids

527 Figure 2: GC-FID patterns of Grob test obtained with columns coated with different stationary phases: a) OV-  
528 1701, b) SLB-IL60i; c) P<sub>66614</sub> Cl, and d) P<sub>66614</sub> NTf<sub>2</sub>. For column characteristics, analysis conditions and peak  
529 identification see experimental

530 Figure 3: Relative area % ratios of Grob Test components measured with the investigated [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] and  
531 [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] NB test columns, and with a OV-1701 column *versus* SLB-IL60i column taken as reference

532 Figure 4: GC-FID patterns of a) menthol model standard mixture analyzed with P<sub>66614</sub> Cl, and [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>]  
533 conventional columns (l: 30m, d<sub>c</sub>: 0.25mm, d<sub>f</sub>: 0.25 μm), and b) phenylpropenoid model standard mixture  
534 analyzed with P<sub>66614</sub> Cl, and [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] NB test columns (l: 5 m, d<sub>c</sub>: 0.10mm, d<sub>f</sub>: 0.1 μm)

535 Figure 5: GC-FID patterns of FFMix obtained with NB test columns coated with different stationary phases: a)  
536 P<sub>66614</sub> Cl, and b) P<sub>66614</sub> NTf<sub>2</sub>. For column characteristics, analysis conditions and peak identification see  
537 experimental

538 Figure 6: GC-FID patterns of AIMix obtained with NB test columns coated with different stationary phases: a)  
539 P<sub>66614</sub> Cl, and b) P<sub>66614</sub> NTf<sub>2</sub>. For column characteristics, analysis conditions and peak identification see  
540 experimental

541 Figure 7: Relative area % ratios of AIMix components measured with the investigated [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] and [P<sub>66614</sub><sup>+</sup>]  
542 [NTf<sub>2</sub><sup>-</sup>] NB test columns, and with a SLB-IL60i column *versus* OV-1701 column taken as reference

543 Figure 8: GC-MS patterns of sage essential oil with [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] (a) and [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] (b) NB test columns.  
544 Temperature program: from 50°C to 200°C (5 min) at 10°/min

545 Figure 9: GC-FID patterns of vetiver essential oil hydrocarbon (in grey) and oxygenated fractions (in black)  
546 analyzed with a) [P<sub>66614</sub><sup>+</sup>] [Cl<sup>-</sup>] NB test column, and b) [P<sub>66614</sub><sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] NB test column.

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548 Table 1: Chromatographic performance of the investigated stationary phases calculated on the analysis of the  
 549 Grob test standard mixture.

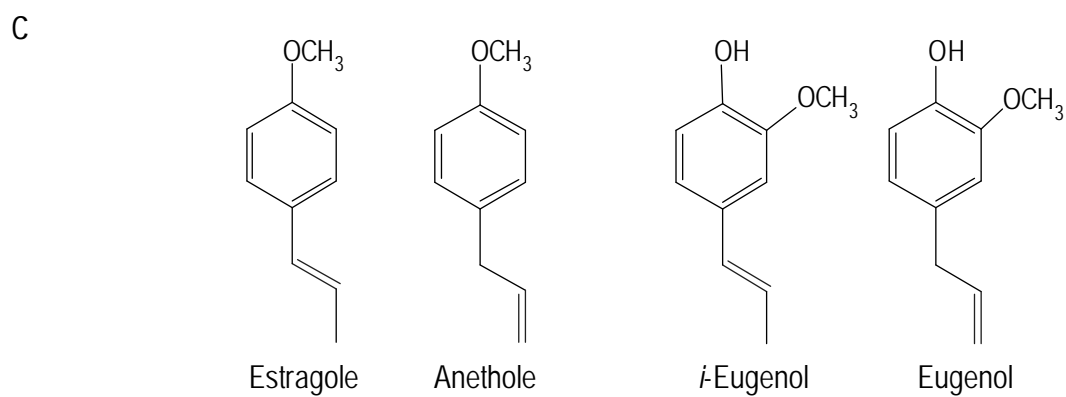
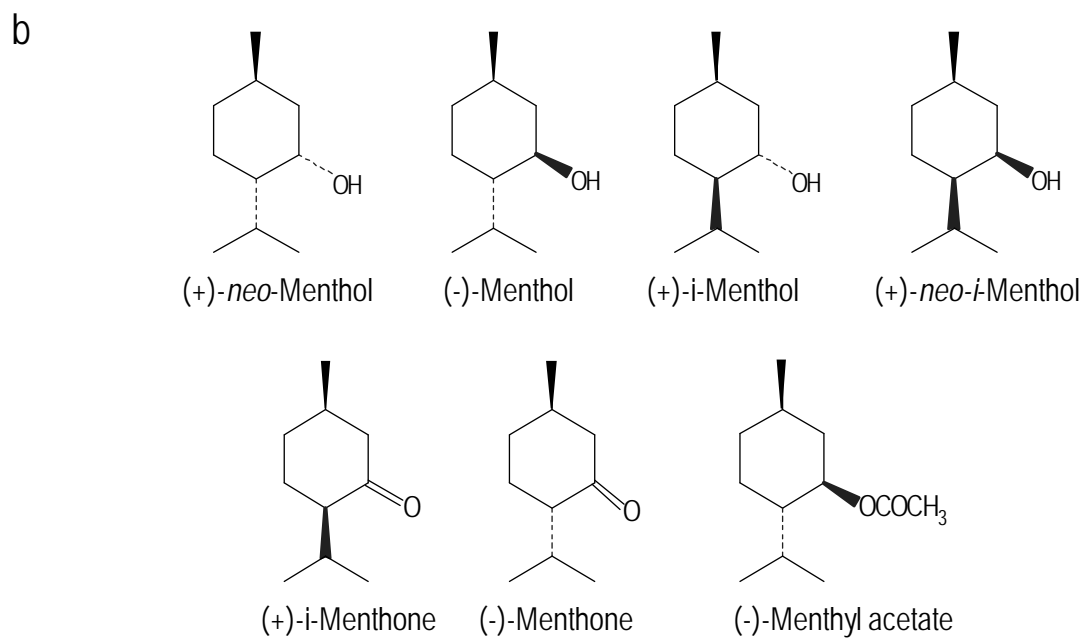
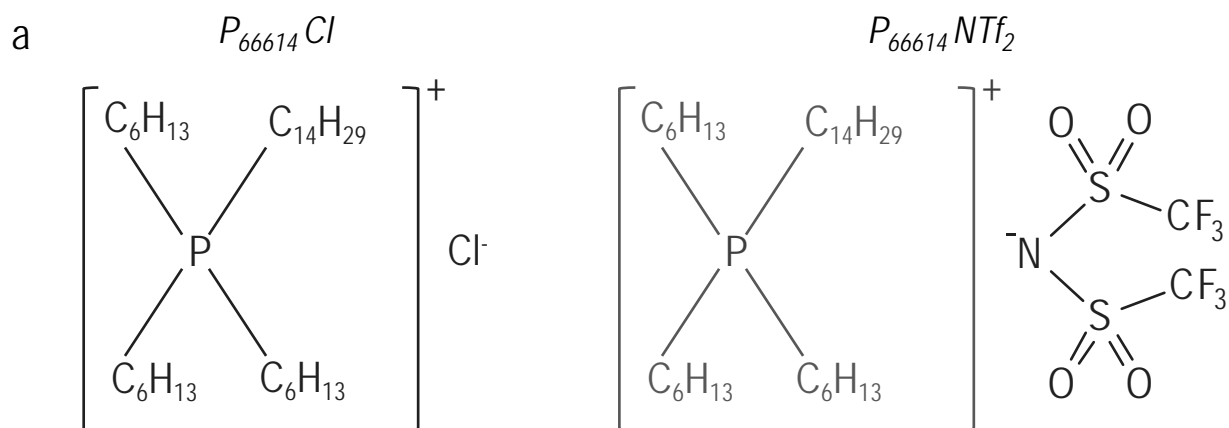
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PN		N		N/m		$\Delta s$		Average $\sigma$	
[P <sub>66614</sub> <sup>+</sup> ] [Cl]	[P <sub>66614</sub> <sup>+</sup> ] [NTf <sub>2</sub> ]	[P <sub>66614</sub> <sup>+</sup> ] [Cl]	[P <sub>66614</sub> <sup>+</sup> ] [NTf <sub>2</sub> ]	[P <sub>66614</sub> <sup>+</sup> ] [Cl]	[P <sub>66614</sub> <sup>+</sup> ] [NTf <sub>2</sub> ]	[P <sub>66614</sub> <sup>+</sup> ] [Cl]	[P <sub>66614</sub> <sup>+</sup> ] [NTf <sub>2</sub> ]	[P <sub>66614</sub> <sup>+</sup> ] [Cl]	[P <sub>66614</sub> <sup>+</sup> ] [NTf <sub>2</sub> ]
37	33	49083	48096	9817	9619	1352	1299	0.045	0.039
Compounds				Retention time		$\sigma$ (min)		Tailing factor	
				[P <sub>66614</sub> <sup>+</sup> ] [Cl]	[P <sub>66614</sub> <sup>+</sup> ] [NTf <sub>2</sub> ]	[P <sub>66614</sub> <sup>+</sup> ] [Cl]	[P <sub>66614</sub> <sup>+</sup> ] [NTf <sub>2</sub> ]	[P <sub>66614</sub> <sup>+</sup> ] [Cl]	[P <sub>66614</sub> <sup>+</sup> ] [NTf <sub>2</sub> ]
1	Decane	1.66	2.26	0.011	0.010	0.833	0.822		
2	Dodecane	6.67	8.29	0.027	0.027	0.818	0.818		
3	1-Octanol	35.56	19.89	0.041	0.042	1.296	1.188		
4	2,3-Butanediol	41.12	22.45	0.070	0.051	3.291	0.857		
5	Methyl decanoate	16.08	26.84	0.039	0.042	0.844	1.200		
6	Methyl dodecanoate	26.93	37.33	0.046	0.044	0.942	1.099		
7	Methyl undecanoate	21.69	32.18	0.041	0.044	0.810	1.133		
8	2,6-Dimethylphenol	52.42	16.74	0.052	0.038	1.568	0.987		
9	2,6-Dimethylaniline	27.27	26.55	0.042	<i>N.C.</i>	1.041	<i>N.C.</i>		
10	Dicyclohexylamine	37.09	<i>N.D.</i>	<i>N.C.</i>	<i>N.D.</i>	<i>N.C.</i>	<i>N.D.</i>		
11	Hexanoic acid, 2-ethyl-	61.68	25.67	0.078	0.052	1.465	1.171		

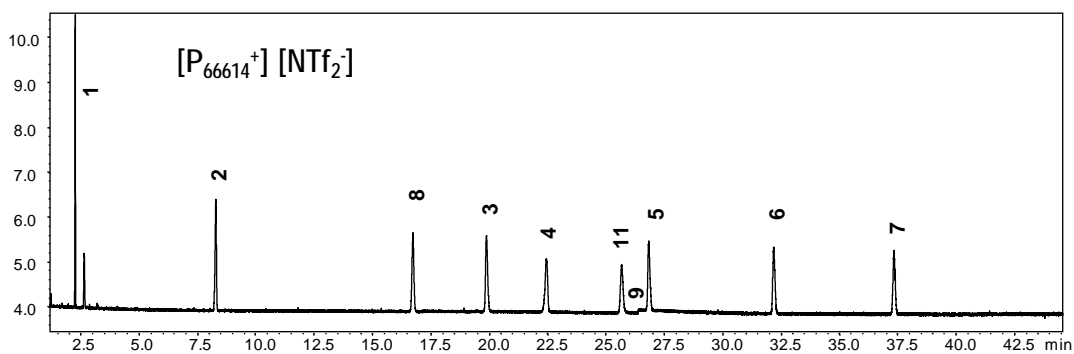
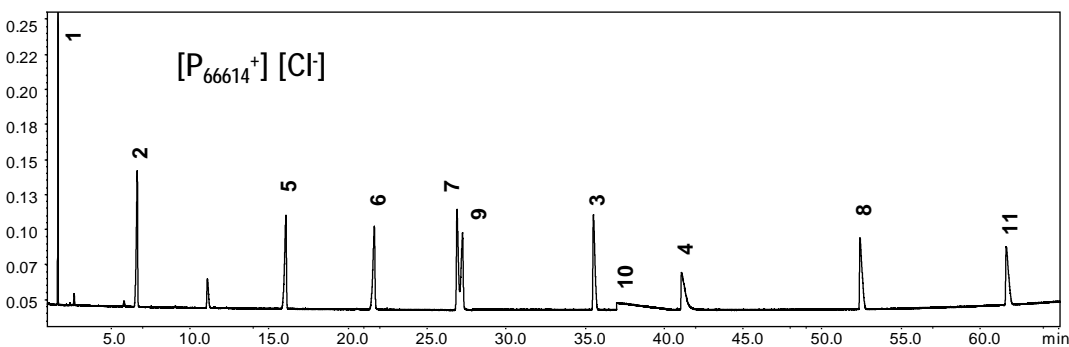
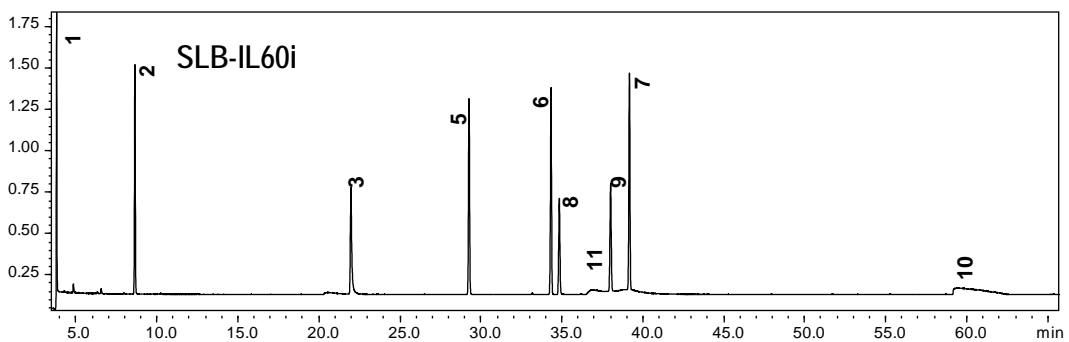
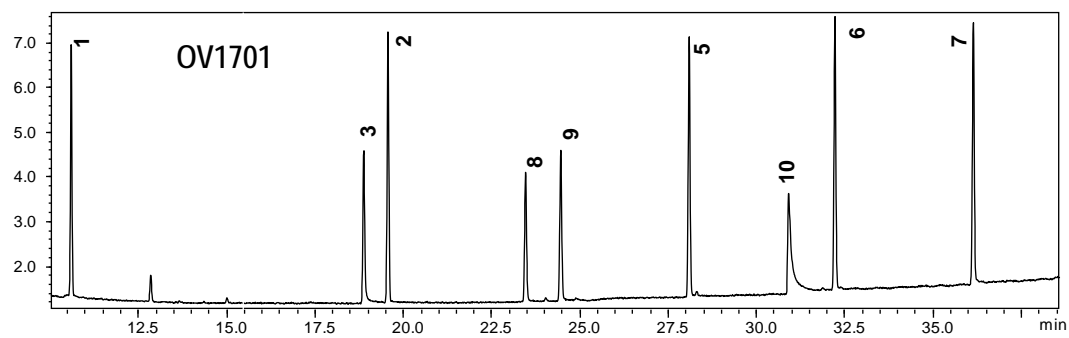
551 *N.C.* not calculable because highly distorted

552 *N.D.* not detectable

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557 Figure 2

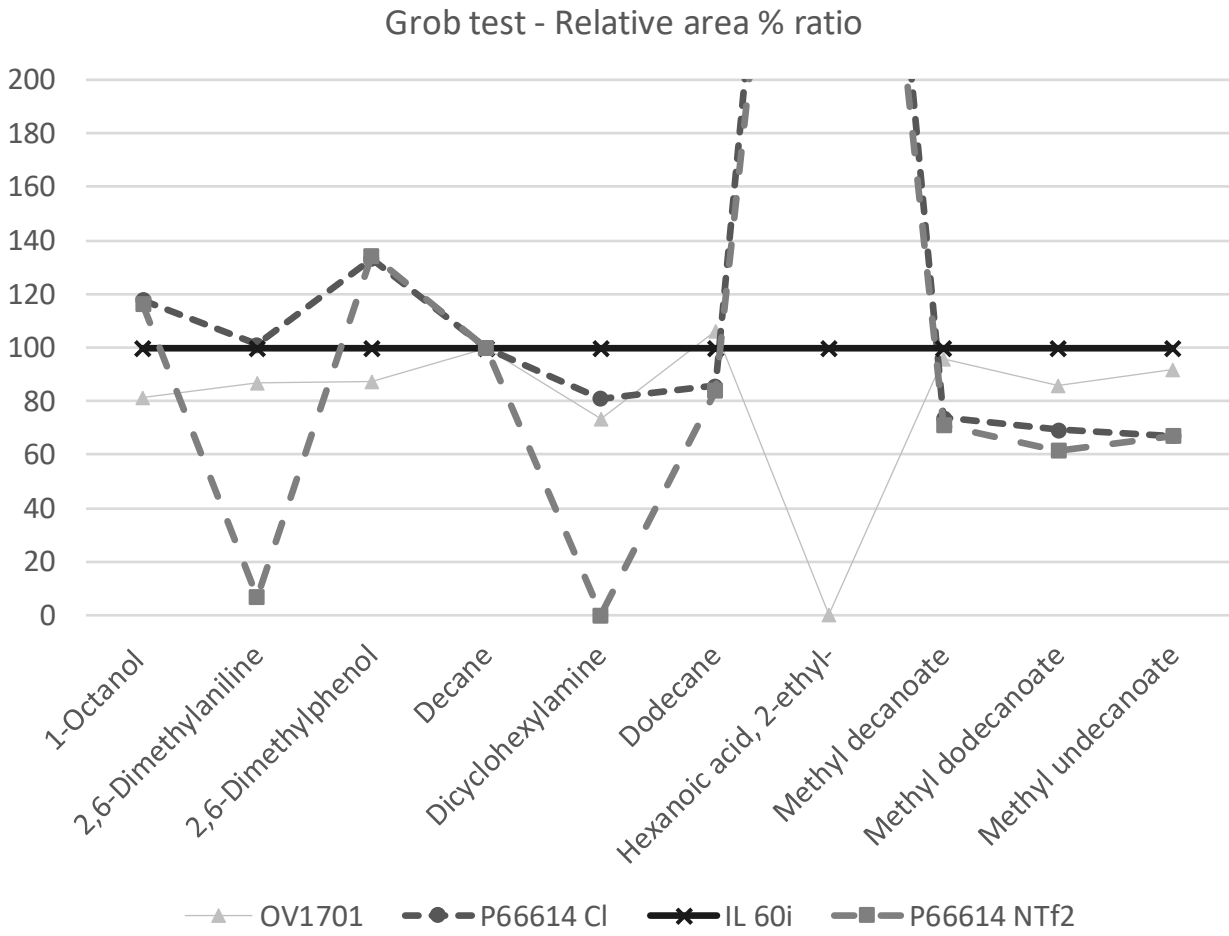


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560 Figure 3

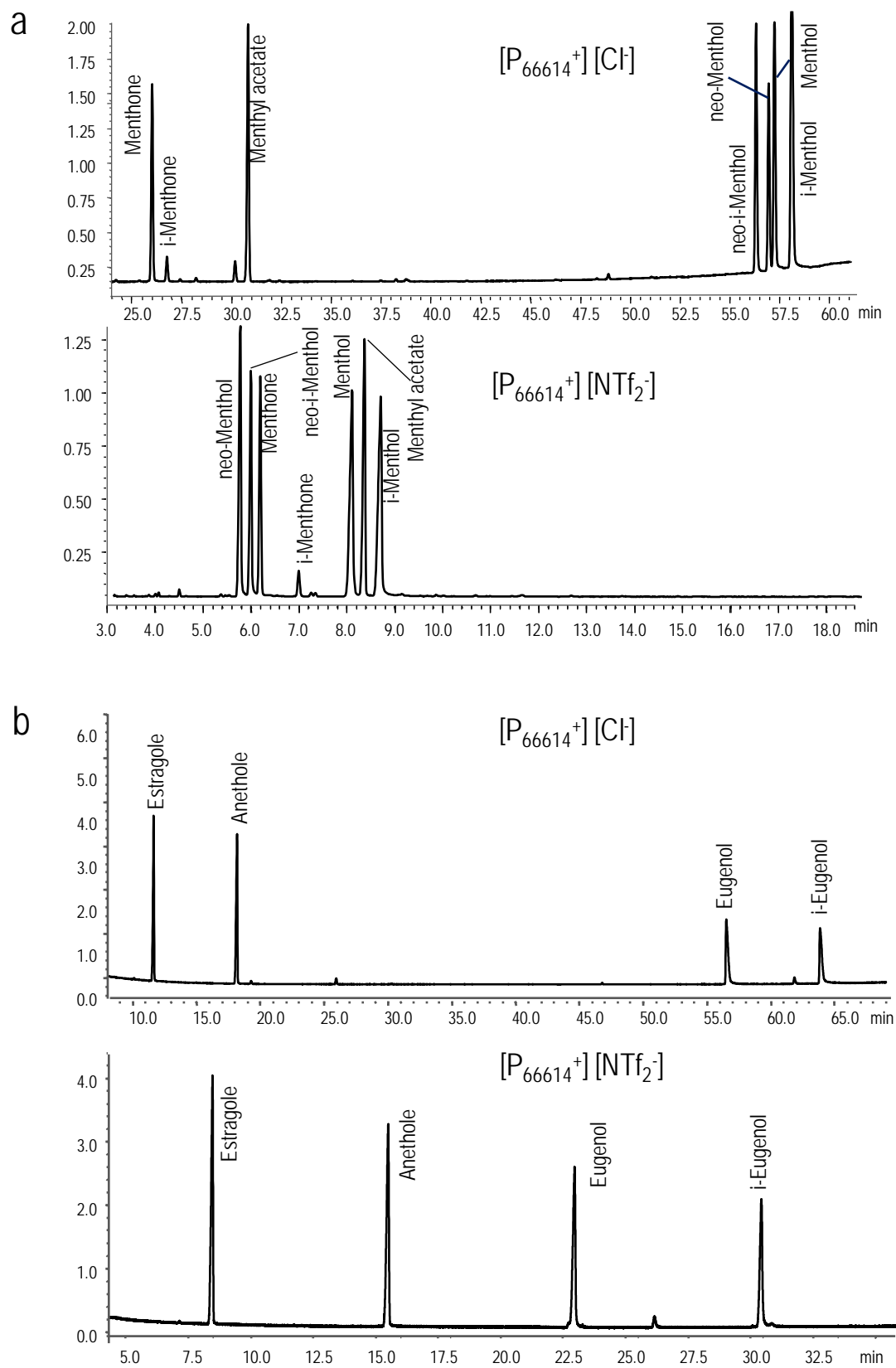
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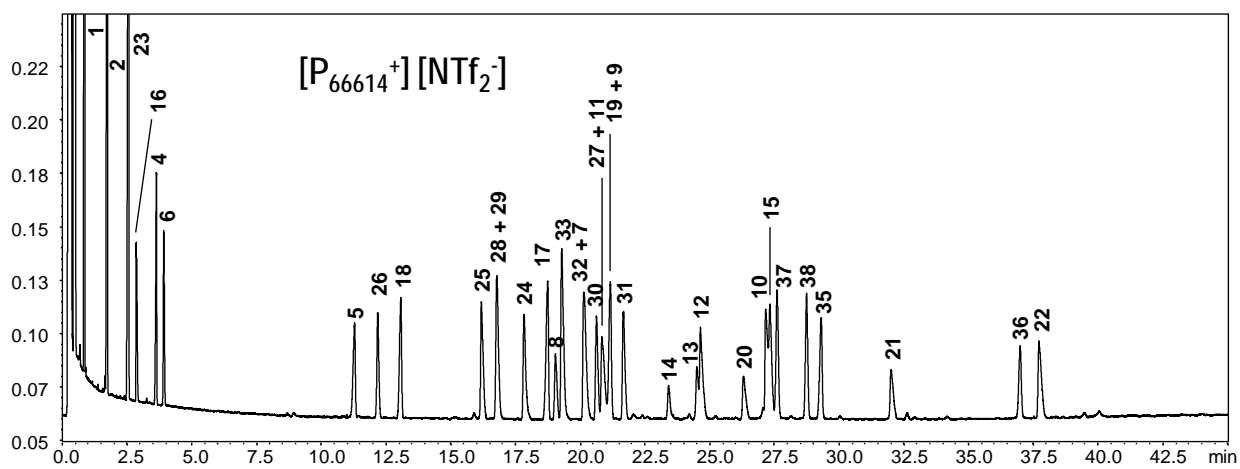
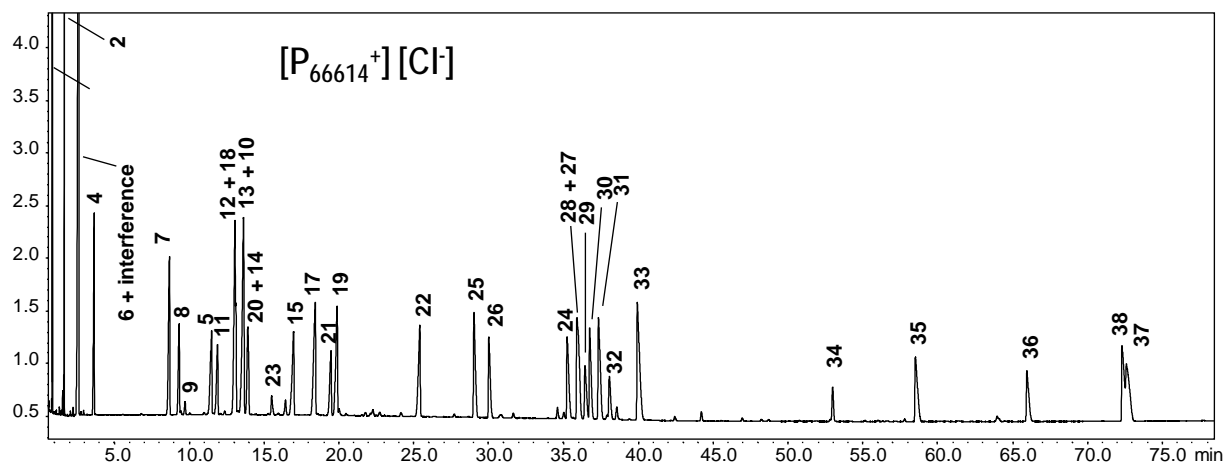




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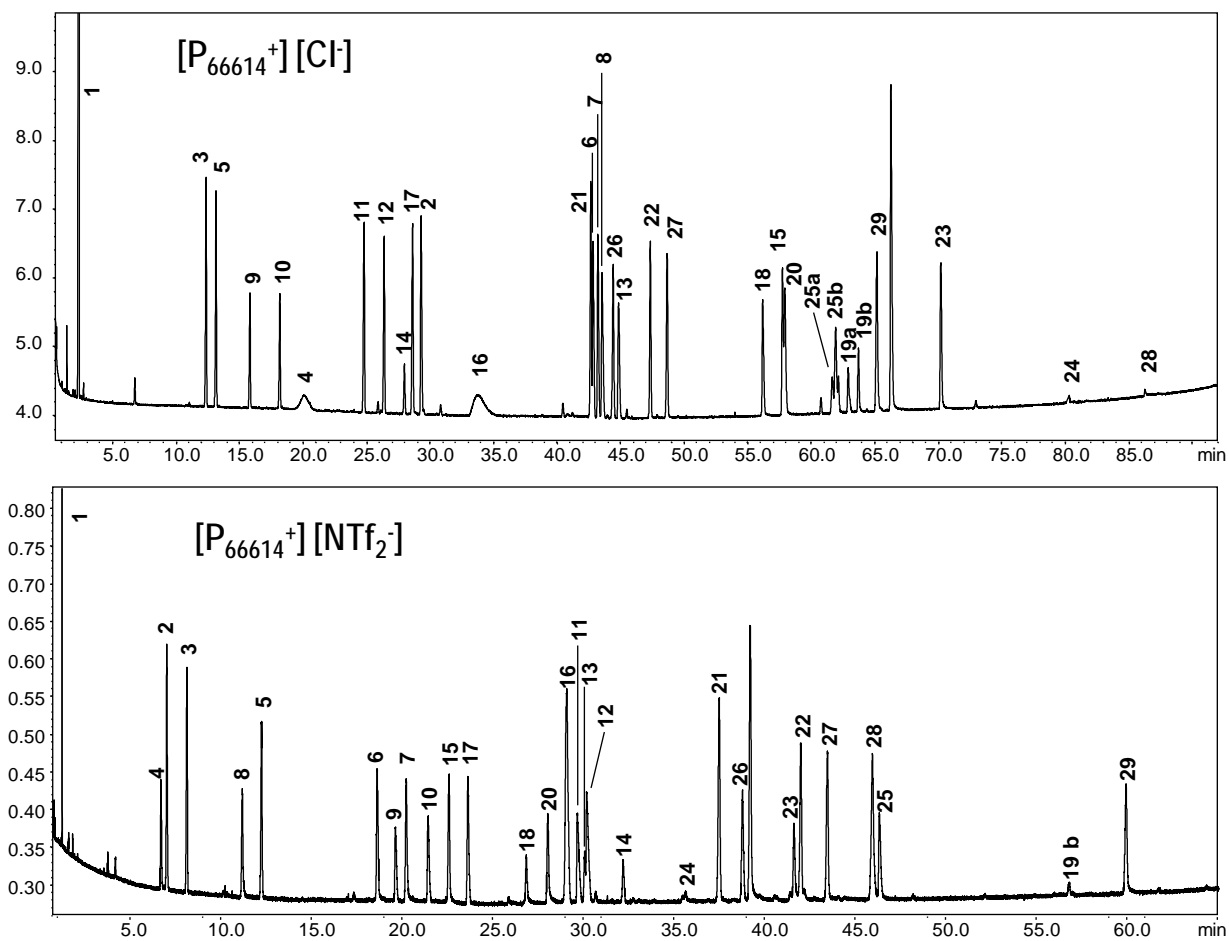
567 Figure 5



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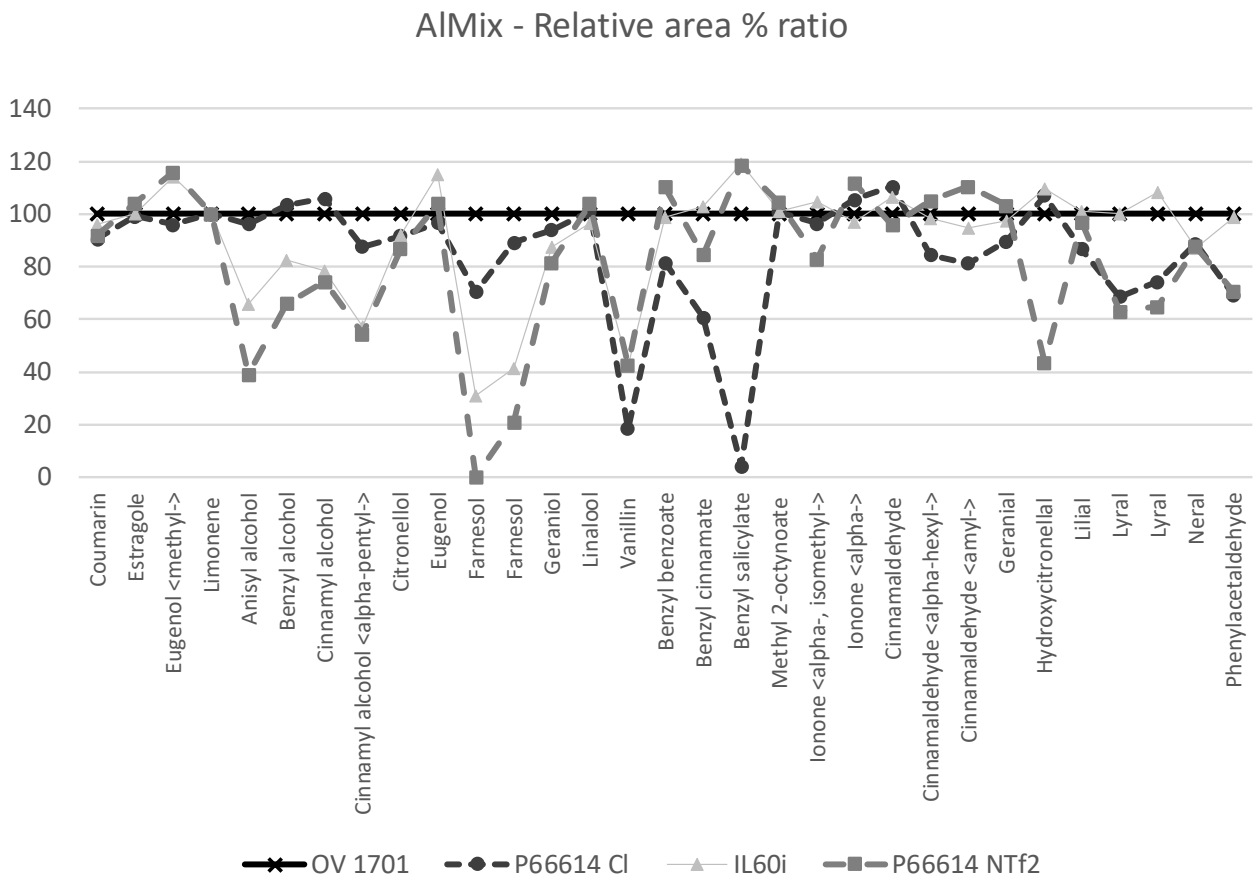
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570 Figure 6



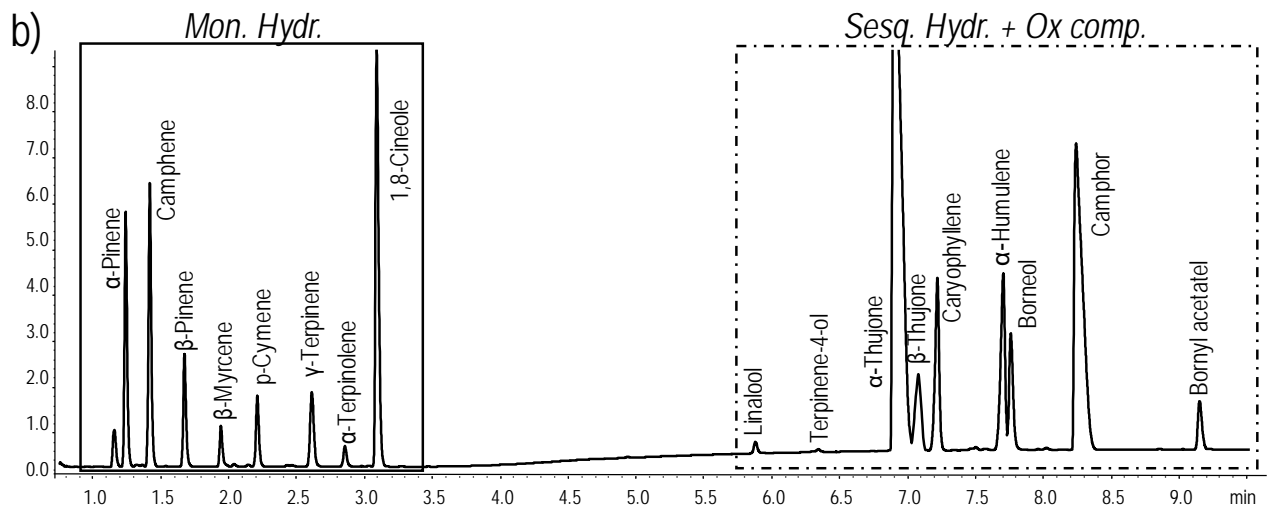
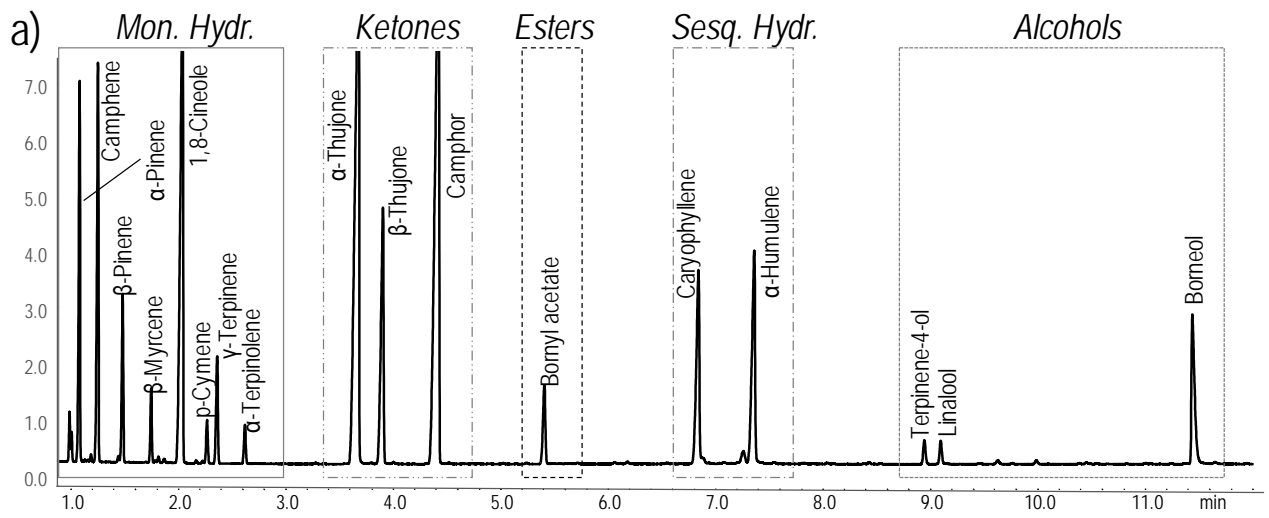
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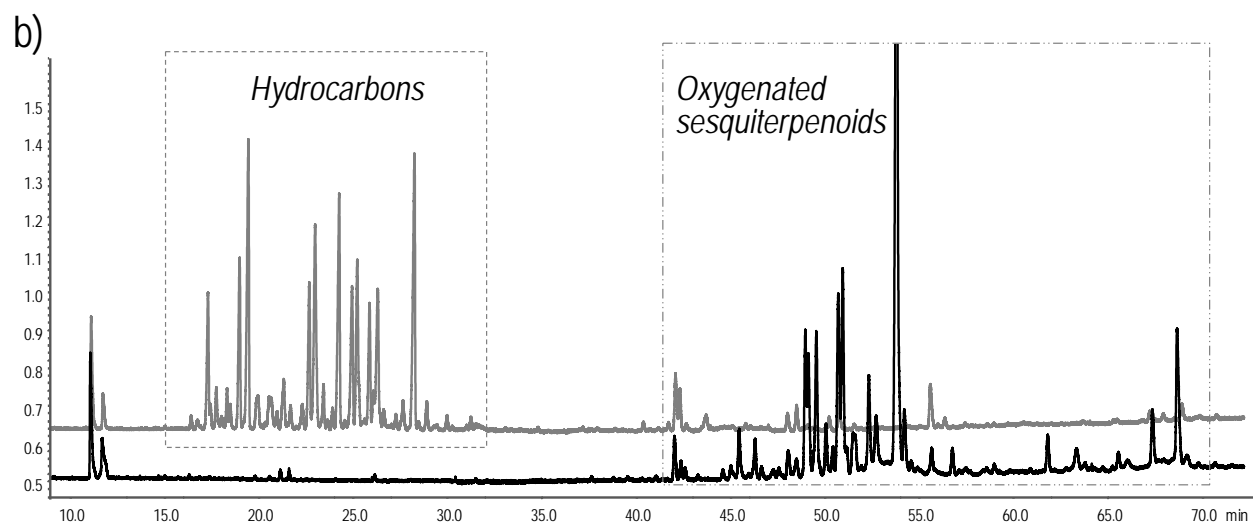
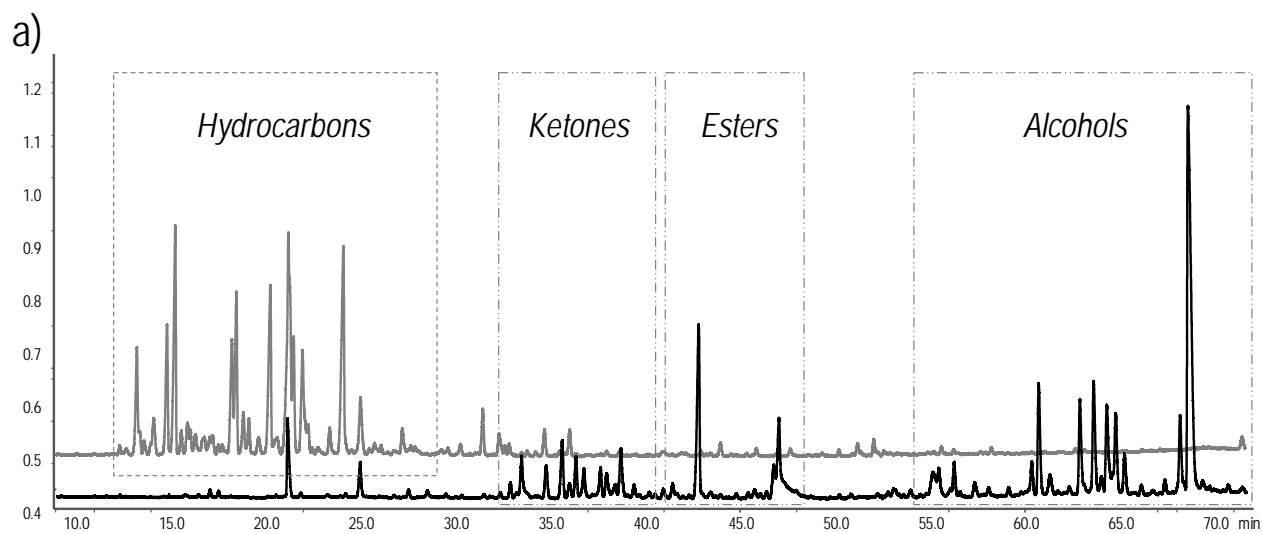
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579 Figure 9



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