NJC

Accepted Manuscript

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Polymerized Phosphonium-Based Ionic Liquids as Stationary Phases in Gas Chromatography: Performance Improvements by Addition of Graphene Oxide

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Keywords: Gas chromatography; Graphene oxide; Phosphonium-based polymeric ionic liquids; Solvation parameter model; Stationary phases.

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1   **ABSTRACT**

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3   Eight new functionalized, polymerizable phosphonium ionic liquids were prepared and

4   applied as polymeric stationary phases in gas chromatography (GC). These coated GC

5   columns exhibit high thermal stability compared to other ionic liquids (220-380ºC), and

6   column efficiencies between 2700 and 3700 plates m^{-1}. The new columns have been

7   characterized using the Abraham model in order to understand the effects of the

8   polymeric cation and the anion on the behavior of the system. These stationary phases

9   show unique selectivity for several types of organic compounds such as alcohols,

10 amines, pesticides and polycyclic aromatic hydrocarbons (PAHs), with good peak

11 symmetries in some cases. Moreover, graphene oxide (GO) sheets have been covalently

12 bonded onto the inner wall surface of fused silica capillary columns using 3-

13 aminopropyl-diethoxymethylsilane (3-AMDS) as a cross-linking agent. The use of GO

14 in the preparation of the capillary columns enhances their efficiency, improving peak

15 symmetries because of the reduction of the unspecific absorptions.

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24   **1. INTRODUCTION**

25   The term "ionic liquid" (IL) is currently used to describe a broad class of salts with

26   wide liquid ranges.

27   Ionic liquids have been developed for a wide variety of applications in different areas

28   due to their unique properties.[1-11] An emerging application of ILs is as stationary phases

29   in gas -chromatography, which is the subject of this paper. The common properties of

30   the ILs, such as high thermal and redox stability, high viscosity and negligible vapor

31   pressure, make these types of compounds very attractive as stationary phases in gas

32   chromatography. The vast majority of ILs previously applied in GC are based on

33   imidazolium cations.[12-22] In contrast, studies focused on novel classes of ILs achieved

34   by a modification of the chemical structure of the cation are scarce. In particular,

35   phosphonium, sulfonium or borenium- based ILs[23-27] have not received the same

36   literature attention than their imidazolium analogs.

37   The higher cost and lower air stability of most phosphines compared with amines, along

38   with the synthetic difficulties to access multi-substituent functionalized phosphonium

39   cations can explain the scarcity of studies focused on phosphonium-based ILs.

40   However, some of their properties (i.e. less dense than water, whereas the density of the

41   nitrogen-based ILs is higher[28]) make them more suitable for some applications such as

42   solvents in organic and inorganic synthesis. In the field of analytical chemistry and,

43   more specifically, in gas chromatography, the phosphonium- based ILs offer great

44   potential due to properties such as higher thermal stability[29,30] than many nitrogen-based

45   ILs. However, the paucity of studies carried out on phosphonium ILs is still not

46   sufficient for a wide range of applications. It is therefore necessary to perform deeper

47   studies on the behavior of phosphonium ILs as stationary phases in gas

48   chromatography.

49   A major problem in the study of new stationary phases based on ILs is the difficulty to

50   obtain highly homogenous coatings that would generate good profiles of peaks and

51   more effective separations. For this reason, in recent years, developments in separation

52   sciences have resulted in a new generation of stationary phases containing carbon

53   nanotubes and GO, which have been found to provide homogeneous coatings. Graphene

54   is a monolayer of sp^2-hybridized carbon atoms tightly arranged into a two-dimensional

55   honeycomb lattice. GO is an aromatic macromolecule containing reactive oxygen

56   functional groups such as epoxide and hydroxyl.[31,32]

57   Zhao et al.[33] demonstrated that singled-walled carbon nanotubes enhanced the

58   enantioseparations on a chiral ionic liquid stationary phase, because the carbon

59   nanotubes increased the superficial area in the inner wall, and therefore favored the

60   interactions between the stationary phase and the analytes.

61   Qu et al. have employed graphene and GO as stationary phases for capillary

62   electrochromatography, capillary liquid chromatography and gas chromatography,

63   obtaining effective separations of neutral, basic and protein mixtures[34], and separations

64   of various types of organic compounds with good separation efficiency.[35]

65   In order to contribute to the development and study of new stationary phases with

66   improved selectivities, in this paper, we present a complete study of the solvation

67   properties of eight monocationic phosphonium-based polymeric ILs (phosphonium

68   PILs).[30] Moreover, with the aim of improving the column efficiency, to eliminate non-

69   specific interaction due to silanol groups, sheets of graphene oxide covalently bonded to

70   the inner wall of the column have been incorporated. For the first time, phosphonium

71   ionic liquids have been polymerized onto this modified inner wall, giving rise to good

72   results. The thermal stability of the new phosphonium PILs stationary phases has been

73   evaluated, and the Abraham model has been used to study the variation of the

74   interactions between the new chromatographic phases and the analytes as the cation and

75   anion are changed.

76

77   **2. MATERIAL AND METHODS**

78   Most chemical reagents were purchased from Sigma-Aldrich and used without further

79   purification. The PAHs mixture was purchased from Restek (Bellefonte, United States).

80   NaBAr'$_4$ (Ar'= 3,5-bis(trifluoromethyl)phenyl) was prepared as previously reported.[36]

81   Methanol, dichloromethane and *n*-hexane were obtained from Merck. Untreated fused

82   silica capillaries (0.25 and 0.10 mm i.d.) were purchased from Supelco (Madrid, Spain).

83   Dichloromethane was distilled from CaH$_2$ and stored under nitrogen in a Young tube

84   and used without further purification. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a

85   Bruker Advance 300, DPX-300, or Advance 400 spectrometer. NMR spectra are

86   referred to the internal residual solvent peak for ^{1}H and ^{13}C {^{1}H} whereas phosphoric

87   acid (H$_3$PO$_4$, 85%) is used as external reference for ^{31}P NMR. NMR samples were

88   prepared under nitrogen using Konte manifolds purchased from Aldrich. All spectra are

89   given in the Supporting Information.

90   **2.1. Synthesis of polymerizable phosphonium ionic liquids.**

91   Some manipulations were performed under an inert atmosphere of dinitrogen using

92   standard Schlenk techniques due to the air sensitivity of n-tributylphosphine.

93   **[(^{n}Bu)$_3$(allyl)P]Br (IL 1).** Allyl bromide (0.83 mL, 9.60 mmol) was added to a solution

94   of n-tributylphosphine (2 mL, 8.00 mmol) in dichloromethane (20 mL), previously

95   cooled to 0º C. The reaction mixture was allowed to reach room temperature and stirred

96 for 1 hour. The resulting solution was evaporated to dryness, and after aprox 6 h. under

97 vacuum IL 1 was obtained as a white solid (2.379 gr, 92%).[23]

98 **[(^{n}Bu)$_3$(allyl)P]NTf$_2$ (IL 2).** LiN(CF$_3$SO$_2$)$_2$ (0.106 g, 0.371 mmol) was added to a

99 solution of [(^{n}Bu)$_3$(allyl)P]Br (IL 1) (0.100 g, 0.309 mmol) in methanol (20 mL), and

100 the resulting slurry was stirred for 48 hours. Methanol was then evaporated under

101 vacuum and the resulting solid residue was extracted with dichloromethane (25 mL).

102 The solution was washed with water (3 × 20 mL) and dried over magnesium sulfate

103 overnight.   Then, the resulting solution was filtered, and evaporated under reduced

104 pressure to yield compound [(^{n}Bu)$_3$(allyl)P]NTf$_2$ (IL 2) as an oil (65%).

105 **[(^{n}Bu)$_3$(allyl)P]OTf (IL 3).** To a solution of [(^{n}Bu)$_3$(allyl)P]Br (IL 1) (0.100 g, 0.309

106 mmol) in CH$_2$Cl$_2$ (20 mL), AgOTf (0.095 g, 0.371 mmol) was added and the mixture

107 was stirred for 48h. Afterwards, the solution was filtered through a short plug of

108 diatomaceous earth, dried under reduced pressure, and after 6 h, IL3 was obtained as an

109 oil (78 %).

110 **[(^{n}Bu)$_3$(allyl)P]BAr'$_4$(IL 4).** Compound IL 4 was prepared as described above for IL 3,

111 starting from IL 1 (0.100 g, 0.309 mmol) and NaBAr'$_4$ (0.329 g, 0.371 mmol). IL 4 was

112 obtained as a white solid, with a melting point of 75 ºC (Yield 70%).

113 **[(^{n}Bu)$_3$(crotyl)P]Cl (IL 5).** Crotyl chloride (0.94 mL, 9.60 mmol) was added to a

114 solution of tri-n-butylphosphine (2 mL, 8.00 mmol) in CH$_2$Cl$_2$ at 0º C. The mixture was

115 allowed to warm to room temperature, stirred for 1 hour and then the solvent was

116 evaporated to dryness under reduced pressure. The residue was dissolved in methanol

117 (20 mL), lithium bis(trifluoromethyl)sulfonamide (2.756 g, 9.60 mmol) was added and

118 the reaction mixture was stirred for 48 h. The solvent was then evaporated under

119 vacuum, the residue extracted with CH$_2$Cl$_2$ (20 mL) and the organic layer was washed

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120 with distilled water (3 × 20 mL). Dichloromethane was evaporated and IL 5 was

121 obtained as colorless oil (63 %).

122 **[(^{n}Bu)$_3$(crotyl)P]NTf$_2$ (IL 6).** Crotyl chloride (0.94 mL, 9.60 mmol) was added to a

123 solution of n-tributylphosphine (2 mL, 8.00 mmol) in CH_2Cl_2 at 0° C. The mixture was

124 allowed to warm to room temperature, stirred for 1 hour and then the solvent was

125 evaporated to dryness under reduced pressure. The residue was dissolved in methanol

126 (20 mL), lithium bis(trifluoromethane)sulfonamide (2.756 g, 9.60 mmol) was added and

127 the reaction mixture was stirred for 48 h. The solvent was then evaporated under

128 vacuum, the residue extracted with CH_2Cl_2 (20 mL) and the organic layer was washed

129 with distilled water (3 × 20 mL). Dichloromethane was evaporated and IL 6 was

130 obtained as a colorless oil (2.709 g, 63 %).

131 **[(^{n}Bu)$_3$(methallyl)P]NTf$_2$ (IL 7).** IL7 was prepared as described above for IL 6,

132 starting from n-tributylphosphine (2 mL, 8.00 mmol), methallyl chloride (0.94 mL, 9.60

133 mmol) and lithium bis(trifluoromethane)sulfonamide (2.756 g, 9.60 mmol). IL 7 was

134 obtained as a colorless oil (57 %).

135 **[(Ph)$_2$(allyl)$_2$P]NTf$_2$ (IL 8).** IL 8 was prepared as described above for IL 6, starting

136 from allyldiphenylphosphine (1.90 mL, 8.00 mmol), allyl bromide (0.83 mL, 9.60

137 mmol)) and LiNTf$_2$ (2.756 g, 9.60 mmol). IL 8 was obtained as colorless oil (66 %).

138 Schemes 1 and 2 show the structures of all the polymerizable phosphonium ILs used in

139 this study (see Supporting Information).

140 **2.2. Methods**

141 **2.2.1. Preparation of polymeric phosphonium-based ILs capillary columns**

142   All capillary columns were coated using the static method on a 10 m capillary column

143   (0.25 mm i.d.) at 40 ℃ using 0.25% (w/v) of ILs dissolved in dichloromethane. Prior to

144   adding the solvent to the IL monomer, 3 mg of AIBN [2,2′-azobis(2-

145   methylpropionitrile)] (~10 wt %) were added as initiator of the radical polymerization.

146   Capillaries were filled with the solution of initiator and ionic liquid. The AIBN

147   decomposition constant is lower than the coating rate at this temperature, so

148   polymerization was almost insignificant during the filling of the column.[37,38] After

149   coating, the ends of the capillary were sealed and the capillaries placed in a GC oven,

150   where the column was heated from 40 to 80 ℃ at 1 ℃/min and then kept at 80 °C for 5

151   h in order to ensure complete polymerization. Equation 2 can be used to approximate

152   the stationary phase film thickness (d_f) of capillaries columns.[22,38]

153   **Equation 2.**

154    $d_f = d_c c/400$

155   where d_c is the diameter of the capillary tubing (in micrometers), and c is the percentage

156   by weight (%) concentration of the stationary phase dissolved in an appropriate solvent.

157   Helium carrier gas was then flushed through the capillary at a rate of 1 mL/min, and the

158   capillary was then conditioned from 30-120 ℃ at 3 ℃/min and held at 120 ℃ for 2 h. A

159   triplicate of each column was prepared and the efficiencies of the IL columns were

160   determined to be higher than 3200 plates/m by using naphthalene at 100 °C.

161   **2.2.2. Preparation of polymeric phosphonium-based ILs capillary columns**

162   **incorporating sheets of graphene oxide bonded to the inner wall columns.**

163   In order to avoid the nonspecific adsorptions due to the low-stability of the graphene

164   dispersion in dichloromethane,[30] GO sheets were covalently bonded onto the inner

165   surface of fused silica capillary columns using 3-aminopropyl-diethoxymethyl-silane

166   (3-AMDS) as cross-linking agent. First, the capillaries were pre-treated with 1 mL 3-

167   AMDS toluene solution (1 vol %) in order to modify the inner surface of the capillary

168   through a covalent interaction between the silanol groups and 3-AMDS.[35] Then, GO

169   sheets were linked to the amino functionalized surface of fused silica capillary column

170   by rinsing the capillary with the GO suspension. To obtain a stable homogeneous

171   colloidal suspension of the GO sheets, a long time of sonication is required (over six

172   hours) in an ultrasound bath, followed by centrifugation at 3000 rpm for 5 min. After

173   coating, the ends of the capillary were sealed and the capillaries were introduced in a

174   GC oven, heating the column from 50 to 120 ºC at 3ºC min^{-1}. After this, the capillaries

175   were filled with the solution of initiator and ionic liquid.

176   Figure 1 shows the SEM images of capillary columns with a mixture of sheets of

177   graphene oxide bonded to the inner wall and phosphonium PILs. As it can be seen, a

178   homogeneous film is formed.
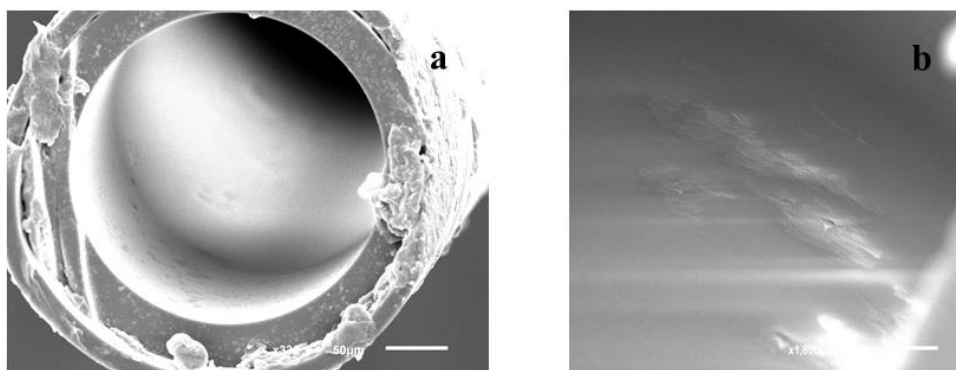
179   **Figure 1.** SEM images of a) the inner wall of capillary with GO sheets covalently bonded and
180   phosphonium PILs b) an amplified zone of the image shown in (a)

181

182   To evaluate the capillary columns, each individual probe molecule (dissolved in

183   dichloromethane) was injected into the column at three different temperatures: 50 ºC, 80

184   ºC and 110 ºC. At 50° C some of the used probe molecules, (particularly the H-bond

185   donors) showed peak asymmetries (As) higher than 1.5 and were therefore rejected

186   from the data set. At 110 ° C some probe solutes coeluted with the solvent; therefore,

187   these results were also discarded.

188   For the determination of the system constants, 43 probe molecules were used, ensuring

189   that a minimum of four test compounds were used to assess each of the parameters

190   under study. Selected compounds differ in size, dipolarity/polarizability, and hydrogen

191   bond donor or acceptor properties. Moreover, the peak asymmetries were from 0.9 to

192   2.3, and the retention times ranged from 2 to 15 min for the probe molecules at 110 ºC.

193   The solute descriptors for the 43 probe molecules are listed in Table 1.

194

195   **Table 1.** Probe molecules and values of solute descriptors used in the characterization of
196   phosphonium PILs stationary phases.

197

Probe molecules	E	S	A	B	L
1-Hexanol	0.21	0.44	0.344	0.52	3.643
Anisole	0.712	0.768	0	0.311	3.808
Cyclohexanone	0.403	0.895	0	0.53	3.759
1,2-Dichlorobenzene	0.872	0.771	0	0.054	4.516
Butylbenzene	0.595	0.499	0	0.139	4.734
Nonanal	0.121	0.636	0	0.414	4.838
Butyl acetate	0.079	0.57	0	0.438	3.409
Iodobenzene	1.182	0.784	0	0.135	4.548
1-Hexyne	0.167	0.274	0.09	0.117	2.544
1-Nitropropane	0.243	0.925	0.049	0.27	2.878
1-Pentanol	0.219	0.44	0.344	0.52	3.128
Pyridine	0.635	0.843	0	0.532	3.006
Benzonitrile	0.742	1.135	0	0.331	4.04
Phenyl acetate	0.648	1.055	0	0.521	4.378
Nitrobenzene	0.846	1.138	0	0.269	4.539
Naphthalene	1.24	0.906	0	0.193	5.154
Heptanal	0.14	0.642	0	0.441	3.856
2-Heptanone	0.123	0.662	0	0.496	3.781
1-Phenylethanol	0.823	0.819	0.351	0.648	4.424
Benzaldehyde	0.813	1.025	0	0.394	4.005
1-Octanol	0.199	0.44	0.344	0.52	4.648
1-Chloronaphthalene	1.419	0.951	0	0.135	6.175

Aniline	0.955	1.003	0.249	0.425	3.956
Fluorene	1.664	1.12	0	0.252	6.921
4-Chloroaniline	1.017	1.128	0.366	0.309	4.972
Benzyl alcohol	0.803	0.882	0.4	0.557	4.244
Butyl benzoate	0.668	0.851	0	0.393	5.974
Cinnamic alcohol	1.119	0.971	0.451	0.606	5.475
Phenol	0.769	0.759	0.716	0.319	3.844
Acetophenone	0.806	1.026	0	0.503	4.533
3-Methyl-1-butanol	0.198	0.423	0.351	0.501	2.963
1-Butanol	0.224	0.44	0.344	0.52	2.578
Ethyl benzoate	0.694	0.886	0	0.444	5.032
2-Phenylethanol	0.787	0.797	0.39	0.636	4.741
1-Decanol	0.191	0.44	0.344	0.52	5.589
Triethylamine	0.101	0.14	0	0.78	3.017
Ethylbenzene	0.613	0.499	0	0.139	3.814
1,3-Dinitrobenzene	0.079	0.57	0	0.438	3.409
Coumarin	1.269	1.61	0	0.524	6.034
Styrene	0.894	0.671	0	0.177	3.86
Undecan-2-one	0.105	0.662	0	0.496	5.732
Methyl hexanoate	0.084	0.564	0	0.456	3.970
4-Chloroaniline	1.0217	1.128	0.366	0.309	4.972

198

199   Probe molecules were injected and retention times were measured in triplicate. Multiple

200   linear regressions were performed using Statgraphics Centurion XV for Windows

201   version 15.2.06. The linearity regression (R^2) for all evaluations was ≥ 0.97. The values

202   of all the system constants are listed in Table 2 for phosphonium PILs.

203   **Table 2.** Regression parameter coefficients of phosphonium PILS

IL	T (°C)	c	e	s	a	b	l	R^2	n	SE	F
IL 1	50	-4.68 (0.12)	-0.20 (0.09)	1.83 (0.12)	5.68 (0.19)	0.09 (0.14)	0.72 (0.03)	0.99	28	0.05	338
	80	-4.32 (0.16)	-0.23 (0.14)	1.74 (0.16)	4.83 (0.20)	-0.64 (0.22)	0.59 (0.02)	0.99	32	0.07	212
	110	-4.61 (0.15)	-0.28 (0.12)	1.22 (0.17)	3.60 (0.26)	-0.66 (0.29)	0.48 (0.03)	0.98	24	0.09	188
IL 2	50	-3.39 (0.19)	-0.12 (0.14)	2.22 (0.19)	1.85 (0.32)	1.28 (0.29)	0.52 (0.05)	0.98	24	0.12	123
	80	-4.32 (0.14)	-0.23 (0.08)	1.27 (0.13)	1.69 (0.16)	0.70 (0.16)	0.58 (0.03)	0.98	27	0.08	175
	110	-4.35 (0.23)	-0.80 (0.13)	1.15 (0.23)	1.32 (0.28)	-1.07 (0.22)	0.55 (0.04)	0.97	33	0.10	66
IL 3	50	-4.73 (0.19)	-0.32 (0.14)	1.80 (0.20)	4.21 (0.32)	-0.37 (0.24)	0.77 (0.05)	0.98	28	0.08	124
	80	-3.99 (0.08)	-0.15 (0.07)	1.74 (0.09)	3.14 (0.16)	-0.64 (0.15)	0.61 (0.02)	0.99	34	0.04	461
	110	-5.48 (0.10)	-0.04 (0.07)	1.31 (0.09)	2.15 (0.11)	-0.79 (0.12)	0.40 (0.02)	0.99	33	0.04	802
IL 4	50	-3.98 (0.11)	-0.14 (0.07)	1.57 (0.08)	4.22 (0.14)	1.27 (0.10)	0.62 (0.03)	0.99	25	0.07	216
	80	-3.38 (0.13)	-0.28 (0.08)	0.96 (0.12)	3.75 (0.18)	0.90 (0.15)	0.55 (0.02)	0.98	26	0.06	120
	110	-5.33 (0.22)	-0.35 (0.16)	0.94 (0.19)	2.93 (0.22)	0.29 (0.23)	0.41 (0.04)	0.98	21	0.11	174
IL 5	50	-4.70 (0.25)	0.09 (0.18)	1.87 (0.25)	7.23 (0.46)	-0.21 (0.28)	0.67 (0.06)	0.97	23	0.15	77
	80	-4.36 (0.09)	-0.28 (0.07)	1.80 (0.10)	5.56 (0.14)	-0.33 (0.15)	0.56 (0.02)	0.99	31	0.04	544
	110	-4.55 (0.13)	-0.36 (0.11)	1.78 (0.15)	4.79 (0.23)	-0.39 (0.28)	0.49 (0.02)	0.99	25	0.07	239
IL 6	50	-3.52 (0.13)	-0.20 (0.09)	1.28 (0.12)	0.97 (0.17)	1.72 (0.11)	0.49 (0.03)	0.98	32	0.08	137
	80	-3.85 (0.11)	-0.21 (0.07)	1.05 (0.08)	0.91 (0.11)	0.97 (0.10)	0.42 (0.02)	0.98	35	0.07	171
	110	-3.99 (0.12)	-0.24 (0.08)	0.90 (0.10)	0.88 (0.11)	0.55 (0.14)	0.40 (0.03)	0.98	30	0.07	116
IL 7	50	-3.86 (0.14)	-0.12 (0.09)	1.57 (0.14)	1.62 (0.21)	0.81 (0.16)	0.67 (0.03)	0.99	31	0.07	214
	80	-3.94 (0.10)	-0.13 (0.03)	1.56 (0.08)	1.42 (0.11)	0.51 (0.07)	0.58 (0.02)	0.99	36	0.03	450
	110	-3.83 (0.16)	-0.24 (0.10)	1.00 (0.16)	0.66 (0.19)	0.04 (0.21)	0.45 (0.03)	0.98	33	0.07	106
IL 8	50	-3.90 (0.20)	-0.06 (0.15)	1.39 (0.21)	1.42 (0.32)	1.40 (0.26)	0.63 (0.04)	0.97	29	0.12	91
	80	-4.26 (0.13)	-0.10 (0.09)	1.33 (0.13)	1.07 (0.16)	1.09 (0.17)	0.51 (0.03)	0.98	32	0.10	193
	110	-3.74 (0.10)	-0.43 (0.08)	1.27 (0.12)	0.08 (0.14)	0.14 (0.16)	0.39 (0.02)	0.98	30	0.06	221

204

205   All separations were performed using a Shimadzu GC-2010 Gas Chromatograph

206   (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector. Analyses of

207   alcohols/amines, PAHs and pesticides were performed with helium as carrier gas at a

208   flow of 1 mL/min and a split ratio of 100/1. The injector and detector temperatures were

209   250 ℃ and 300 ℃, respectively. Methane was used to measure the column hold-up

210   time.

211   **3. RESULTS AND DISCUSSION**

212   Phosphonium-based ionic liquids (IL 1-8) have been synthesized by quaternization of

213   phosphines, and in several cases by a subsequent methatesis reaction to allow the anion

214   exchange. With the new ILs in hand, we have determined the influence of both cation

215   and anion on the properties of the ionic liquids, as well as in their performance as

216   stationary phases in GC.

217   **3.1. Optimization of film thickness capillary columns**

218   The variation of the column efficiency as a function of the film thickness was evaluated

219   using naphthalene as a probe solute. As can be seen in Figure 2, a percentage of 0.25%

220   w/v PIL provides greater separation efficiency. This percentage corresponds to a PIL

221   film thickness of about 0.16 microns. Therefore, capillary columns were prepared with a

222   thickness of approximately 0.16 microns film (0.25, w/v %) for all subsequent studies.

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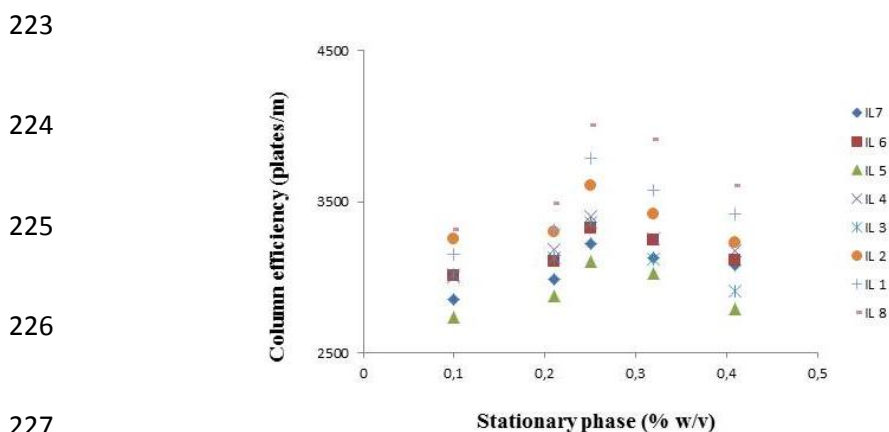
228   **Figure 2.** Representation of efficiency variation of phosphonium PILs stationary phases.

229

230   **3.2. Thermal stability**

231   Thermal stability is highly dependent on both the anion and the cation of the IL, and

232   directly determines the operating temperature range and lifetime of the GC column.

233   Figure 3 shows the loss of stationary phase due to the ILs decomposition or

234   volatilization. As seen in Figure 3, PIL 8, which has two allyl groups, shows the highest

235   thermal stability, presumably due to crosslinking during polymerization. PILs 1, 4, 5

236   and 7 show lower thermal stability. It is well known that the presence of halides in the

237   ILs lowers the thermal stability of the resulting stationary phases due to their

238   nucleophilic nature, which opens the way to decomposition via S_N1 and S_N2 processes.[39]

239   PIL 4 shows lower stability than PIL 1 because of the instability of the tetrakis[3,5-

240   bis(trifluoromethyl)phenyl]borate anion. On the other hand, PILs with NTf_2^- and OTf^-

241   anions show higher thermal stabilities, except in the case of PIL 7, a fact that could

242   indicate instability due to the methallyl group. For PIL 6, the slight increase in the

243   length of the aliphatic chain compared to PIL 2 makes the thermal stability somewhat

244   higher.

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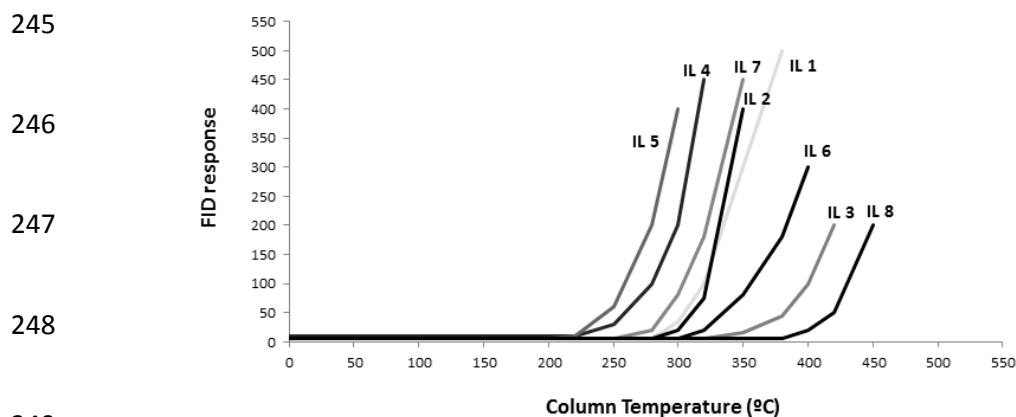
250   **Figure 3.** Thermal stability of the phosphonium PILs stationary phases.

251

252   These results provided a rough idea of the thermal stability of the ILs studied. To

253   evaluate quantitatively the thermal stability of PILs stationary phases a study was

254   conducted using an isothermal method. Thus the GC column was held at a series of

255   constant temperatures for at least 12 h, and the retention of probe compounds were

256   measured at a lower temperature before and after the isothermal conditioning.

257   Table 3 shows the isothermal measurements for naphthalene at different temperatures

258   with the phosphonium PILs. As it can be seen, the thermal stabilities of these PILs

259   ranged from 220 to 380 ºC, and are higher than those of other stationary phases based

260   on ILs.[18,40,41]

261   **Table 3.** Variation of naphthalene retention factor with phosphonium PILs columns using the
262   isothermal method.

T (ºC)	IL 1	IL 2	IL 3	IL 4	IL 5	IL 6	IL 7	IL 8
100	0.64	0.70	0.97	0.83	0.35	0.28	0.59	0.61
150	0.52	0.65	0.92	0.76	0.28	0.24	0.54	0.56
180	0.47	0.57	0.84	0.69	0.23	0.20	0.50	0.52
200	0.43	0.46	0.80	0.62	0.17	0.17	0.45	0.49
220	0.38	0.37	0.74	0.55	0.20[a]	0.15	0.38	0.45
250	0.31	0.31	0.69	0.59[a]	*	0.10	0.31	0.39
270	0.40[a]	0.27	0.61	*		0.08	0.39[a]	0.33
300	*	0.36[a]	0.52			0.22[a]	*	0.26
320		*	0.46			*		0.21
330			0.51[a]					0.18
350			*					0.11
380								0.20[a]
400								*

263   [a] Peaks tailing were observed. * No retention was observed for naphthalene

264   **3.3. IL solvation parameters: effect of the anion and the cation on the system**

265   **constants.**

266   A number of methods have been developed to characterize the solvation behaviour of

267   liquids.[20,42] In this study, the solvation parameter model developed by Abraham[43] has

268   been used to characterize the interactions between molecules of solute and stationary

269   phases.

270   **Equation 1.** Abraham solvation parameter model Equation

271    $log\ k = c + eE + sS + aA + bB + lL$

272   According to Equation 1, the retention factor (k) of a given solute at a specific

273   temperature is determined chromatographically. E, S, A, B, and L are solute descriptors

274   that represent excess molar refraction, dipolarity, H-bond acidity, H-bond basicity and

275   the gas-hexadecane partition coefficient at 298 K, respectively. Poole and co-workers[44]

276   optimized these descriptors by gas chromatography, reversed-phase liquid

277   chromatography and micellar electrokinetic chromatography. The system constants

278   from equation 1 are defined as: e indicates the ability of the stationary phase to interact

279   with the π- and n-electrons of the solvent; s is a measurement of the

280   dipolarity/polarizability of the solvent; a and b define the solvent hydrogen bond

281   basicity and acidity, respectively. Finally, l is a measurement of the phase ability to

282   distinguish between, or to separate members of any homologous series.

283   The system constants for the tested stationary phases were obtained by the use of the

284   inverse GC method and are listed in Table 2. Two of the five interaction parameter

285   coefficients, namely s (dipole-type interactions) and a (H-bond basic interactions) have

286   the larger magnitude for all ILs studied. This fact has been already observed for

287   imidazolium-based ILs[19] and phosphonium PILs.[29] It is well known that hydrogen bond

288   basicity and dipolarity of ILs are determined by the nature of the counter-anion.   The

289   cross-correlation between descriptors were checked and low correlations between

290   descriptors (<0.5 in absolute value) were observed.

291   Hydrogen bond basicity values ranged from 0.66 to 5.56 at 80ºC. The a-term of PILs 1

292   and 5 were higher in comparison with the other PILs, since the high electron density of

293   chloride and bromide makes them strong hydrogen bond acceptors. The other studied

294   PILs showed lower hydrogen bond basicities due to the large delocalization of the

295   negative charge in NTf_2^-, OTf^- and tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate

296   anions. This observation has already been made for imidazolium cations.[16,19,23,45-47]

17

297   It was observed that the value of the coefficients decrease as the temperature is

298   increased, showing that the solute retention decreases as a function of temperature, as

299   usually occurs in gas chromatography analysis.

300   The values obtained for the *b-term* were negative for some of the PILs tested. Negative

301   b-terms have been also reported for some of the imidazolium ILs, despite the fact that

302   the imidazolium cation possesses the ability to act as a hydrogen bond donor. In this

303   case, it seems that these unrealistic values cannot be explained by the structure of the

304   PILs because none of them have acidic hydrogens that could act as strong hydrogen

305   bond donors. Therefore, *b-term* was forced to be zero and the regression was performed

306   using *e*, *s*, *a* and l terms. The results obtained for the correlation coefficient and system

307   constants remained unchanged, implying that the b-term does not affect the model. It is

308   important to note that this phenomenon has been reported previously for other

309   phosphonium ILs.[29,30]

310   On the other hand, all the PILs that we have studied have shown low values for non-

311   bonding and π-electron interactions (e-term). The negative values of this system

312   constant are related to the way in which the solute descriptor E is determined.[42] The

313   comparison of phosphonium and imidazolium ILs shows that the e-term values are

314   lower for phosphonium ILs tested here, due to the π-electron-rich imidazolium cation,

315   implying that the e-term is dominated by the cation. Other phosphonium PILs studied

316   show similar values for the e-term (from -0.28 to 0.12 at 70ºC). The positive values are

317   due to the presence of lone pair electrons on the oxygen atoms of the ether chain.[29]

318   In the case of PIL 8, which contains two phenyl groups in its structure, negative values

319   of the e-term can be explained by the presence of π-stacking interactions between the

320   phenyl groups.

321　The values obtained for s-term were similar for all PILs studied. For PILs 1-4, the anion

322　changes, whilst the cation remains constant. There are no major changes in the s-term

323　and this implies that the dipolar interactions did not appear to be significantly

324　influenced by the anion type. When the cation is changed (PILs 6-8), no changes were

325　observed and it can be concluded that all phosphonium PILs will interact through

326　dipole-type interactions

327　The *l* coefficient is a combination of exoergic and endoergic processes. The magnitude

328　of this term indicates how well the IL will separate compounds in a homologous series.

329　As the studied PILs had positive *l* coefficients, the dispersion interaction seems to

330　dominate. The term values fall within the range 0.61 to 0.42 at 80 °C. These values are

331　similar to those of most of the studied phosphonium PILs. Therefore, dispersion

332　interactions must not be significantly influenced by the cation, and the dipolarities (s-

333　term) of these PILs are nearly identical.

334　**3.4. Separation of complex mixtures.**

335　In order to study the chromatographic behavior of these IL columns, different standard

336　mixtures were prepared and injected on phosphonium PILs stationary phases.

337　As an example, the chromatograms of a mixture of amines and alcohols using PIL 1 and

338　PIL 6 coated columns are displayed in Figure 4. Good symmetries for PILs 1 (from 0.8

339　to 1.9) and 6 (from 0.8 to 1.5), compared to those obtained with other stationary phases

340　based on imidazolium and phosphonium ILs[17,18,21,35] are diagnostic of a homogeneous

341　distribution of the polymerized ILs on the capillary inner wall. The higher tailing peaks

342　for PIL 1 compared to those of PIL 6 is in agreement with the higher values of a- and b-

343　term observed for PIL 1, due to the presence of the bromide anion, which makes this

344　PIL a relatively strong hydrogen bond acceptor. Moreover, variations of the retention

345   factor are observed for some analytes. Alcohols exhibited an increase in the retention

346   time on the IL 6 stationary phase compared to IL 1, due to the presence of hydrogen

347   bond-donating moieties.
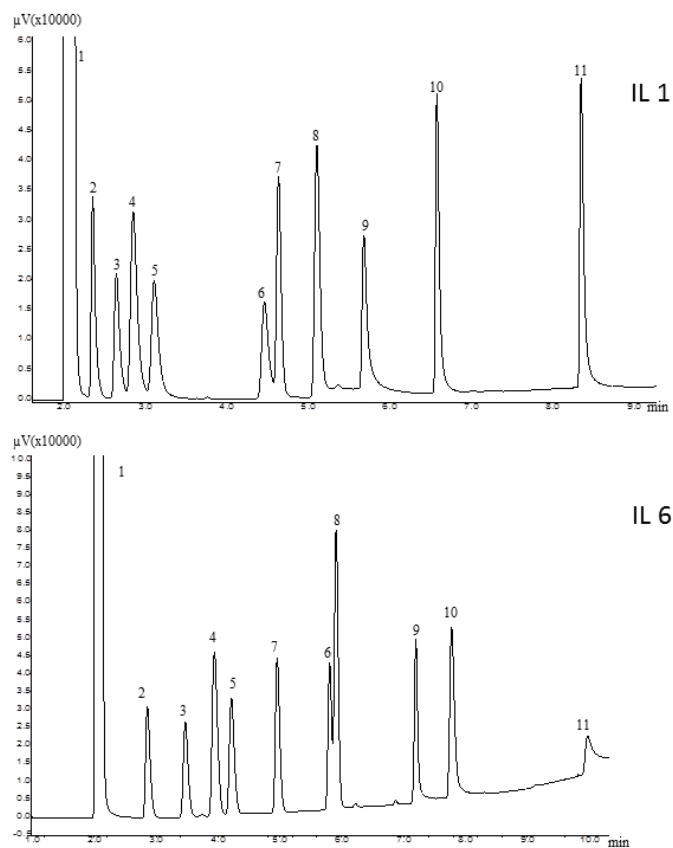
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349   **Figure 4.** Separation of a mixture containing alcohols and amines using IL 1 and IL 6: 1.

350   Hexane; 2. 1-Butanol; 3. 1-Pentanol; 4. 2-Methylpentanol; 5. 1-Hexanol; 6. 1-Octanol; 7.

351   Aniline; 8. Diisopropylamine; 9. 1-Decanol; 10. 2-Phenylethanol; 11. Cinnamic alcohol.

352   Program temperature: initial oven column temperature 100 ºC for 2 min, increased at a rate of

353   25 ºC min^{-1} to 200 ºC and then held at this temperature for 2 min.

354

355   The chromatograms obtained with the other phosphonium PILs studied are in the

356   Supporting Information. As it is shown there, some stationary phases (PILs 4 and 8)

357   show high peak asymmetries (As > 2.0) for alcohols, which is indicative of a non-

358   homogeneous IL film on the capillary wall. Moreover, PIL 5 shows the highest

359   retention times for polar compounds due to their increased ability to interact through

360   hydrogen bonds with this stationary phase (higher value of the a-term).

361

362   Figure 5 shows the chromatograms for the separation of a PAHs mixture employing

363   PILs 1 and PIL 6. It has been demonstrated[48] that some PAHs display high carcinogenic

364   and mutagenic activity, and have been listed as contaminants in wastewater, solid waste

365   and sediments.

366   As can be seen in Figure 5, PIL 1 column allowed to separate Indeno(1,2,3-cd)pyrene,

367   Dibenz(a,h)anthracene and Benzo(g,h,i)perylene in less than 30 minutes, with a

368   resolution value of 3.4 for Indeno(1,2,3-cd)pyrene and Dibenz(a,h)anthracene; and a

369   resolution of 1.2 for Dibenz(a,h)anthracene and Benzo(g,h,i)perylene. It is important to

370   stress that this column is able to get good results for the separation of PAHs using only

371   10 m of column.

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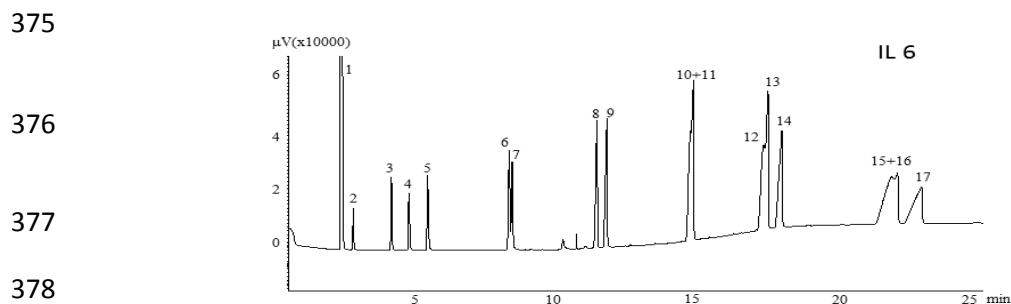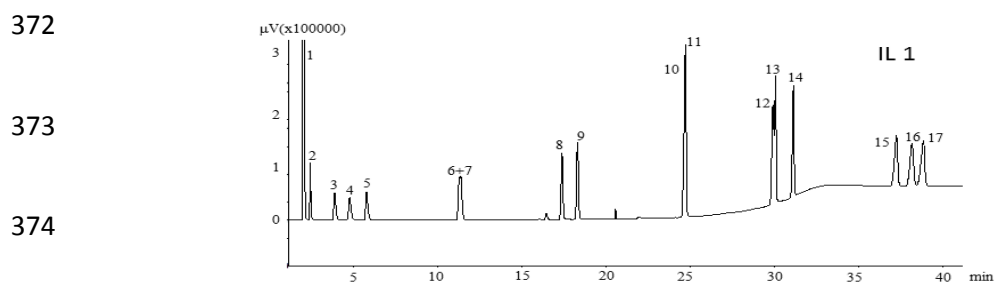
379   **Figure 5**. Separation of Polycyclic Aromatic Hydrocarbons mixture with IL 1 and IL 6. 1.

380   Hexane; 2. Naphthalene; 3.Acenaphthylene; 4. Acenaphthene; 5. Fluorene; 6. Phenanthrene; 7.

381   Anthracene;   8.Fluoranthene;   9.   Pyrene;   10.   Benz[a]anthracene;   11.   Chrysene;

382   12.Benzo[b]fluoranthene;   13.Benzo[k]fluoranthene;   14.Benzo[a]pyrene;   15.   Indeno(1,2,3-

383   cd)pyrene; 16. Dibenz(a,h)anthracene; 17. Benzo(g,h,i)perylene. Program temperature: initial

384   oven column temperature 90 ºC for 2 min, increased at a rate of 15ºC min^{-1} to 255 ºC and held at

385   this temperature for 20 min.

386

387   The presence of the fronting peaks 12, 15, 16 and 17 with PIL 6 may be due to a strong

388   interaction between these compounds and the column, saturating the column even at

389   low concentrations.

390   The chromatograms obtained with other phosphonium PILs under study herein are

391   showed in the Supporting Information. All stationary phases show the same elution

392   order, except stationary phase based on PIL 4. In this case, Dibenz(a,h)anthracene

393   eluted before the Indeno(1,2,3-cd)pyrene. This behaviour could be explained due to the

394   nature of the anion (BAr'$_4$$^-$) having four aromatic rings in its structure. Steric effects

395   seem to be the responsible of this inverted elution order, as for the non-linear indene

396   compound would be more difficult to go through the PIL 4 column than for the less

397   bulky dibenz(a,h)anthracene, the former being therefore more retained than the latter.

398   **3.5. Incorporation of graphene oxide on phosphonium-based polymeric ionic**

399   **liquids**

400   The addition of a GO dispersion to the phosphonium PILs prior to use them to separate

401   a pesticide mixture by GC analysis improves notably the chromatographic profile.[30] The

402   elution order remains the same for all pesticides, indicating that the employment of GO

403   does not change the nature of the stationary phase, its effect being to increase the

404   surface area, affording a more homogeneous film of polymer ionic liquid along the

405   capillary wall.

406 Despite these improvements, the GO dispersion in dichloromethane exhibited a low

407 stability against agglomeration and sedimentation, and this implies that the film of GO

408 along the capillary wall was far from homogeneous. Considering that a more

409 homogeneous GO coating would further improve column performance, GO sheets were

410 covalently bonded onto the inner surface of fused silica capillary columns using 3-

411 aminopropyldiethoxymethylsilane as a cross-linking agent. The column efficiencies of

412 these new stationary phases have been evaluated, and in all cases an improvement of the

413 efficiencies has been observed, so that an impressive 4200 plates m^{-1} were found for

414 some PILs. When naphthalene was injected at 100 ºC, the retention time was measured

415 every 50 runs, and the results indicated that the columns coated with the new phases

416 endured series of 450 runs without loss of activity.

417 The thermal stabilities of these new stationary phases were evaluated. As shown in

418 Figure 6, when GO sheets are covalently bonded to the inner wall of capillary columns,

419 a slight increment of the thermal stability is observed, compared to that of the

420 phosphonium PILs capillary columns. This phenomenon could be explained because

421 GO displays hydroxyl (-OH) and carboxylic groups (-COOH) that allow π-π, n- π and

422 halogen-π interactions with phosphonium PILs. This fact implies that the adsorption of

423 the PILs into the GO is stronger than into silica.

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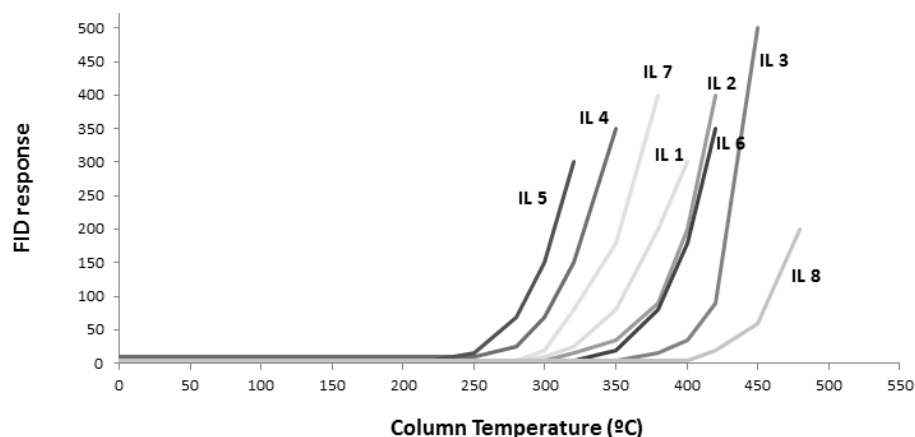
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428 **Figure 6.** Thermal stability for the mixtures of phosphonium PILs and GO sheets covalently

429 bonded to inner wall stationary phases.

430

431 GO-PIL 8 was chosen to test the effect of the covalently bonded GO into the ability of

432 the PILs columns to separate different types of compounds by GC. The choice of this

433 PIL 8 in particular was based on it displaying the worst symmetry peaks in the

434 separation of the mixtures described above, so that clearly an improvement was needed.

435 Tables 4 shows the resulting system constants values for GO-PIL 8 stationary phase.

436 The *a* and *b* terms are lower than those of PIL 8 (with no GO). This can be attributed to

437 the generation of a more homogeneous film along the capillary as a consequence of the

438 covalently bonded GO sheets to the inner wall, and to the existence of a lower number

439 of free silanol groups thus reducing the non-specific absorptions.

440 **Table 4.** Regression parameter coefficients of mixture of PIL 8 and GO sheets covalently
441 bonded to inner wall stationary phase.

IL	T (ºC)	c	e	s	a	b	l	R^2	n	SE	F
IL 8	50	-3.90 (0.18)	-0.10 (0.12)	1.45 (0.18)	1.05 (0.12)	1.11 (0.23)	0.79 (0.03)	0.99	30	0.11	561
	80	-4.30 (0.12)	-0.16 (0.19)	1.21 (0.17)	0.82 (0.08)	0.86 (0.10)	0.68 (0.03)	0.98	34	0.08	227
	110	-4.68 (0.10)	-0.39 (0.10)	1.09 (0.20)	0.11 (0.14)	0.19 (0.17)	0.61 (0.02)	0.97	36	0.07	105

24

442   The chromatograms obtained when alcohol/amine and pesticide mixtures were injected

443   in the column coated with covalently linked GO sheets and phosphonium PIL 8, are

444   depicted in Figures 7 and 8, respectively. As shown in Figure 7, the good peak

445   symmetries obtained (As < 1.1) compared to those observed by the use of a dispersion

446   of graphene for the alcohols/amines mixture constitute a clear improvement, and

447   strongly suggest that the phosphonium PIL film is homogeneously distributed on the

448   capillary inner wall.

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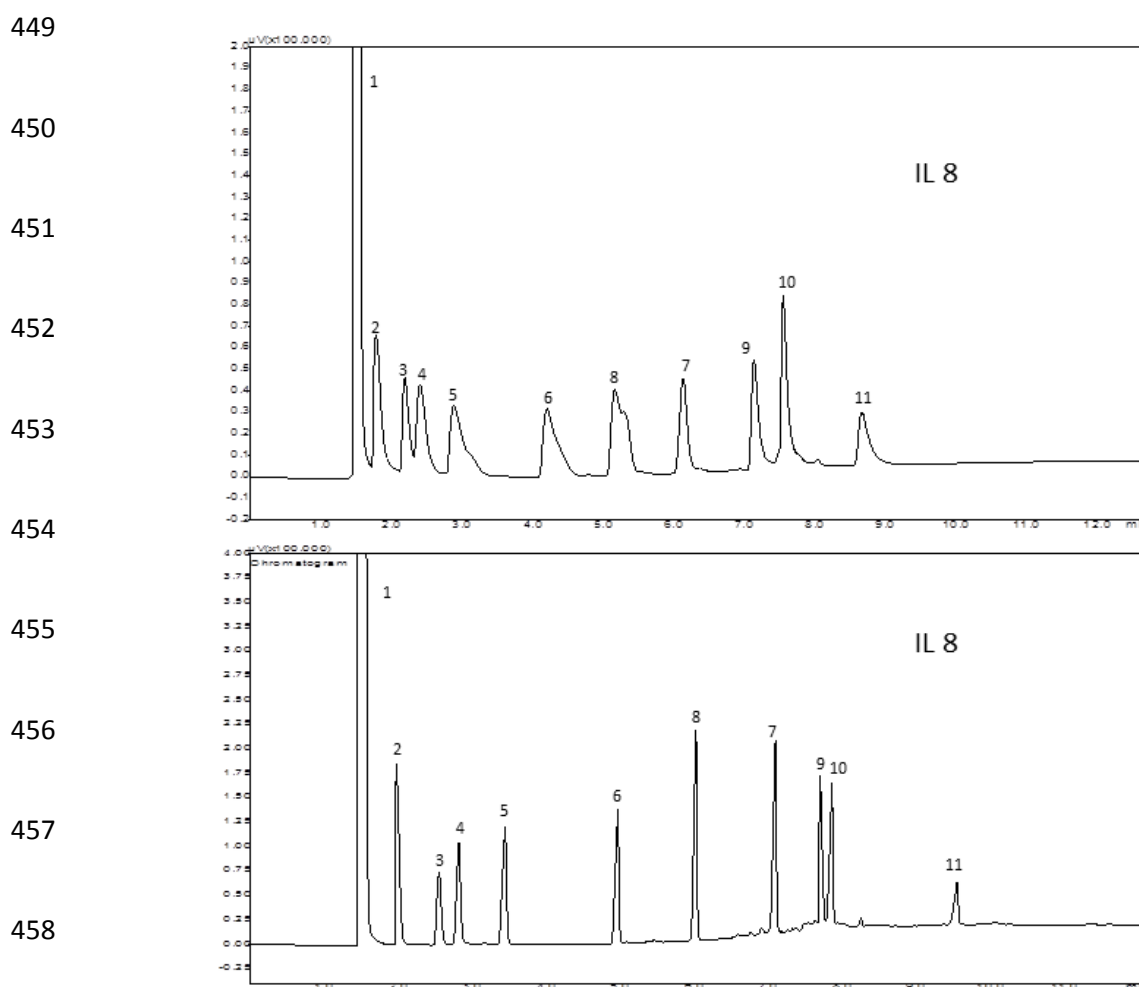
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460   **Figure 7.** Separation of a mixture containing alcohols and amines on a) polymeric IL 8 and

461   graphene dispersion column; b) polymeric IL 8 and graphene oxide covalently bonded column :

462   1. Hexane; 2. 1-Butanol; 3. 1-Pentanol; 4. 2-Methylpentanol; 5. 1-Hexanol; 6. 1-Octanol; 7.

463   Aniline; 8. Diisopropylamine; 9. 1-Decanol; 10. 2-Phenylethanol; 11. Cinnamic alcohol.

25

464 Program temperature: initial oven column temperature 100 ºC for 1 min, increased at a rate of

465 30 ºC min^{-1} to 200 ºC and then held at this temperature for 2 min.

466

467 In agreement with the formation of a very homogeneous film along the capillary wall,

468 Figure 8 shows also a good peak tailing compared to the stationary phase based on GO

469 dispersion and PIL. As a result, the new stationary phase allows the separation of some

470 pesticides that previously, using the columns discussed above, co-eluted and could not

471 be separated.
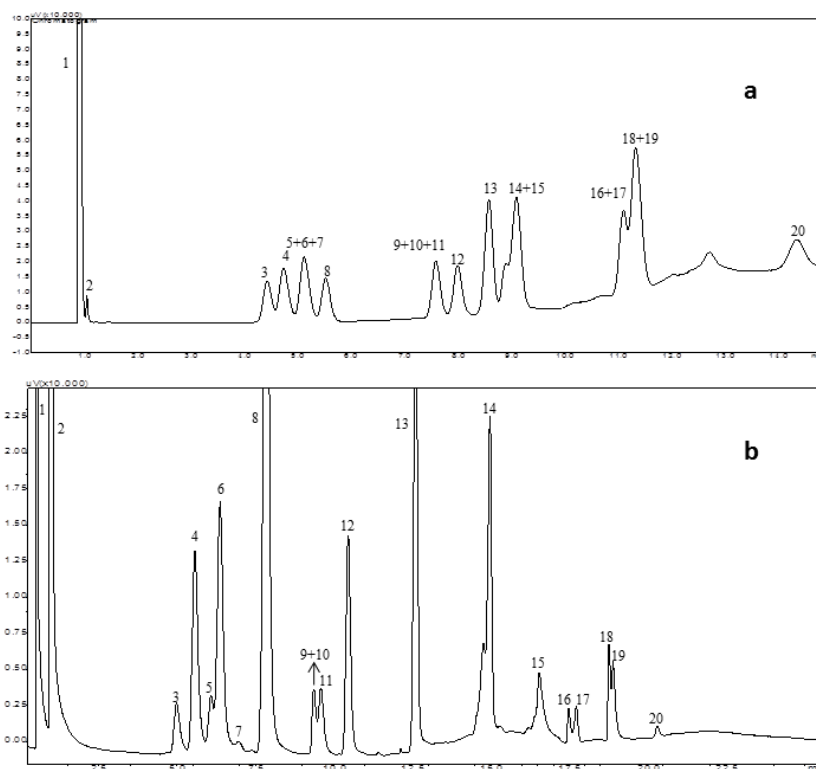
481 **Figure 8**. Separation of a pesticide mixture on: a) mixture of graphene oxide dispersion and

482 PIL 8 column; b) a mixture of covalently bonded graphene oxide and polymerized IL 8 column:

483 1. Hexane; 2. Hexachlorobenzene; 3. Aldrin; 4. Bromocyclen; 5. HCH; 6. Heptachlor; 7.

484 Endrin; 8. Isodrine; 9. Chlorophenothan; 10. Endosulfan; 11. 4,4-DDE; 12. Dieldrin; 13. DDD;

485 14. Metoxychlor; 15. Bromacil; 16. Coumaphos; 17. Dialifos; 18. Ruelene; 19. Carbaril; 20.

486   Pyraclofos. Program temperature: initial oven column temperature 130 ℃ for 2 min. and a

487   heating rate of 10 ℃ /min to 250 ℃ and then held at this temperature for 15 min.

488

4. CONCLUSIONS

490   In this study, eight polymeric phosphonium ionic liquid stationary phases were prepared

491   and their chromatographic properties when used for gas chromatography analysis have

492   been studied. The thermal stabilities observed for all the stationary phases based on the

493   phosphonium ionic liquids studied are higher than those of stationary phases based on

494   traditional imidazolium monocationic ionic liquids, therefore allowing separations at

495   higher temperatures than imidazoliums ionic liquids.

496

497   Moreover, the incorporation of graphene oxide sheets through covalent bonds to

498   phosphonium PILs clearly improved their properties and behavior as gas

499   chromatography stationary phases, due to the formation of a more homogeneous film

500   along the capillary. This fact implies an enhancement of the interactions with the

501   analytes and a decrease in non-specific interactions. As a consequence, the new phases

502   allowed separations of several types of organic compounds with good separation

       efficiencies.

503

504   This research should lead to the development of a wide range of chromatographic

       columns displaying improved selectivities.

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The incorporation of graphene oxide sheets to phosphonium ionic liquids stationary phases led to a great improvement of their separation efficiencies