

1 **Polymeric metal-containing ionic liquid sorbent coating for the determination of**
2 **amines using headspace solid-phase microextraction**

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13 **Abstract**

14 This study describes the design, synthesis, and application of polymeric ionic liquid sorbent
15 coatings featuring nickel metal centers for the determination of volatile and semi-volatile amines from
16 water samples using headspace solid-phase microextraction. The examined polymeric ionic liquid
17 sorbent coatings were composed of two ionic liquid monomers (tetra(3-vinylimidazolium)nickel
18 bis[(trifluoromethyl)sulfonyl]imide $[\text{Ni}^{2+}(\text{VIM})_4] 2[\text{NTf}_2^-]$ and 1-vinyl-3-hexylimidazolium
19 $[\text{HVIM}^+][\text{NTf}_2^-]$), and an ionic liquid crosslinker (1,12-di(3-
20 vinylimidazolium)dodecane $[(\text{VIM})_2\text{C}_{12}^{2+}] 2[\text{NTf}_2^-]$). With these ionic liquid monomers and
21 crosslinkers, three different types of coatings were prepared: PIL 1 based on the neat
22 $[\text{Ni}^{2+}(\text{VIM})_4] 2[\text{NTf}_2^-]$ monomer; PIL 2 consisting of the $[\text{Ni}^{2+}(\text{VIM})_4] 2[\text{NTf}_2^-]$ monomer with
23 addition of crosslinker, and PIL 3 comprised of the $[\text{HVIM}^+][\text{NTf}_2^-]$ monomer and crosslinker.
24 Analytical performance of the prepared sorbent coatings using headspace solid-phase microextraction
25 GC-MS was compared with the polydimethylsiloxane and polyacrylate commercial coatings. The
26 PIL 2 sorbent coating yielded the highest enrichment factors ranging from 5500 to over 160000 for
27 the target analytes. The developed headspace solid-phase microextraction GC-MS method was

28 applied for the analysis of real samples (the concentration of amines was 200 $\mu\text{g L}^{-1}$), producing
29 relative recovery values in the range of 90.9-120.0 % (PIL 1) and 83.0-122.7 % (PIL 2) from tap
30 water, and 84.8-112.4 % (PIL 1) and 79.2-119.3 % (PIL 2) from lake water.

31

32 **Keywords**

33 Amines; polymeric metal-containing ionic liquids; nickel ions; solid-phase microextraction.

34

35 **Article Related Abbreviations:**

36 2,6-DTBP, 2,6-di-tert-butylpyridine; DAROCUR 1173, 2-hydroxy-2-methylpropiophenone; EF,
37 enrichment factor; HS-SPME, headspace solid-phase microextraction; IL, ionic liquid; LLE, liquid-
38 liquid extraction; MCILs, metal-containing ionic liquid; NaCl, sodium chloride; PA, polyacrylate;
39 PDMS, polydimethylsiloxane; PIL, polymeric ionic liquid; R^2 , coefficient of determination; RR,
40 relative recovery; $[\text{HVIM}^+][\text{NTf}_2^-]$, 1-vinyl-3-hexylimidazolium
41 bis[(trifluoromethyl)sulfonyl]imide); $[\text{Ni}^{2+}(\text{VIM})_4] 2[\text{NTf}_2^-]$, tetra(3-vinylimidazolium)nickel
42 bis[(trifluoromethyl)sulfonyl]imide; $[(\text{VIM})_2\text{C}_{12}^{2+}] 2[\text{NTf}_2^-]$, 1,12-di(3-
43 vinylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide.

44

45 **1. INTRODUCTION**

46 Amines are well-known environmental pollutants that are widespread throughout the world.
47 They can be released from a variety of anthropogenic (chemicals, pesticides, pharmaceuticals,
48 automobiles, dyestuff, etc.) and natural sources (biomass burning, oceans, and vegetation) [1].
49 Amines are easily released to the environment through groundwater, rivers, lakes, and soil as well as
50 industrial effluents or chemical decomposition products [2]. Most compounds of this class are
51 hazardous and toxic to humans and animals. They can react with nitrosylating agents and, as a
52 consequence, be converted to carcinogenic n-nitroamines [3]. Even though contamination of amines
53 can exist in the environment at trace levels, they may have a mutagenic and toxic effect on animals

54 and humans. Therefore, the concentration of amines in the surrounding water must be continuously
55 monitored, and it is vital to find fast, easy, effective, and sensitive methods for their determination.

56 Solid-phase microextraction (SPME) is a solvent-free extraction technique and is an alternative
57 to conventional extraction methods, such as liquid-liquid extraction (LLE) and solid-phase extraction
58 (SPE) [4]. The procedure for extracting analytes from an aqueous solution using SPME consists of
59 the following three main steps: a) exposing the fiber to the sample by direct-immersion (DI) or the
60 headspace (HS) above the sample, b) absorbing/adsorbing the analytes by the sorbent, and c)
61 desorption of the analytes from the coating by thermal or solvent extraction. The SPME method has
62 become widely used to determine a wide range of analytes from complex matrices, such as samples
63 of food products, biological substances, pharmaceuticals, and environmental samples [5-8]. SPME
64 has numerous advantages over other extraction methods, such as being simple, rapid, easily
65 automated, eliminates the use of toxic solvents, and allows for the collection of samples in-situ and
66 in-vivo. One of the most important limitations of the method is the choice of commercially-available
67 SPME sorbent coatings. Therefore, on-going research in the field is focused on developing new
68 sorbent coatings that extend the range of analytes that can be effectively extracted. Various materials
69 such as nanoparticles of noble metals, sorbents based on silica (silicon dioxide), ionogels, molecularly
70 imprinted polymers, conductive polymers, carbon nanotubes, metal and/or metal oxide nanoparticles,
71 graphene and graphene oxide, metal organic frameworks, ionic liquids (ILs), and polymeric ionic
72 liquids (PILs) [9-17] hold promise due to their desired tunability. The above drawbacks are related to
73 the general limitations of the SPME method. However, in the case of amine determination by SPME
74 coupled to gas chromatography (GC), a number of additional problems arise due to their high aqueous
75 solubility, volatility, polarity, and highly basic character (i.e., stronger sorption to polar stationary
76 phases is observed with the decrease in the molecular mass of amines) [18].

77 ILs are a well-known group of materials that have been used as SPME sorbent coatings. These
78 compounds consist of a bulky organic cation and a smaller inorganic/organic anion and are present
79 as liquids below 100 °C. The physical and chemical properties of ILs are highly tunable based on
80 selecting an appropriate anion and cation pair. When ILs are used as a polymerizable monomer, PILs

81 are formed and retain many of the unique physico-chemical properties of ILs as well as additional
82 advantages that include higher thermal and chemical stability, and a negligible change in viscosity
83 when subjected to high temperatures [19, 20]. PILs have been used for the determination of various
84 classes of analytes, including polycyclic aromatic hydrocarbons, fatty acid methyl esters, esters and
85 benzene derivatives, carbon dioxide, estrogens, alcohols and amines, genotoxic or structurally
86 alerting alkyl halides and aromatics, pyrethroids, and contaminants of emerging concern [10, 11,
87 1621].

88 Another interesting subclass of ILs is metal-containing ionic liquids (MCILs). MCILs are formed
89 by incorporating transition and/or rare earth metals into their chemical structure [22]. In addition to
90 possessing fundamental properties of ILs, the paramagnetic metals in MCILs impart magnetic,
91 catalytic, and optical properties, which significantly increases the scope of their applications [23, 24].
92 MCILs have been used in various areas of analytical chemistry including extractions and
93 microextractions, chromatographic separations, membrane applications and gas absorption,
94 electrochemistry, and sensors [25, 26]. Incorporation of metal ions (Ni^{2+} , Mn^{2+} , Co^{2+} , Dy^{3+} , Gd^{3+} ,
95 Nd^{3+}) into the IL chemical structure significantly influences their interactions with analytes
96 originating from different organic subclasses such as alcohols, ketones, chlorinated alkanes, aromatic
97 compounds and amines [22, 27]. It has been observed that nickel-containing MCILs exhibit unique
98 selectivity towards amines [27]. The viscosity of MCILs drop significantly with an increase of
99 temperature, rendering them impractical in SPME. To overcome this obstacle, the creation of a
100 polymerizable sorbent coating is required. A procedure using vinylimidazole ligands coordinated to
101 silver ion and subsequent free radical polymerization to form a polymeric metal-containing ionic
102 liquid was previously reported [28].

103 Using this approach, nickel-based PILs were synthesized in this study with or without the
104 addition of crosslinker to investigate its effect on amine extraction performance. According to a
105 previous study by Ho et al. [29], crosslinked PILs possess higher durability, stability, and robustness
106 compared to linear PIL-based coatings. The effect of nickel cation in the PIL chemical structure was
107 studied by further comparing the extraction performance to a structurally-similar PIL coating lacking

108 the metal center. To benchmark the sorbent coatings, extractions of the targeted amine analytes were
109 compared to commercially-available fibers consisting of PDMS and PA sorbent coatings. The
110 developed HS-SPME-GC-MS method was finally applied for the analysis of real samples, including
111 tap and lake water.

112

113 **2. MATERIALS AND METHODS**

114 **2.1. Reagents and materials**

115 The group of studied amines included pyridine (99.8 %), triallylamine (99.0 %), tripropylamine
116 ($\geq 98.0\%$), 3-ethylpyridine ($\geq 98.0\%$), aniline (99.5 %), and 2,6-di-tert-butylpyridine (2,6-DTBP,
117 $\geq 97.0\%$), all purchased from Sigma-Aldrich (St. Louis, MO, USA). Table SM-1 of the
118 supplementary material (SM) shows the structures and various physico-chemical properties of the
119 analytes. Stock solutions of the individual analytes were prepared in acetonitrile (99.8 %, Sigma-
120 Aldrich) at a concentration of 2000 mg L^{-1} . The intermediate solutions in acetonitrile were prepared
121 by diluting the set of individual stock solutions to a level of 100 mg L^{-1} for each analyte. GC-MS
122 calibration curves were obtained using a set of solutions prepared so that the volume of injected
123 standard solutions were equal to $1\text{ }\mu\text{L}$. Working solutions were prepared by spiking the intermediate
124 solution into the ultrapure or real water samples containing sodium chloride (NaCl, $\geq 99.5\%$,
125 purchased from Fisher Scientific, Fair Lawn, NJ, USA). Ultrapure water ($18.2\text{ M}\Omega\text{ cm}$) was obtained
126 from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

127 For the synthesis of monomers and crosslinkers, the following reagents were used: 1-
128 vinylimidazole ($\geq 99.0\%$), nickel(II) chloride (98.0 %), 1,12-dibromododecane (98.0 %), 1-
129 bromohexane (98.0 %), all purchased from Sigma-Aldrich. Lithium bis[(trifluoromethyl)sulfonyl]
130 imide (LiNTf₂) was acquired from SynQuest Laboratories (Alachua, FL, USA). The reagent 2-
131 hydroxy-2-methylpropiophenone ($> 96.0\%$, DAROCUR 1173, Sigma-Aldrich) was used as an
132 initiator in the polymerization reaction. Methanol (99.8 %), ethyl acetate (99.8 %), isopropanol
133 (99.5 %), and dichloromethane ($\geq 99.8\%$) were purchased from Sigma-Aldrich.

134 The commercial SPME fibers, featuring polyacrylate (PA, 85 μm) and polydimethylsiloxane
135 (PDMS, 100 μm) coatings, were provided as gifts from Millipore-Sigma. Elastic nitinol wires were
136 used as solid supports in the preparation of the SPME fibers (Nitinol Devices & Components,
137 Fremont, CA, USA). Blank SPME assemblies (24 Ga) were provided by Millipore-Sigma
138 (Bellefonte, PA, USA).

139 Real water samples were collected from the laboratory tap in Ames (IA, USA) and from Lake
140 LaVerne on the campus of Iowa State University, respectively. The samples were stored in the dark
141 using glass bottles at 4 $^{\circ}\text{C}$ before use. Prior to analysis, NaCl was added to a concentration of 30 %
142 (w/v).

143

144 **2.2. Instrumentation**

145 Amine separations were carried out using an Agilent Technologies 7890B GC equipped with a
146 5977A MS detector (single quadrupole) on a CP-Sil8 CB capillary column (length 30 m, 0.25 mm
147 ID, 0.25 μm film thickness). Ultrapure helium was used as carrier gas at a flow rate of 1 mL min^{-1} .
148 The inlet was operated in splitless mode with an inlet temperature of 190 $^{\circ}\text{C}$. The following oven
149 program was used: initial temperature equal to 40 $^{\circ}\text{C}$, then the temperature was increased at
150 2 $^{\circ}\text{C min}^{-1}$ up to 80 $^{\circ}\text{C}$, followed by an increase to 270 $^{\circ}\text{C}$ at 30 $^{\circ}\text{C min}^{-1}$, and finally held for 1 min.
151 The MS employed electron ionization (EI) at 70 eV and gain factor mode. The transfer line
152 temperature was set at 250 $^{\circ}\text{C}$, while the source and quadrupole temperatures were fixed at 230 $^{\circ}\text{C}$
153 and 150 $^{\circ}\text{C}$, respectively. Data were acquired in single ion monitoring (SIM) mode. Identification of
154 the amines was accomplished by considering the retention time, presence of quantifier and qualifier
155 ions for each analyte (see Table SM-1 of SM), and the ratio between those ions. The peak area
156 corresponding to the quantifier ion was used for quantitative purposes.

157 Scanning electron microscopy (SEM) images of the nickel-based PIL fibers were obtained using
158 a FEI Quanta-250 microscope (FE-SEM).

159

160 **2.3. Synthesis of ionic liquid monomers and crosslinker**

161 Two IL monomers, namely, 1-vinyl-3-hexylimidazolium bis[(trifluoromethyl)sulfonyl]imide
162 $[\text{HVIM}^+][\text{NTf}_2^-]$ and tetra(3-vinylimidazolium)nickel bis[(trifluoromethyl)sulfonyl]imide
163 $[\text{Ni}^{2+}(\text{VIM})_4] 2[\text{NTf}_2^-]$, as well as the 1,12-di(3-vinylimidazolium)dodecane
164 bis[(trifluoromethyl)sulfonyl]imide $[(\text{VIM})_2\text{C}_{12}^{2+}] 2[\text{NTf}_2^-]$ IL crosslinker were synthesized and used
165 in the study.

166 The $[\text{Ni}^{2+}(\text{VIM})_4] 2[\text{NTf}_2^-]$ IL monomer was synthesized using a modification of a previously
167 published procedure [26]. One equivalent (millimolar) of anhydrous nickel (II) chloride was added
168 to four equivalents of 1-vinylimidazole in methanol with stirring at room temperature overnight. After
169 reaction, solvent was removed by rotary evaporation. The resulting solid material was dried under
170 vacuum for 24 h at 40 °C. The obtained solid ($[\text{Ni}^{2+}(\text{VIM})_4] 2[\text{Cl}^-]$) was then reacted with LiNTf₂ at
171 a 1:4 molar ratio, respectively, in acetone and water by stirring at room temperature for 5 hours. The
172 solvent was subsequently evaporated and the material dried under vacuum. After drying, the material
173 was dissolved in dichloromethane, and remaining lithium chloride was removed by liquid-liquid
174 extraction with ultrapure water. In the final step, dichloromethane was evaporated under vacuum for
175 24 h at 40 °C. Elemental analysis (CHN): Calculated % for C₂₄H₂₄F₁₂N₁₀NiO₈S₄, Calculated; C,
176 28.96; H, 2.43; N, 14.07; S, 12.88. Found; C, 34.56; H, 3.17; N, 13.85; S, 9.34.

177 The $[\text{HVIM}^+][\text{NTf}_2^-]$ IL monomer and $[(\text{VIM})_2\text{C}_{12}^{2+}] 2[\text{NTf}_2^-]$ IL crosslinker were synthesized
178 according to previously published methods [30, 31]. The monomer and crosslinker were characterized
179 using ¹H NMR and electrospray ionization (ESI)-MS and spectra are shown in Figures SM 1-5 of the
180 SM.

181

182 **2.4. Preparation of solid-phase microextraction fibers**

183 All coatings were prepared by on-fiber UV-initiated polymerization following previously
184 described procedures [29]. The composition and mass ratio of components used for the preparation
185 of the IL-based coatings are shown in Table 1 and Figure 1. Three types of coatings were prepared:
186 PIL 1 consisting of pure $[\text{Ni}^{2+}(\text{VIM})_4] 2[\text{NTf}_2^-]$ monomer; PIL 2 with monomer and
187 $[(\text{VIM})_2\text{C}_{12}^{2+}] 2[\text{NTf}_2^-]$ crosslinker, and PIL 3 based on the $[\text{HVIM}^+][\text{NTf}_2^-]$ monomer and

188 crosslinker. The PIL3 coating was used as a reference to study the effect of Ni^{2+} metal center in the
189 PIL on extraction performance. The IL monomer, IL crosslinker (if applied), and free radical initiator
190 were mixed in appropriate proportions at 55 °C. The homogenous mixture was manually placed on
191 the surface of a previously derivatized nitinol support. Derivatization of elastic nitinol wires was
192 carried out according to a previously published method [32] and glued into a commercial SPME
193 device. The coatings were exposed to UV irradiation (360 nm) for two hours to promote
194 polymerization. Finally, the obtained fibers were thermally conditioned in the GC injection port at
195 200 °C for 30 min.

196

197 **2.5. Headspace solid-phase microextraction procedure**

198 Samples for HS-SPME were placed in 20 mL glass vials closed with open-top caps and
199 polytetrafluoroethylene/silicone septa (Supelco). For all experiments, the sample volume was
200 maintained at 10 mL. Before exposure of the SPME fiber, samples were thermostated at the
201 temperature of extraction for 15 min using a hotplate with an accuracy of ± 0.5 °C. Subsequently,
202 samples were spiked with required volumes of the stock solution and mixed at 800 rpm for 5 min. A
203 Corning PC-420D magnetic stirring hotplate (Corning, NY, USA) and a stir bar (1 cm length \times 0.5 cm
204 diameter, Fisher Scientific) were used for mixing. The fiber was exposed to the headspace of the
205 sample solution for 10-70 min at 25-70 °C. After extraction, the fibers were immediately inserted into
206 the GC injection port for thermal desorption at 190 °C for 10 min. The temperature and desorption
207 time were optimized in advance by studying carry-over effects.

208 The amino functional groups within amine molecules are responsible for strong and specific
209 interactions with silane groups and siloxane bridges. Consequently, this leads to their strong retention,
210 which often results in broad, asymmetrical chromatographic peaks and low sensitivity. To avoid these
211 issues, it is necessary to choose an optimal GC column. The following capillary columns were
212 examined to identify the most effective separation of amines: HP-5ms (30 m, 0.25 mm ID, 0.25 μm
213 film thickness), DB-WAX (30 m, 0.25 mm ID, 0.25 μm film thickness), and CP-Sil8 CB

214 (30 m, 0.25 mm ID, 0.25 μ m film thickness). The CP-Sil8 CB column has demonstrated superior
215 performance in amine separation and was selected for further studies.

216

217 3. RESULTS AND DISCUSSION

218 3.1. Characterization of nickel-based polymeric ionic liquid fibers

219 The introduction of transition metals into the IL chemical structure may significantly affect its
220 interactions with organic compounds, thereby influencing extraction properties. This feature was
221 exploited in the determination of phenolics, polycyclic aromatic hydrocarbon, insecticide compounds
222 and lipophilic organic UV filters using MCILs in micro-liquid extraction techniques [33, 34]. More
223 systematic studies evaluating the selectivity of MCILs were performed by studying the retention of
224 analytes obtained from inverse gas chromatography when the MCIL is used as a stationary phase [27].
225 MCILs with anions containing metals (Ni^{2+} , Mn^{2+} , Co^{2+} , Dy^{3+} , Gd^{3+} , Nd^{3+}) with acetylacetone
226 ligands were investigated. The results indicated an exceptionally high affinity of amines (especially
227 pyridine) for nickel-containing MCILs. However, due to their liquid state, these compounds cannot
228 be directly applied as extraction phases in SPME. In this study, the structural features of the MCIL
229 were modified by incorporating 1-vinylimidazole ligands featuring terminal double bonds that can be
230 polymerized while exploiting the amine function of the ligand to coordinate to the nickel metal ion.
231 A similar approach has been used successfully to produce UV curable SPME PIL coatings featuring
232 silver ion for the selective extraction of unsaturated compounds [28].

233 In the current study, the following three types of SPME sorbent coatings were prepared: (1)
234 polymerized neat $[\text{Ni}^{2+}(\text{VIM})_4][\text{NTf}_2^-]$ monomer (PIL 1), (2) $[\text{Ni}^{2+}(\text{VIM})_4][\text{NTf}_2^-]$ monomer with the
235 addition of 50 % w/w of $[(\text{VIM})_2\text{C}_{12}^{2+}][\text{NTf}_2^-]$ as crosslinker (PIL 2), and (3) $[\text{HVIM}^+][\text{NTf}_2^-]$
236 monomer and a crosslinker (PIL 3). The goal was to investigate the effect of added crosslinker (PIL 1
237 vs. PIL 2) and the presence of nickel cation (PIL 2 vs. PIL 3) on the extraction performance for a
238 variety of amines. The chemical structures and physical properties of the fiber coatings are shown in
239 Table 1.

240 As the analytes should be released from the fiber by thermal desorption, the thermal stability of
241 PIL sorbent coating is very important. The fibers were tested by exposure to the GC inlet. All PIL
242 fibers were stable up to 200 °C. In comparison, non-polymerized ILs with the same anion and
243 containing Ni^{2+} ion showed significantly lower decomposition temperatures of 164 and 178 °C,
244 respectively [22]. It can be concluded that the increased thermal resistance in the tested coatings
245 results from the formation of a stable polymer structure [35].

246 The visual appearance, thickness, and regularity of the developed nickel-based PIL sorbent
247 coatings were evaluated using scanning electron microscopy (SEM). Figure 2 shows the images of
248 fibers with and without added crosslinker.

249

250 **3.2. Optimization of the extraction procedure**

251 When optimizing extraction methods in SPME, the most important parameters are extraction and
252 desorption times, sampling and desorption temperatures, salt concentration, and sample agitation. In
253 the case of compounds that dissociate in aqueous solutions, sample solution pH should also be taken
254 into account.

255 Amines are weak bases and can undergo hydrolysis in aqueous solutions. To facilitate their
256 transfer to the headspace, they must remain undissociated. Thus, the pH of the aqueous samples must
257 be adjusted accordingly. The pKa values describing acidity of protonated amines are listed in Table
258 SM-1. Tripropylamine lies at the upper limit with a pKa equal to 10.58. According to the general rule
259 of equilibrium, it is widely accepted that keeping the pH of the solution two units above the pKa value
260 of analytes ensures its quantitative presence in the neutral form [36]. Therefore, the pH of the aqueous
261 solution was increased by the addition of a strong base (NaOH) to 13.

262 The values of some parameters mentioned above were assumed *a priori*. The thermal desorption
263 temperature of the analytes should permit their quickest possible transfer to the chromatographic
264 column. Typically, the limitation is the thermal stability of the sorbent material and analytes. Based
265 on the previously determined durability of the fibers (approximately 200 °C), it was assumed that
266 analytes could still be desorbed at a slightly lower temperature of 190 °C.

267 The optimal time for thermal desorption was determined using a pre-determined temperature of
268 the GC injection port. For optimization purposes, extraction of analytes using the tested fibers was
269 carried out from samples using a concentration two times higher than the planned working range (i.e.,
270 400 $\mu\text{g L}^{-1}$). The desorption studies were carried out using times ranging from 2 to 20 minutes. The
271 longest desorption time of 10 min was required for PIL 1 to avoid carry-over effects. To ensure
272 uniform conditions for all investigated fibers, the identical desorption time was applied in all further
273 experiments.

274 Stirring using a magnetic stir bar was utilized as the sample agitation method. It is well-known
275 that increasing agitation of the sample is often accompanied by an increase in the mass transfer caused
276 by convection [5]. In this study, the highest stirring speed was limited by the formation of droplets of
277 samples on the fiber surfaces caused by too vigorous agitation. Thus, an optimal stir rate of 800 rpm
278 was used for all experiments in the study.

279

280 **3.2.1. Influence of salt content**

281 Previous HS-SPME studies reported that the addition of salts can affect the extraction efficiency
282 due to the salting out effect [37]. The interaction of water with these additional ions may have a
283 significant impact on the extraction process as their solubility in water can be expected to increase or
284 decrease. Amines may be particularly susceptible to the salting out effect [5]. Since the change in
285 solubility of analytes in water is related to the sample-headspace equilibrium, the salting out effect
286 was investigated with fibers containing the PIL 1 and PIL 2 sorbent coatings. Aqueous samples that
287 did not contain NaCl yielded very low extraction efficiency and high experimental error (RSD >
288 15 %). Hence, NaCl concentrations of 5, 15, and 30 % (w/v) were evaluated at 40 °C with an
289 extraction time of 30 min. The obtained results are shown in Figure SM-6. The results indicate that
290 in the case of the tested amines, the addition of salt significantly reduced their solubility in water and
291 increased their extraction efficiency from the headspace. The most pronounced effect was observed
292 for pyridine using PIL 1 where the chromatographic peak area increased by 44-fold; in contrast, the
293 extraction efficiency for 2,6-DTBP using PIL 2 increased only by 2-fold. For the analyzed analytes,

294 the effect of NaCl addition was qualitatively and quantitatively similar for both PIL 1 and PIL 2.
295 Based on obtained results, solutions with a concentration of 30 % (w/v) were chosen for further
296 experiments.

297

298 **3.2.2. Influence of extraction temperature**

299 It is known that an increase in the extraction temperature often leads to an increase in the
300 diffusion coefficient, thereby increasing the rate of mass transfer to the headspace [5]. The effect of
301 extraction temperature on the extraction efficiency was investigated in the temperature range from 25
302 to 70 °C (in 15 °C increments) for 30 min using 30 % (w/v) NaCl in the aqueous sample solution.
303 The obtained extraction temperature profiles are shown in Figure SM-7 of SM. In the case of the HS
304 mode, an equilibrium is formed for the analyte between the aqueous solution, headspace, and sorbent
305 coating. Partitioning of the analytes between the solution and the fiber depends on the values of the
306 partition coefficients between the sample and the headspace as well as the headspace and fiber
307 coating. As can be observed, the extraction efficiency evolves with increasing temperature in four
308 ways: reaches a maximum (3-ethylpyridine, pyridine), decreases (triallylamine, 2,6-DTBP), increases
309 (tripropylamine), and remains constant (aniline). Increasing extraction temperature may also impede
310 analyte absorption on sorbents because of it being an exothermic process [38]. A decreasing trend in
311 extraction efficiency for volatile analytes (i.e., triallylamine, 2,6-DTBP, and pyridine) at higher
312 temperatures is likely due to their absorption on PIL sorbents being more hindered compared to the
313 case of less volatile analytes at the given conditions. The profiles obtained for both fibers (PIL 1 and
314 PIL 2) follow a similar trend, except for tripropylamine, where in the case of the crosslinked sorbent
315 coating the extraction efficiency increases significantly with temperature. A compromised
316 temperature condition of 45 °C was identified and chosen for all amines.

317

318 **3.2.3. Influence of extraction time**

319 The optimal extraction time was determined by analyzing the analyte extraction efficiency upon
320 exposing the fiber to the sample headspace at times varying from 10 to 70 minutes using an extraction

321 temperature of 45 °C and 30 % (w/v) NaCl in the aqueous sample solution. Figure SM-8 of SM shows
322 the effect of extraction time on the extraction efficiency of PIL 1 and PIL 2 sorbent coatings. It can
323 be observed that for different analytes, various trends were obtained. For aniline and 2,6-DTBP, the
324 extraction efficiency did not change significantly when extraction times longer than 10 min were
325 tested. Pyridine, tripropylamine, and 3-ethylpyridine were more efficiently extracted at longer
326 extraction times, while a drop in extraction efficiency occurred for triallylamine.

327 There is no single physico-chemical property that explains the differences in time profiles
328 obtained for different analytes as the most volatile analyte (pyridine) does not reach equilibrium in
329 the tested time range, while the least volatile 2,6-DTBP undergoes equilibration after 10 min. Also,
330 it could be expected that for compounds with higher values of the enrichment factor their transport
331 within the fiber coating will require an extended equilibration time. Meanwhile, triallylamine shows
332 even a slight decrease in extraction efficiency in PIL 2 with time, while the less efficiently extracted
333 tripropylamine is far from equilibrium. In determining the optimal extraction time, the compounds
334 that did not reach equilibrium within the studied time (tripropylamine, 3-ethylpyridine, and pyridine)
335 were taken into account. For those compounds, extending the extraction time from 50 to 70 minutes
336 increased the sum of chromatographic peaks areas by less than 20 %. Thus, in further studies, an
337 extraction time of 50 minutes was used for all fibers.

338

339 **3.3. Analytical performance of the developed headspace solid-phase microextraction method** 340 **and evaluation of extraction efficiency**

341 Partial validation of the HS-SPME method utilizing the PIL and commercial fibers involved
342 determination of coefficient of determination (R^2), limits of detection (LOD), limits of quantification
343 (LOQ), repeatability (relative standard deviation, RSD), and relative recovery (RR). The working
344 ranges for all amines and each of the investigated SPME fibers are presented in Table SM-2. A
345 working range from 5 to 200 $\mu\text{g L}^{-1}$ was used for the studied PIL and commercial fibers. For all fibers
346 within the working range, satisfactory linearity with the R^2 values above 0.990 was found (see Table
347 SM-2 of SM). Table SM-3 shows the sensitivities of the methods expressed by the calibration slope

348 for each fiber. In the case of most amines (with the exception of 2,6-DTBP), the nickel-based fibers
349 (PIL 1 and PIL 2) exhibited higher sensitivity than commercial fibers and the PIL 3 fiber.

350 The LODs were calculated on the basis of a signal-to-noise ratio of three, and the LOQs as ten
351 times the above-mentioned ratio. The LOD values of 2,6-DTBP for all fibers were significantly lower
352 compared to other amines with a maximum of $0.0037 \mu\text{g L}^{-1}$ for PIL 1 and a minimum of
353 $0.000077 \mu\text{g L}^{-1}$ for PIL 2. LODs of the other amines ranged from $0.05-1.56 \mu\text{g L}^{-1}$ for PIL 1, 0.02 to
354 $0.84 \mu\text{g L}^{-1}$ for PIL 2, $0.01-1.41 \mu\text{g L}^{-1}$ for PIL 3, $1.02-12.76 \mu\text{g L}^{-1}$ for PA, and $0.08-6.48 \mu\text{g L}^{-1}$ for
355 PDMS (Table 2). LODs of pyridine, triallylamine, tripropylamine, and aniline obtained with the PIL-
356 based SPME method were similar to or lower than the LOD values measured with other analytical
357 methods such as capillary electrophoresis, GC-MS, and dispersive liquid-liquid microextraction
358 coupled with GC-MS, which ranged from 0.07 to $42 \mu\text{g L}^{-1}$ [39-42]. The LOQ values for all fibers
359 are shown in Table SM-4 of SM.

360 The repeatability of the methods was calculated by performing triplicate extractions of aqueous
361 samples spiked with amines at a concentration $200 \mu\text{g L}^{-1}$, and are presented in Table 2. The RSD
362 values for PIL fibers did not exceed 15 % for all analytes and are comparable with those obtained
363 using commercial fibers. Relative recovery was calculated as the ratio of the concentrations of spiked
364 solutions to its value determined in the course of the analytical procedure. Calculated RR values are
365 summarized in Table SM-5 of SM. The RRs ranged from 84.5 to 116.3 % for all fibers, proving the
366 usefulness of the PIL fibers in analytical applications. The performance of each type of PIL fiber
367 began to decrease after ~ 70 extraction/desorption cycles. Therefore, 60 cycles was selected as the
368 optimal lifetime of the sorbent coatings.

369 In addition, a comparison was made between the extraction efficiency of the developed nickel-
370 based PIL fibers and selected commercial fibers (PA and $100 \mu\text{m}$ PDMS) using the enrichment factor
371 (EF) [43]. This parameter is a suitable tool for comparing the extraction ability by considering the
372 nature of the sorption coatings of fibers, regardless of its geometrical dimensions. The EF parameter
373 was calculated as the ratio of the analyte concentration in the fiber and the analyte concentration in
374 the aqueous sample. The obtained values of EFs are shown in Table SM-6 and represented in Figure 3

375 . An example chromatogram is shown in Figure SM-9 of SM. The EF values for both nickel-based
376 PIL fibers (PIL 1 and PIL 2) are higher than those obtained for the both commercial fibers (PA and
377 PDMS) and standard PIL fiber (PIL 3) in the case of all target analytes, with the exception of 2,6-
378 DTBP for the PIL 1 fiber. For most analytes, the EF values of PIL 2 were higher than PIL 1. This is
379 due to the increased surface area of the crosslinked PIL 2 resulting in enhanced analyte-sorbent
380 interactions [44, 45]. Therefore, the PIL 2 fiber was most suitable for the extraction of amines by HS-
381 SPME in this work. This sorbent coating may be a particularly attractive alternative to commercially-
382 available coatings for the determination of volatile amines.

383

384 **3.4. Analysis of real samples**

385 Lake and tap water were analyzed to evaluate the matrix effect of environmental samples on the
386 performance of the developed nickel-based PIL fibers and the HS-SPME-GC-MS method for the
387 determination of amines. The water samples were spiked with amines at a concentration of $200 \mu\text{g L}^{-1}$
388 and extracted under optimal conditions using the PIL 1 and PIL 2 fibers. The matrix effect was
389 evaluated in terms of relative recovery and repeatability (Table 3). The RRs of lake water ranged
390 from 84.8 to 112.4 % for PIL 1 and from 79.2 to 119.3 % for PIL 2. For spiked tap water samples,
391 the RRs varied between 90.9-120.0 % for PIL 1 and 83.0-122.7 % for PIL 2. The obtained RSD
392 values for both fibers and both types of water samples were acceptable and were less than 15 %.
393 Based on both parameters, no significant matrix effects were identified.

394

395 **4. CONCLUSIONS**

396 In this work, two nickel-based PIL sorbent coatings were successfully developed and applied in
397 HS-SPME coupled to GC-MS for the determination of volatile and semi-volatile amines, including
398 pyridine, triallylamine, tripropylamine, 3-ethylpyridine, aniline, and 2,6-DTBP, from water samples.
399 After optimizing the extraction parameters, the extraction efficiency of the developed fibers (PIL 1
400 and PIL 2) was evaluated and compared with commercial fibers using the EF normalization

401 parameter. The nature of the nickel-based sorbent coatings provided higher efficiencies than the
402 conventional PIL coating as well as commercial PA and PDMS coatings for all of the analytes studied.

403 Additionally, the results from this study show that the analytical performance of the nickel-based
404 PIL, PA, and PDMS (100 μm) fibers were comparable in terms of working range, coefficient of
405 determination, LOD, LOQ, reproducibility, and RR. Low LODs were achieved for developed fibers,
406 and ranged from 0.003717 to 1.56 mg L^{-1} and from 0.000077 to 0.84 $\mu\text{g L}^{-1}$ for PIL 1 and PIL 2,
407 respectively. Finally, the developed HS-SPME-GC-MS method was applied for the analysis of real
408 samples, including tap and lake water. The RRs of PIL 2 ranged from 83.0 to 122.7 % for tap water
409 and from 79.2 to 119.3 % for lake water.

410

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416

417 **CONFLICT OF INTEREST**

418 The authors have declared no conflict of interest.

419

420 **REFERENCES**

421 [1] Kataoka H., Derivatization reactions for the determination of amines by gas chromatography and
422 their applications in environmental analysis. *J. Chromatogr. A* 1996, **733**, 19–34.

423 [2] Zhu Y., Wang M. H., Du H. Y., Wang F., Mou S. F., Haddad P. R., Organic analysis by ion
424 chromatography: 1. Determination of aromatic amines and aromatic diisocyanates by cation-
425 exchange chromatography with amperometric detection. *J. Chromatogr. A* 2002, **956**, 215–220.

426 [3] Chung K. T., Mutagenicity and carcinogenicity of aromatic amines metabolically produced from
427 azo dyes. *Environ. Carcino. & Ecotox. Revs.* 2000, *C18*^H, 51–74.

428 [4] Arthur C. L., Pawliszyn J., Solid phase microextraction with thermal desorption using fused silica
429 optical fibers. *Anal. Chem.* 1990, **62**, 2145–2148.

430 [5] Pawliszyn J., *Handbook of Solid Phase Microextraction*. Elsevier, Waltham, MA, USA 2012.

431 [6] Kataoka H., Lord H. L., Pawliszyn J., Applications of solid-phase microextraction in food
432 analysis. *J. Chromatogr. A* 2000, **880**, 35–62.

433 [7] Chary N. S., Fernandez-Alba A. R., Determination of volatile organic compounds in drinking and
434 environmental waters. *Trends Anal. Chem.* 2012, **32**, 60–75.

435 [8] Snow N. H., Solid-phase micro-extraction of drugs from biological matrices. *J. Chromatogr. A*
436 2000, **885**, 445–455.

437 [9] Hashemi B., Zohrabi P., Shamsipur M., Recent developments and applications of different
438 sorbents for SPE and SPME from biological samples. *Talanta* 2018, **187**, 337–347.

439 [10] Yu H., Ho T. D., Anderson J. L., Ionic liquid and polymeric ionic liquid coatings in solid-phase
440 microextraction. *Trends Anal. Chem.* 2013, **45**, 219–232.

441 [11] Patinha D. J., Silvestre A. J., Marrucho I. M., Poly (ionic liquids) in solid phase microextraction:
442 Recent advances and perspectives. *Prog. Polym. Sci.* 2019, **98**, 101148.

443 [12] Yavir K., Marcinkowski Ł., Marcinkowska R., Namieśnik J., Kłoskowski A., Analytical
444 applications and physicochemical properties of ionic liquid-based hybrid materials: A review. *Anal.*
445 *Chim. Acta* 2019, **1054**, 1–16.

446 [13] Gutiérrez-Serpa, A., Rocío-Bautista P., Pino V., Jiménez-Moreno F., Jiménez-Abizanda, A. I.,
447 Gold nanoparticles based solid-phase microextraction coatings for determining organochlorine
448 pesticides in aqueous environmental samples. *J. Sep. Sci.* 2017, **40**, 2009–2021.

449 [14] Luo Z., Chen G., Li X., Wang L., Shu H., Cui X., Chang C., Zeng A., Fu Q., Molecularly
450 imprinted polymer solid-phase microextraction coupled with ultra high performance liquid
451 chromatography and tandem mass spectrometry for rapid analysis of pyrrolizidine alkaloids in herbal
452 medicine. *J. Sep. Sci.* 2019, **42**, 3352–3362.

453 [15] Li G., Row K., Ternary deep eutectic solvent magnetic molecularly imprinted polymers for the
454 dispersive magnetic solid-phase microextraction of green tea. *J. Sep. Sci.* 2018, **41**, 3424–3431.

455 [16] Wan Ibrahim W. N., Sanagi M. M., Mohamad Hanapi N. S., Kamaruzaman S., Yahaya N., Wan
456 Ibrahim W. A., Solid-phase microextraction based on an agarose-chitosan-multiwalled carbon
457 nanotube composite film combined with HPLC-UV for the determination of nonsteroidal anti-
458 inflammatory drugs in aqueous samples. *J. Sep. Sci.* 2018, *41*, 2942–2951.

459 [17] Abolghasemi M. M., Yousefi V., Piryaei M., Synthesis of a metal-organic framework confined
460 in periodic mesoporous silica with enhanced hydrostability as a novel fiber coating for solid-phase
461 microextraction. *J. Sep. Sci.* 2015, *38*, 1187–1193.

462 [18] Zeeuw J., Vonk N., Buyten J., Heijnsdijk P., Clarisse R., The Analysis of Volatile Amines by
463 Capillary Gas Chromatography. Varian, Middelburg, Netherlands 2000.

464 [19] Qian W., Texter J., Yan F., Frontiers in poly(ionic liquid)s: syntheses and applications. *Chem.*
465 *Soc. Rev.* 2017, *46*, 1124–1159.

466 [20] Yuan J., Mecerreyes D., Antonietti M., Poly(ionic liquid)s: an update. *Prog. Polym. Sci.* 2013,
467 *38*, 1009-1036.

468 [21] Mei M., Huang X., Chen L., Recent development and applications of poly (ionic liquid)s in
469 microextraction techniques. *Trends Anal. Chem.* 2019, *112*, 123–134.

470 [22] Chand D., Farooq M. Q., Pathak A. K., Li J., Smith E. A., Anderson J. L., Magnetic ionic liquids
471 based on transition metal complexes with N-alkylimidazole ligands. *New J. Chem.* 2019, *43(1)*, 20–
472 23.

473 [23] Santos E., Albo J., Irabien A., Magnetic ionic liquids: synthesis, properties and applications.
474 *RSC Adv.* 2014, *4*, 40008–40018.

475 [24] Wang H., Yan R., Li Z., Zhang X., Zhang S., Fe-containing magnetic ionic liquid as an effective
476 catalyst for the glycolysis of poly (ethylene terephthalate). *Catal. Commun.* 2010, *11*, 763–767.

477 [25] Sajid M., Magnetic ionic liquids in analytical sample preparation: a literature review. *Trends*
478 *Anal. Chem.* 2019, *113*, 210–223.

479 [26] Clark K. D., Nacham O., Purslow J. A., Pierson S. A., Anderson J. L., Magnetic ionic liquids in
480 analytical chemistry: a review. *Anal. Chim. Acta.* 2016, *934*, 9–21.

481 [27] Nan H., Peterson L., Anderson J. L., Evaluating the solvation properties of metal-containing
482 ionic liquids using the solvation parameter model. *Anal. Bioanal. Chem.* 2018, *410*(19), 4597–4606.

483 [28] Trujillo-Rodríguez M. J., Anderson J. L., Silver-based polymeric ionic liquid sorbent coatings
484 for solid-phase microextraction: Materials for the selective extraction of unsaturated compounds.
485 *Anal. Chim. Acta* 2019, *1047*, 52–61.

486 [29] Ho T. D., Yu H., Cole W. T., Anderson J. L., Ultraviolet photoinitiated on-fiber
487 copolymerization of ionic liquid sorbent coatings for headspace and direct immersion solid-phase
488 microextraction. *Anal. Chem.* 2012, *84*, 9520–9528.

489 [30] Anderson J. L., Armstrong D. W., Immobilized ionic liquids as high-selectivity/high-
490 temperature/high-stability gas chromatography stationary phases. *Anal. Chem.* 2005, *77*, 6453–6462.

491 [31] Anderson J. L., Ding R., Ellern A., Armstrong D. W., Structure and properties of high stability
492 geminal dicationic ionic liquids. *J. Am. Chem. Soc.* 2005, *127*, 593–604.

493 [32] Ho T. D., Toledo B. R., Hantao L. W., Anderson J. L., Chemical immobilization of crosslinked
494 polymeric ionic liquids on nitinol wires produces highly robust sorbent coatings for solid-phase
495 microextraction. *Anal. Chim. Acta* 2014, *843*, 18–26.

496 [33] Yu H., Merib J., Anderson J. L., Faster dispersive liquid–liquid microextraction methods using
497 magnetic ionic liquids as solvents. *J. Chromatogr. A* 2016, *1463*, 11–19.

498 [34] Chisvert A., Benedé J. L., Anderson J. L., Pierson S. A., Salvador A., Introducing a new and
499 rapid microextraction approach based on magnetic ionic liquids: Stir bar dispersive liquid
500 microextraction. *Anal. Chim. Acta* 2017, *983*, 130–140.

501 [35] Pierson S. A., Nacham O., Clark K. D., Nan H., Mudryk Y., Anderson J. L., Synthesis and
502 characterization of low viscosity hexafluoroacetylacetone-based hydrophobic magnetic ionic
503 liquids. *New J. Chem.* 2017, *41*, 5498–5505.

504 [36] Sarafraz-Yazdi A., Ardaki M. S., Amiri A., Determination of monocyclic aromatic amines using
505 headspace solid-phase microextraction based on sol–gel technique prior to GC. *J. Sep. Sci.* 2013, *36*,
506 1629–1635.

507 [37] Vila M., Celeiro M., Lamas J. P., Dagnac T., Llompart M., Garcia-Jares C., Determination of
508 fourteen UV filters in bathing water by headspace solid-phase microextraction and gas
509 chromatography-tandem mass spectrometry. *Anal. Methods* 2016, *8*, 7069–7079.

510 [38] Sarafraz-Yazdi A., Vatani H., A solid phase microextraction coating based on ionic liquid sol–
511 gel technique for determination of benzene, toluene, ethylbenzene and o-xylene in water samples
512 using gas chromatography flame ionization detector. *J. Chromatogr. A* 2013, *1300*, 104–111.

513 [39] Hattori T., Okamura H., Asaoka S., Fukushi K., Capillary zone electrophoresis determination of
514 aniline and pyridine in sewage samples using transient isotachophoresis with a system-induced
515 terminator. *J. Chromatogr. A* 2017, *1511*, 132–137.

516 [40] Liu, S., Wang W., Chen J., Sun J., Determination of aniline and its derivatives in environmental
517 water by capillary electrophoresis with on-Line concentration. *Int. J. Mol. Sci.* 2012, *13*, 6863–6872.

518 [41] Tsukioka T., Ozawa H., Murakami T., Gas chromatographic-mass spectrometric determination
519 of lower aliphatic tertiary amines in environmental samples. *J. Chromatogr. A* 1993, *642*, 395–400.

520 [42] Diao C. P., Wei C. H., Rapid determination of anilines in water samples by dispersive liquid–
521 liquid microextraction based on solidification of floating organic drop prior to gas chromatography–
522 mass spectrometry. *Anal. Bioanal. Chem.* 2012, *403*, 877-884.

523 [43] Pena-Pereira F., Marcinkowski Ł., Kłoskowski A., Namieśnik J., Silica-based ionogels:
524 nanoconfined ionic liquid-rich fibers for headspace solid-phase microextraction coupled with gas
525 chromatography–barrier discharge ionization detection. *Anal. Chem.* 2014, *86*, 11640–11648.

526 [44] Trujillo-Rodríguez M. J., Nan H., Anderson J. L., Expanding the use of polymeric ionic liquids
527 in headspace solid-phase microextraction: Determination of ultraviolet filters in water samples. *J.*
528 *Chromatogr. A* 2018, *1540*, 11–20.

529 [45] Ho T. D., Yu H., Cole W. T. S., Anderson J. L., Ultraviolet photoinitiated on-fiber
530 copolymerization of ionic liquid sorbent coatings for headspace and direct immersion solid-phase
531 microextraction. *Anal. Chem.* 2012, *84*, 9520–9528.

532

533 **SUPPORTING INFORMATION**

534 Additional supporting information may be found online in the Supporting Information section at the
535 end of the article.

536 **FIGURE LEGENDS**

537 **Figure 1.** Chemical structures of the cations, anion, and UV initiator (DAROCUR 1173) used for the
538 preparation of sorbent coatings investigated in this study.

539 **Figure 2.** Scanning electron microscopy (SEM) images of the nickel-based PIL fibers examined in
540 this study: PIL 1 ($500\times$) $\approx 8\pm1.3$ μm (A) and PIL 2 ($500\times$) $\approx 11\pm1.9$ μm (B).

541 **Figure 3.** Enrichment factors calculated for the studied amines using five different SPME fibers
542 featuring highly varied sorbent coating chemistries.

543

544 **TABLE LEGENDS**

545 **Table 1.** Composition of sorbent coaings and dimensions of fibers examined in this study.

546 **Table 2.** Limits of detection (LOD) and relative standard deviation (RSD) obtained for amines when
547 performing HS-SPME-GC-MS using different SPME fibers.

548 **Table 3.** Analysis of lake and tap water using the HS-SPME-GC-MS method with nickel-based PIL
549 fibers.