Selective isolation of pesticides and cannabinoids using polymeric ionic liquid-based sorbent coatings in solid-phase microextraction coupled to high-performance liquid chromatography

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Abstract

The high abundance of cannabinoids within cannabis samples presents an issue for pesticide testing as cannabinoids are often co-extracted with pesticides using various sample preparation techniques. Cannabinoids may also chromatographically co-elute with moderate polarity pesticides and inhibit the ionization of pesticides when using mass spectrometry. To circumvent these issues, we have developed a new approach to isolate commonly regulated pesticides and cannabinoids from aqueous samples using tunable, crosslinked imidazolium polymeric ionic liquid (PIL)-based sorbent coatings for direct immersion solid-phase microextraction (DI-SPME). The selectivity of four PIL sorbent coatings towards 20 pesticides and six cannabinoids, including cannabidiol and Δ^9-THC, was investigated and compared against a commercial PDMS/DVB fiber. Extraction and desorption conditions, including salt content, extraction temperature, pH, extraction time, desorption solvent, and desorption time, were optimized using high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection. Under optimized conditions, the PIL fiber consisting of 1-vinylbenzyl-3-octylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($[VBIMC_8^+][NTf_2^-]$) and 1,12-di(3-vinylbenzylimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide ($[(VBIM)_2C_{12}^{2+}]2[NTf_2^-]$) sorbent coating provided the best selectivity towards pesticides compared to other PILs and the PDMS/DVB fibers and was able to reach limits of detection (LODs) as low as 1 μg/L. When compared to a previously reported PIL-based SPME HPLC-UV method for pesticide analysis, the amount of cannabinoids extracted from the sample was decreased 9-fold while a 4-fold enhancement in the extraction of pesticides was achieved. Additionally, the PIL-based SPME method was applied to samples containing environmentally-relevant concentrations of pesticides and cannabinoids to assess its feasibility for cannabis quality control testing. Relative recoveries between 95% to 141% were obtained using the PIL sorbent coating while recoveries ranging from 50% to 114% were obtained using the PDMS/DVB fiber.

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1. Introduction

The genus Cannabis currently includes one species, *Cannabis sativa* L. with three varieties, *C. sativa* var. *indica*, *C. sativa* var. *afghanica*, and *C. sativa* var. *sativa*, based on the most recent investigation into the taxonomy of Cannabis by McPartland [1]. The variation *C. sativa* var. *sativa* has been used to produce industrial hemp due to its low Δ^9-tetrahydrocannabinol (Δ^9-THC) content, while *C. sativa* var. *indica* has been cultivated for medical marijuana use [2]. However, crossbreeding of these variations has produced hybrid plants that challenge this understanding [3]. Regardless, the Δ^9-THC content must fall below 0.3% by dry weight to be classified as hemp, otherwise, the plant is considered marijuana [4]. These guidelines are driven by the psychoactive nature of Δ^9-THC, which interacts with the cannabinoid receptors in the brain and results in an altered mindset [5]. For this reason, the use of cannabis has been criminalized in many countries until only recently [6-8]. Over the past two decades, a surge of countries have begun to legalize cannabis for medical and/or recreational use [9], leading to the establishment of cannabis farms [10] and the need for accurate quality control methodologies [11].

Within the United States (U.S.), many state regulations require monitoring of cannabinoid potency, pesticide residues, terpene profiles, and the presence of mycotoxins and heavy metals [12-16]. Cannabis poses a complex matrix for pesticide analysis due to the presence of various biomolecules (i.e., proteins, nucleic acids, lipids, fatty acids), flavonoids, terpenes, and cannabinoids [17-18]. Many studies have been conducted to overcome biological matrix effects, including headspace analysis [19] and solid-phase extraction (SPE) cleanup steps [20]. However, in most sample preparation techniques, cannabinoids and terpenes are extracted with pesticide residues due to the similar hydrophobicity of these matrix components [21]. Even more pressing, the greater abundance of cannabinoids often results in their co-elution with multiple pesticide

residues during chromatographic analysis, making quantification challenging without highly sensitive and selective detectors [22].

QuEChERS - quick, easy, cheap, effective, rugged, and safe - has been used as an exhaustive sample preparation technique to capture pesticide residues [23]. This technique involves a liquid-liquid extraction (LLE) step followed by a dispersive solid-phase extraction clean-up step. Though QuEChERS is widely used in cannabis testing, hydrophobic matrix components, such as cannabinoids and terpenes, are often extracted into the organic layer [24-25]. In addition, the incomplete recovery of some pesticides has been reported [24, 26]. Pérez-Parada *et al*. explored three modified QuEChERS methods for the recovery of 61 pesticide residues spiked onto dried marijuana samples [24]. Relative recoveries ranging between 70-120% with relative standard deviations (RSDs) less than 20% were reported for 46 compounds using their most successful method. However, clean-up methods employing both primary-secondary amine (PSA) and graphitized carbon black (GCB) solid phases resulted in signal suppression, which was speculated to be due to the presence of co-eluting matrix components [24]. Another method similar to QuEChERS, known as quick, easy, cheap, effective, rugged, safe, efficient and robust (QuEChERSER), has been used to capture pesticides from various hemp matrices including powder, oils, pellets, and plant material for a high throughput approach [25]. Compared to QuEChERS, this technique involves a similar LLE step using a larger amount of solvent per sample followed by more specified sample clean-up steps that can better differentiate analytes amenable to gas chromatographic (GC) and liquid chromatographic (LC) separations. It was found that more polar analytes that could not be extracted with QuEChERS were extracted with this approach, but was limited by the capture of more matrix components.

Microextraction techniques have become popular sample preparation techniques due to their high enrichment factors, low cost, and simple execution [27]. Compared to the previously described methods, they require less reagents and fewer steps and are based predominately on the partitioning of analytes to the extraction phase. Solid-phase microextraction (SPME) has been used to preconcentrate analytes at low concentrations levels, allowing for analytes to be detected using chromatographic methods with various detectors [27]. The compatibility of SPME with chromatographic separations provides a convenient means for performing quantitative analysis [28-29]. For this reason, SPME has found applications in multiple residue monitoring (MRM) [30], air quality analysis [31-32], biological assays [33], and has recently been applied in the capture of different components found in cannabis [21,34-35]. Most often, headspace (HS)-SPME has been employed to isolate compounds of interest from interfering matrix components [36]. However, cannabis plant materials contain numerous matrix compounds such as terpenes, flavonoids, and cannabinoids that can also partition into the headspace. In this case, the development of a SPME method that exploits the selectivity of the sorbent coating is critical to ensure quantitation at low concentration levels. Many studies have demonstrated that the PDMS sorbent coating is better suited to extract cannabinoids compared to other commercially available sorbent coatings due to its affinity for non-polar analytes [37-39], whereas polyacrylate (PA) is more selective for pesticides and other polar molecules [40]. However, to our knowledge, no such study has explored the selectivity of these sorbents towards pesticides while concurrently monitoring their selectivity for cannabinoids.

Sorbent coatings comprised of ionic liquids (ILs) can be designed to exhibit unique and tailored selectivity towards analytes of interest. Their tunable nature allows for specific interactions to dominate the extraction mechanism by incorporating certain functional groups

within the IL chemical structure. In previous studies, ILs have been shown to undergo electrostatic [41], hydrophobic [42], π-π stacking [43], and/or hydrogen bonding interactions [44] with analytes. By incorporating vinyl groups into the IL chemical structure, they can be transformed into polymeric ionic liquids (PILs) and be chemically bound to a functionalized support using free radical polymerization [42,45]. Highly robust crosslinked sorbent coatings featuring good thermal and chemical stability have been developed by incorporating dicationic IL crosslinkers into the polymer network [46]. The sorbent coatings have been shown to withstand over 150 extraction and desorption steps as well as reach low limits of quantification (1-5 μg/L), which are generally well below the action level of pesticides monitored for cannabis testing [13, 47]. Additionally, the selectivity of PILs can be tuned by modifying the functional group substituents of the IL monomers and dicationic IL crosslinkers, making them viable candidates to isolate analytes of interest for cannabis testing [48].

Herein, we demonstrate the use of chemically tunable PIL-based sorbent coatings for the selective extraction of pesticides from cannabinoids coupled to high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection. Four imidazolium-based PIL sorbent coatings containing various substituent groups, including alkyl chains of varying lengths and/or benzyl moieties, are compared under optimized extraction conditions to identify structural features that play a significant role in controlling PIL selectivity. Under optimal conditions, the PIL sorbent coatings were able to decrease by up to 9-fold the amount of cannabinoids extracted and enhance the amount of pesticides extracted by 4-fold compared to unoptimized conditions. This method was applied to samples containing both cannabinoids and pesticides at environmentally-relevant concentrations to assess any matrix effects that cannabinoids impart on the extraction of pesticides. The relative recoveries for the pesticides using the PIL sorbent coating were compared with those

obtained using the commercial polydimethylsiloxane/divinylbenzene (PDMS/DVB) sorbent coating.

2. Experimental Section

2.1 Working Solutions of Pesticides and Cannabinoids

Type I water from a Milli-DI system was used to obtain 18.2 MΩ·cm Type II water from a MilliQ system, both of which were acquired from MilliporeSigma. Type II water was used for all extraction experiments and HPLC-UV separations. Extractions were carried out in 10 mL screw cap vials (22.5 x 46 mm) with PTFE/Butyl septa caps (18 mm) purchased from MilliporeSigma. Neodymium magnets (3/16" x 3/8", DIA) from K&J Magnetics (Pipersville, PA, USA) functioned as stir bars for all extractions. A set of Oregon pesticide standards as well as cannabinoid standards were provided as gifts by Restek Corporation (Bellefonte, PA, USA). The set of pesticide standards contained six ampules with analytes at a concentration of 600 μg/mL in acetonitrile. A working solution was prepared by combining all six ampules to produce a mixture of 59 pesticides at a concentration of 100 μg/mL. Cannabinoid standards containing 1000 μg/mL of cannabidiol, cannabinol, and Δ^9-THC and individual standards of Δ^8-THC, cannabigerol, and cannabichromene were used to prepare a working solution containing a concentration of 100 μg/mL for each analyte. Table 1 shows a list of pesticides and cannabinoids that were monitored in this work and conditions used in their detection. For select experiments, a 100 μg/mL cannabinoid mixture containing dipentyl phthalate as an internal standard was prepared with methanol.

2.2 Instrumentation

A Varian MR-400 MHz nuclear magnetic resonance (NMR) spectrometer (Palo Alto, CA, USA) was used to obtain ^{1}H NMR spectra to characterize the final purified IL products. All spectra were collected in deuterated dimethyl sulfoxide. A Rayonet photochemical reactor (RPR-100)

158 from Southern New England Ultraviolet Company (Brandford, CT, USA) containing 16 lamps
159 aligned within the perimeter of the reactor was used for IL monomer polymerization at 350 nm.
160 Sorbent coating film thicknesses and volume were determined from scanning electron micrographs
161 obtained by a JEOL JSM-IT200 microscope (Peabody, MA, USA).

162 Two Agilent Technologies 1260 Infinity HPLC systems (Santa Clara, CA, USA) equipped
163 with a quaternary pump and a thermostatted column compartment were used in conjunction with
164 a 20 μL Rheodyne manual injector for the separation of cannabinoids and pesticides. A variable
165 wavelength detector was used for the quantification of cannabinoids and a diode-array detector
166 was used for the quantification of pesticides. The cannabinoids were analyzed on a Restek Raptor
167 ARC-18 column (150 x 4.6 mm I.D.) with a 5 μm particle size and a Raptor ARC-18 guard
168 cartridge (5 x 4.6 mm I.D.) in an EXP Direct Connect Holder. Separations were carried out in
169 reverse phase mode using water and acetonitrile at 1.0 mL/min. The separation began with an
170 isocratic hold at 65% acetonitrile for 0.75 min followed by a gradient increase to 75% acetonitrile
171 in 1 min that was held until 10 min. Pesticides were analyzed on a Restek Raptor biphenyl column
172 (150 x 4.6 mm I.D.) with a 5 μm particle size and a Raptor biphenyl guard cartridge (5 x 4.6 mm
173 I.D.) in an EXP Direct Connect Holder. Separation conditions for the pesticides are summarized
174 in Table S1. Table 1 lists the detection wavelengths used to monitor the pesticides and
175 cannabinoids. Representative chromatograms of the two separations are shown in Figure S1 and
176 Figure 1. Figure S2 provides the chromatograms demonstrating the separation of pesticides at the
177 four different wavelengths.

178 An Agilent 1260 Infinity binary pump with a HiP autosampler and a 6230 time-of-flight
179 mass spectrometer with a dual electrospray ionization (ESI) source functioned to identify the
180 elution order of the pesticides using the Raptor biphenyl column and guard column. The same

separation method described in Table S1 for the pesticides was used with 0.1% formic acid added to the mobile phases with a decreased flow rate of 0.6 mL/min. Conditions for electrospray ionization are described in Table S2. Elution order was confirmed by retention times from the separation of the 6 individual pesticide mixtures used to make the working solution.

2.3 Ionic Liquid Synthesis and Characterization

Chemical structures of the 1-vinyl-3-octylimidazolium dibis[(trifluoromethyl)sulfonyl]imide ([$OVIM^+$][NTf_2^-]), 1-vinyl-4-dodecylimidazolium ([$VIMC_{12}^+$]) [NTf_2^-], 1,12-di(3-vinylimidazolium)dodecane ([$(VIM)_2C_{12}^{+2}$]) 2[NTf_2^-], and 1-vinylbenzyl-3-octylimidazolium ([$VBIMC_8^+$]) [NTf_2^-] ILs are shown in Table 2. All IL reactions were carried out under similar conditions according to previously reported procedures [42,49], except for 1,12-di(3-vinylbenzylimidazolium)dodecane ([$(VBIM)_2C_{12}^{+2}$]) 2[NTf_2^-], which employed a different reaction scheme [50]. Synthetic details, NMR spectra of the ILs, procedure for constructing PIL SPME fibers, and SEM micrographs of Fiber **2**, representing data obtained for all PIL fibers, are provided in the Supporting Information (SI).

2.4 Optimization of SPME Extraction Parameters

Using PIL Fiber **3** (Table 3) and a PDMS/DVB fiber, the following SPME parameters were optimized using a one-variable-at-a-time approach: sample pH, salt and temperature, extraction time, desorption time, and desorption solvent. Fiber **3** demonstrated higher extraction efficiency for both cannabinoids and pesticides, and for this reason, was chosen as the representative fiber for optimization. PDMS/DVB was chosen as the commercial sorbent since it can extract a wide range of polarities [51]. The fibers were evaluated based on their performance under initial and optimal conditions. The initial conditions, which were used to begin optimization, were reported for imidazolium-based PIL sorbents when used in DI-SPME for the extraction of pesticides and

non-steroidal anti-inflammatory drugs (NSAIDs) [47]. These conditions consisted of a 30 min conditioning step in methanol to ensure no carryover was present between experiments, followed by a second conditioning step in water for 10 min to remove solvent from the sorbent coating. These same conditioning steps were applied to all fibers used in this current study prior to all extractions. For extraction, 10 mL of DI water (pH adjusted) was spiked with 20 µL of the working solution, which was homogenized with 2 min of stirring. The fiber was exposed to the sample for 60 min at a stirring rate of 600 rpm. The analytes were desorbed from the fiber in 30 µL of methanol over a 15 min period. For this study, the same sample concentration of 200 µg/L was used for all experiments. The desorption volume was maintained at 30 µL to obtain the best peak response. For the PDMS/DVB fiber, acetonitrile was determined to be the better desorption solvent for pesticides studied previously [47]; therefore, conditioning was performed using acetonitrile until a desorption solvent was selected.

To determine optimal conditions, HPLC compatible organic solvents, including methanol, acetonitrile, and acetone, were examined as desorption solvents. Extraction times were varied between 5 min to 80 min and the desorption time was studied using a time-course ranging between 1 and 15 min. Temperatures ranging from 20°C (room temperature, RT) to 80°C and salt content from 0% to 30% (w/v) NaCl were optimized to improve the extraction of most pesticides. Additionally, pH conditions of 2, 5, and 8 were chosen to study electrostatic interactions between the PIL fiber and charged analytes. To develop a universal method for an entire class of analytes (i.e., pesticides), the optimal parameters need to be representative of most analytes. The sum of the individual peak areas for each class of analytes, denoted as the total peak area, was used to assess the trends for the pesticides and cannabinoids. For most extraction conditions, all analytes responded similarly.

227 The optimal PIL-based SPME method consisted of exposing the fibers to a 10 mL aqueous
228 sample adjusted to pH 2 and containing 30% (w/v) NaCl for 5 min at 40°C and 600 rpm. The
229 spiked sample was allowed to equilibrate for 10 min to reach the 40°C extraction temperature prior
230 to exposing the fiber. The desorption step involved a 1 min wash step with water to remove salt
231 from the fiber followed by a 30 s desorption in 30 μL methanol. For the PDMS/DVB fiber, the
232 fiber was exposed to a 10 mL sample at pH 8 containing 10% (w/v) NaCl for 30 min at 40°C.
233 Afterward, the fiber was placed in water for 1 min and subsequently placed in 30 μL of methanol
234 for 5 min.

235 **2.5 Extraction from Complex Samples**

236 The working range and limits of detection (LOD) for the SPME-LC-UV method were
237 determined for all monitored pesticides and cannabinoids at optimal conditions using Fiber **4**
238 (Table 4). The sorbent coating of Fiber **4** demonstrated a greater affinity towards the pesticides
239 than the other PIL sorbent coatings, which was not discovered until after optimization. Samples
240 spiked with an analyte concentration of 30 μg/L were extracted at optimal conditions and the
241 resulting data were used to calculate percent recoveries. Studies comparing the effectiveness of
242 this method in isolating pesticides from cannabinoids were conducted using samples containing
243 both pesticides at 30 μg/L and cannabinoids at 10 mg/L concentrations. These concentrations were
244 chosen to represent cases where neutral cannabinoids are present in high abundance compared to
245 pesticides, in which case the cannabinoid concentration can be up to 10,000-fold higher than the
246 action level of most pesticides (0.1 μg/g) according to the literature [13, 52]. To prepare these
247 samples, 1 mL of the cannabinoid working solution was added to a sample vial and the organic
248 solvent was evaporated off under a gentle stream of air to reduce the amount of organic solvent

249 present in the extraction. The resulting concentrate was redissolved in 100 µL of methanol
250 followed by the addition of the aqueous matrix and 3 µL of the pesticide working solution.
251
252 **3. Results and Discussion**
253 **3.1 Choice of Analytes**
254 The cannabinoids chosen for this study are based on their prevalence in cannabis and
255 represent commonly co-extracted matrix components when testing for pesticide residues on
256 cannabis plant material [53]. The Oregon pesticide standards were selected as these analytes are
257 commonly monitored within the U.S. and Canada during cannabis testing [12-13, 54]. Therefore,
258 these 59 analytes are representative of all regulated pesticides. Peak purity analysis was carried
259 out by comparing the UV spectra across multiple wavelengths for each detected peak. Peaks that
260 passed peak purity analysis and that were not expected to co-elute with the cannabinoids were
261 considered for monitoring throughout this study to allow for accurate quantification when
262 extracted from complex samples. The resulting list of 20 monitored pesticides, shown in Table 1,
263 was chosen to represent different classes of pesticides based on their elution order in the separation
264 and possess various structural features including aromatic and electronegative atoms that result in
265 assorted retention times, as labeled in Figure S2.
266 **3.2 Choice of Chemically-Tunable PIL-based Sorbents**
267 Imidazolium-based IL monomers were chosen due to their ease of structural tunability.
268 Once polymerized and crosslinked, PIL sorbent coatings often exhibit minimal swelling in water
269 and increased stability in organic solvents [46], making them ideal for applications in DI-SPME.
270 The chemical structures of IL monomers used to create the sorbents are shown in Table 2 and the
271 composition of the PIL sorbents, and the respective fibers tested in this study, are provided in

Table 3. The length of the alkyl substituent (i.e., octyl and dodecyl) was varied to examine the effects of hydrophobic interactions on extraction selectivity. PILs featuring aromatic moieties (Fiber **3** and Fiber **4**) and lacking aromatic groups (Fiber **1** and Fiber **2**) were designed to explore the effect of π-π stacking interactions on extraction selectivity.

To determine the sorbent exhibiting highest selectivity towards pesticides, triplicate extractions were carried out using previously reported conditions, which were optimal for extracting pesticides using similar PIL sorbents [47]. The peak areas of the analytes were used to evaluate the extraction efficiencies, or the mass of analyte extracted relative to the mass in the sample. Since the analyte concentration within the sample was kept constant throughout the study, a comparison between sorbent coatings can be made using peak areas, which represent the mass of analyte extracted. This method was also used to determine the performance of the sorbent in extracting cannabinoids. As shown in Figure S10, all sorbents were able to extract the cannabinoids; however, sorbents containing aromatic moieties exhibited higher extraction efficiencies for all cannabinoids, likely due to the π-π interactions between the sorbent and cannabinoids. Overall, for the pesticides, Fiber **3** provided the highest average total peak area, and for this reason, was chosen as the model fiber to optimize the extraction method. The reproducibility of Fiber **3** was evaluated by using the initial extraction conditions for the cannabinoids. RSDs for the cannabinoids ranged from 6-17%.

Additionally, interesting trends were observed between the sorbent coatings. Firstly, pesticides 2, 4, 7, 8, and 13 from Table 1 had lower peak areas compared to the other monitored pesticides under these conditions for all fibers. For pesticides 1-16 that were able to be detected, higher extraction efficiencies were observed with Fiber **2** compared to Fiber **1**; however, for pesticides 17-20, extraction efficiencies comparable to Fiber **4** were observed for Fiber **1**,

295 suggesting that the alkyl chain length might play an important a role in extracting these analytes.
296 Additionally, for pesticides 1, 3, 5, 6, and 10, comparable extraction efficiencies were observed
297 for Fibers **3** and **4**, but for analytes 11-20, higher extraction efficiencies were observed for Fiber
298 **3**. All but one monitored analytes contained aromatic groups; therefore, differences in their
299 extraction are expected to be facilitated by other types of interactions. It has been previously
300 observed by Ho *et al.* that sorbents containing aromatic groups in both the monomer and
301 crosslinker exhibited a higher affinity for more polar analytes [46]. For this reason, nonpolar
302 analytes were not extracted as well as with Fiber **4** compared to Fiber **3** and showed to have a
303 higher affinity for the pesticides compared to the other sorbent coatings investigated in this study
304 (discussed further in section 3.4).
305
306 **3.3 Optimization of PIL Fiber for Cannabinoids and Pesticides**
307 **3.3.1 Desorption Solvent**
308 Methanol, acetonitrile, and acetone were tested as desorption solvents; however, acetone
309 adversely affected the resolution of the cannabinoids in the separation due to its higher solvent
310 strength and was not further tested. Based on the average total peak areas presented in Figure S11,
311 methanol was observed as the optimal solvent for desorbing both cannabinoids and pesticides from
312 Fiber **3** as well as for the commercial PDMS/DVB fiber (Figure S12). Acetonitrile (being slightly
313 less polar than methanol) was expected to solubilize cannabinoids better than methanol [66];
314 however, methanol can hydrogen bond with the phenolic cannabinoids, resulting in better
315 solubilization of cannabinoids.
316 **3.3.2 Temperature and Salt Conditions**

To maximize the amount of polar pesticides extracted by the sorbent, various salt and temperature conditions used in the extraction were explored. It is well-known that sodium chloride acts as an effective salting-out agent [55]. As shown in Figure S13, employing a higher percentage of salt resulted in significantly higher peak areas for all monitored pesticides. However, some charged analytes can be better solubilized in water with the addition of salt [67]; therefore, salt conditions between 0% and 30% (w/v) NaCl were explored. For Fiber **3**, 30% (w/v) NaCl resulted in the highest enrichment of analytes while for the PDMS/DVB fiber 10% (w/v) NaCl was optimal, as shown in Figure S14. Likewise, the effect of temperature in the presence of 30% (w/v) NaCl for Fiber **3** and 10% w/v NaCl for the PDMS/DVB fiber was studied to enhance the performance of the extraction method by increasing the diffusion of analytes to the fibers. Four different temperature conditions (20°C, 40°C, 60°C, and 80°C) were explored for the extraction of pesticides, and the results are shown in Figure 2A. Higher extraction temperatures resulted in enhanced extraction efficiency for all pesticides compared to results observed for Fiber **3** when using the same temperature conditions in the absence of salt. Using the PDMS/DVB fiber, extraction of analytes 1, 2, and 6 were adversely affected when using higher extraction temperatures while analytes 4, 7, 8, and 11 showed no change in peak area. For this reason, an extraction temperature of 80°C was not explored for this sorbent. The peak areas of all other analytes increased with an increase in temperature and the results are shown in Figure S15. An extraction temperature of 40°C was used to continue optimization with the PDMS/DVB fiber to give some enhancement in the extraction efficiency without sacrificing the extraction of pesticides 1, 2, and 6.

Due to the presence of chloride ions in the aqueous solution and the ionic nature of the sorbent, ion exchange between the [NTf_2^-] anion of the sorbent and [Cl^-] ions from the matrix was

investigated. If [Cl^-] ions were to exchange with [NTf_2^-] ions to become part of the sorbent's composition, a change in the extraction efficiency would be expected due to an alteration of the sorbent's hydrogen bond basicity [68]. To explore this, a study was conducted to establish a range of temperature conditions and salt content in which the extraction behavior of the sorbent was not changed. At higher temperatures, the PIL sorbent may be prone to swelling, resulting in more rapid diffusion of ions [46]. These effects were determined by comparing triplicate extractions in the absence of salt before and after a 1-hour exposure period to both 10% and 30% (w/v) NaCl solutions for temperatures ranging from 20-80°C. For temperatures of 20 °C and 40°C, the total peak areas remained comparable to the control at both salt conditions. Upon reaching higher temperatures, the reproducibility (relative standard deviation, RSD) of the sorbent was higher than 15%, as shown in Figure S16. For the 10% (w/v) salt condition and 60°C, the total peak area was also comparable to the control; however, for the 30% (w/v) salt condition, the reproducibility increased to 37%. Likewise, after exposure to salt at 80°C, the reproducibility for both the 10% and 30% (w/v) salt conditions increased to 28% and 24%, respectively. These results suggest that exposure to salt at higher temperatures adversely affected the reproducibility and may potentially alter the sorbent composition. Additionally, upon repeated exposure to higher temperature conditions (i.e., 60°C, 80°C) in the presence of salt, the appearance of the sorbent coating changed from a yellow to an orange/red color, indicating alteration of the sorbent coating. Therefore, 40°C was chosen as the optimal temperature condition along with a salt content of 30% (w/v) for the extraction of pesticides using PIL sorbent coatings.

Since the aim of this work is to examine the selectivity of PIL sorbents for pesticides, the optimal conditions were based on the stability of the fibers as well as conditions in which pesticides exhibited higher extraction efficiencies compared to cannabinoids. It has been previously reported

363 that increased salt concentration results in a decreased extraction efficiency of cannabinoids using
364 commercial SPME fibers [36,56]. This was evaluated for both Fiber **3** and the PDMS/DVB fiber
365 by extracting cannabinoids in the presence of 10% and 30% (w/v) NaCl solutions adjusted to pH
366 5 under RT conditions (20°C). For Fiber **3**, no difference in extraction efficiency was observed
367 between the 0% and 10% (w/v) salt conditions; however, a significant decrease was observed for
368 the 30% (w/v) salt condition as shown in Figure 3A. Likewise, the PDMS/DVB sorbent showed
369 diminished extraction efficiencies in the presence of both 10% and 30% (w/v) NaCl. Cannabinoids,
370 such as cannabigerol and cannabidiol (possessing two hydroxyl groups), exhibited the most drastic
371 drops in peak area, whereas cannabichromene had higher peak areas in the presence of salt. A
372 previous study has reported that the increased viscosity of the sample from the addition of NaCl
373 resulted in slower diffusion of the cannabinoids to the PDMS (100 μm) fiber [36].

374 **3.3.3 Sample pH**

375 It is well-known that the extraction behavior of many pesticides is influenced by the pH of
376 the aqueous sample matrix [57]. Pesticides in aqueous samples are reported to be better extracted
377 by the sorbent if the analytes are in their neutral state [57]. In a previous study using crosslinked
378 imidazolium PIL-based sorbents, pesticides exhibited higher extraction efficiencies when the
379 aqueous solution was adjusted to pH values below 2.5 [47], which provided motivation for
380 examining a pH range from 2 to 8 for this study. The effects of different pH conditions on the
381 extraction of pesticides are shown in Figure 2B. Higher peak areas were obtained at pH 2 for
382 almost all pesticides using Fiber **3** while higher peak areas were obtained at pH 8 using the
383 PDMS/DVB fiber. Out of the 20 pesticides listed in Table 1, myclobutanil was the only pesticide
384 having a pKa (2.30 ± 0.10) within this pH range; however, the peak areas were consistent across
385 the three pH values. Pesticides 2, 5, 11-15, and 17-20 are expected to be in a neutral state while

pesticides 1, 3, 4, 6-7, 9-10, and 16 have pKa values of 10 or higher, indicating these analytes remain predominantly ionized at pH values of 2, 5, and 8. The observed trends were not consistent with the ionizable nature of the analytes. Therefore, differences in peak areas across the three pH values for these pesticides are likely due to other interactions, such as hydrogen bonding, with the aqueous solution. The hydrogen bond acidity or basicity of analytes tends to dictate their solubility in water, and, therefore, their partitioning into more nonpolar phases [69]. The pesticides examined in this study have many hydrogen bond basic functional groups. A study analyzing the solvation characteristics of a reverse phase HPLC stationary phase, comprising of 1-butylimidazolium bromide, which was chemically bonded to silica particles with a heptane linker, was previously conducted at various mobile phase compositions from 50% to 100% methanol [70]. According to Sun et al., the hydrogen bond acidity of 1-butylimidazolium bromide is around -0.9 and the hydrogen bond basicity is around -0.1 across all mobile phase compositions, which suggests that this phase does not interact well with basic analytes under neutral pH conditions [70], and it is possible that other imidazolium-based phases, such as the PIL sorbent coatings, have similar properties. Therefore, basic analytes could be driven to interact more strongly with the aqueous phase instead of the PIL sorbent under pH 8 conditions.

More unexpectedly, phenolic cannabinoids, which are assumed to be neutral with predicted pKa values ranging from 9.40-9.83 [60-65], exhibited some variation in extraction efficiency with the pH of the sample. The total peak area of analytes extracted was enhanced when the pH of the aqueous sample was increased (see Figure 3B), and the same trend was also observed for the commercial PDMS/DVB sorbent, as shown in Figure S17. Interestingly, another study using crosslinked graphene oxide modified with IL sorbent coatings for DI-SPME noted a similar observation for phenolic compounds and attributed this behavior to electrostatic interactions

between the IL and the phenolic compounds [71]. Based on the observed trends, pH 2 was used for optimization of the pesticides and pH of 8 was used for optimization of the cannabinoids with the Fiber **3**.

3.3.4 Extraction Time

Sorption-time profiles were generated for pesticides and cannabinoids to determine the extraction time at which all analytes attained equilibrium between the sorbent and the aqueous sample matrix. Sorption-time profiles for pesticides and cannabinoids are shown in Figure 2C and Figure 3C, respectively. For pesticides, equilibration between the sample and the sorbent was initially observed to occur very quickly (within a minute). It is hypothesized that this result is due to the strong salting-out effect, contributing to very fast sorption kinetics. By decreasing the NaCl content of the sample to 10% (w/v), an equilibration time of 5 min was observed, as shown in the sorption-time profile in Figure 2C, suggesting that pesticides are extracted more rapidly with increasing salt content. Cannabinoids, on the other hand, required up to 60 min to reach equilibrium in the absence of salt. The difference in extraction kinetics between the cannabinoids and pesticides for the PIL sorbent coating offers a unique advantage over other traditional sorbents (i.e., PDMS/DVB) in selectively isolating pesticides. For optimization, 5 min was used as the extraction time for pesticides while 60 min was used for cannabinoids.

For the PDMS/DVB fiber, equilibration was not reached within an extraction time of 80 min (Figure S18), suggesting that the cannabinoids exhibit slower sorption kinetics to the sorbent coating compared to Fiber **3**. Additionally, operating in the kinetic region of the sorption-time profile should result in a decreased amount of cannabinoids extracted, which can be beneficial in selectively isolating pesticides from cannabinoids. Therefore, the sorption-time profile was not extended to include longer extraction times and a maximum extraction time of 80 min was used to

assess desorption conditions for the cannabinoids. For pesticides, equilibration was reached within 45 min, as shown in Figure S19. Since the equilibration time is longer than that of Fiber **3**, further analysis was required to determine the extraction time that would provide the largest benefit in selectively extracting pesticides. The total peak area for pesticides at each time point was divided by the respective total peak area of the cannabinoids to provide a ratio of the amount extracted. This data was plotted over the sorption-time profile and is shown in Figure S19. Extraction times of 15 and 30 min provided the highest ratio indicating that better selectivity can be obtained for pesticides at these time points. Since the total peak areas of the pesticides are higher at 30 min, this time point was chosen as the optimal extraction time as lower detection limits can be obtained.

3.3.5 Desorption Time

Desorption profiles were also generated for each class of analytes and are shown in Figure S20. Complete desorption of pesticides from Fiber **3** was obtained within 5 s for all analytes. For cannabinoids, desorption equilibrium was obtained within 2 min, as shown in the desorption-time profile. Carryover was assessed by re-immersing the sorbent after desorption into a separate 30 μL aliquot of methanol, allowing a comparison of average peak areas to those obtained from the initial desorption. The average percent carryover ranged from 1.5-2.5%, depending on the specific analyte. A similar desorption trend was observed for cannabinoids using the PDMS/DVB fiber, also resulting in a desorption time of 2 min (Figure S21). For pesticides, the desorption profile for the PDMS/DVB fiber is shown in Figure S22 and indicates equilibration being reached at approximately 5 min.

3.4 Sorbent Coating Selectivity Towards Pesticides and Cannabinoids

Based on the forementioned results, it is apparent that cannabinoids and pesticides prefer different extraction conditions when PIL sorbents are used, which is favorable when developing a

455 selective extraction method. Pesticides prefer lower pH conditions, higher salt and temperature
456 conditions, and can be extracted within a minute; meanwhile, cannabinoids prefer higher pH
457 conditions, lower salt content, and required longer extraction times. For this reason, the optimal
458 extraction conditions for isolating pesticides from cannabinoids using PIL sorbents included an
459 extraction time of 5 min at 40 °C from samples adjusted to pH 2 and containing 30% (w/v) NaCl
460 followed by desorption in 30 µL of methanol for 30 s. This desorption time was chosen so that
461 minor deviations in time provide less error compared to a 5 s desorption time. For the PDMS/DVB
462 fiber, optimal conditions consisted of a 30 min extraction time at 40 °C from samples adjusted to
463 pH 8 and with 10% (w/v) NaCl (see Figures S23 and S24). Complete desorption was obtained
464 using 30 µL of methanol and a desorption time of 5 min. Results for the extraction of cannabinoids
465 and pesticides using all fibers are shown in Figure 4. To assess the sorbent's affinity for these
466 analytes, the peak areas were divided by the volumes of each fiber as the volume of the sorbent
467 coating can greatly affect the extraction efficiency of the fiber. The coating volume was chosen
468 instead of film thickness as the normalizing factor as the PIL sorbent coatings form droplets when
469 using higher film thicknesses. Fiber **2** had the highest coating volume followed by Fiber **3**, Fiber
470 **1**, and Fiber **4,** which had about a third the coating volume of Fiber **1**. Previously, it was mentioned
471 that Fiber **3** and Fiber **4** had similar extraction efficiencies. After considering the effect that the
472 volume of each sorbent coating has on the extraction efficiencies, Fiber **4** appeared to possess the
473 best sorbent composition for extracting pesticides. Fiber **1**, Fiber **2,** and Fiber **3** showed a
474 considerably lower affinity towards the pesticides compared Fiber **4**, which indicates that having
475 the aromatic moieties in both the monomer and crosslinker plays a significant role in the extraction
476 of pesticides. Although Fiber **3** that had the highest total average peak areas, this sorbent coating

actually possessed the lowest affinity for the pesticides. The higher extraction efficiencies observed previously were likely due to the higher coating volume.

Compared to initial conditions, the optimized conditions afforded a 9-fold decrease in the extraction efficiencies of cannabinoids using Fiber **4** and a 4-fold increase in the extraction efficiencies of pesticides. The average total peak area for cannabinoids was 1,257 under initial extraction conditions and was decreased to 148 under optimal extraction conditions; meanwhile, the total peak area for the pesticides was 991 under initial conditions and increased to 3,793 under optimal conditions. Only a small increase in the extraction efficiencies of pesticides was observed for the PDMS/DVB fiber from 3,490 to 4,242. The nature of sorbent coating for Fiber **4** also appears to have 2 times the affinity for pesticides compared to the PDMS/DVB fiber, as shown in Figure 5. The optimal conditions were also used to construct the working range for the two fibers. The working ranges, LODs, and relative recoveries are listed in Table 4 (Fiber **4**) and Table S3 (PDMS/DVB). Chromatograms of the pesticides at the low LODs for Fiber **4** are shown in Figure S25.

3.5 Extraction from Complex Samples

Cannabinoids are known to be present in cannabis samples in concentration ranges from 100-1 mg/g, which is significantly higher than the action level of most pesticides in the lower μg/g level [13, 52]. If not selectively extracted, the more abundant cannabinoids co-elute with many of the pesticide as shown in Figure S26. The chromatograms reflect the relative abundance of pesticides and cannabinoids that are present within the complex sample (a 333-fold difference in concentration) if not selective extraction.

To explore the reliability of this extraction method when applied to samples containing a high concentration of cannabinoids, recovery experiments were preformed from aqueous samples

containing 10 mg/L of cannabinoids and 30 μg/L of pesticides. Chromatograms of these extractions are shown in Figure S27. The average total peak area for the cannabinoids recovered from the complex sample was 40,108 when extracted using the PDMS/DVB fiber. However, when extracted using Fiber **4**, the average total peak area was only 8,189 for the cannabinoids. For the pesticides, the total peaks areas were 455 and 406, respectively. Although the extraction efficiencies of the pesticides between the two fibers were comparable, there was a significant difference in the amount of cannabinoids extracted.

The relative recoveries obtained from complex samples were compared to the relative recoveries from samples containing only the pesticides. For Fiber **4**, a positive matrix effect was observed for all analytes with relative recoveries ranging from 94% to 141% for complex samples and 79% to 120% for pesticide-only samples. For the PDMS/DVB fiber, the relative recoveries from complex samples ranged from 50% to 114%. Most pesticides showed a decrease in the relative recoveries compared to the control (78-117%) with pesticides 10, 11, 14, and 15 falling below 80%. Since PDMS/DVB follows an adsorptive extraction mechanism and was more selective towards cannabinoids than Fiber **4**, the available sites for analyte adsorption were likely occupied by the cannabinoids decreasing the extraction of some pesticides. The positive matrix effect observed with Fiber **4** is beneficial for increasing the extraction efficiency of the method, but matrix-matched calibration will require for accurate quantification if applied to real samples.

Conclusions

Crosslinked imidazolium-based PIL SPME sorbent coatings were developed in this study for the selective extraction of pesticides monitored in cannabis pesticide testing and compared against a commercial PDMS/DVB fiber using HPLC-UV. The method effectively enhanced the extraction of pesticides while minimizing the extraction of cannabinoids. The PIL sorbent coating consisting of aromatic moieties in both the monomer and crosslinker demonstrated the best selectivity across

all four PIL sorbent coatings and showed the highest affinity for the pesticides. A 4-fold increase in the extraction of pesticides and a 9-fold decrease in the extraction of cannabinoids was observed compared to data obtained using a previously reported pesticide PIL-DI-SPME method. However, the sorbent coating containing only aromatic groups within the IL monomer exhibited low affinity for the pesticides. The PIL sorbent coating was able to reach low part-per-billion levels of pesticides and had relative recoveries from 79% to 120% at 30 μg/L from aqueous samples. When applied to samples containing a cannabinoid concentration of 10 mg/L, the relative recoveries ranged from 94% to 141%, indicating a positive matrix effect. Compared to the commercial PDMS/DVB fiber, the sorbent coating of Fiber **4** showed a greater selectivity compared to the PDMS/DVB sorbent. However, the more polar pesticides that eluted at the beginning of the separation were not extracted by any of the fibers.

To employ the developed method for use with real world samples, homogenization of the sample in an aqueous solution or a solid-liquid extraction step would be required. Future work will focus on modifying the structure of the sorbent coatings and the extraction platform to enhance the selectivity of the sorbent coating and extract the full range of pesticides. A future goal is to apply this method to a model plant matrix.

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Supporting Information. Synthetic details for the IL monomers and crosslinkers, SEM micrographs of PIL fibers, chromatograms of pesticide and cannabinoid separations, graphs

showing the effect of extraction conditions for both PIL and PDMS/DVB fiber, and ^{1}H NMR spectra for IL monomers and crosslinkers used to construct PIL sorbent coatings.

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Figure Legends:

Figure 1. Overlay of chromatograms at 230 nm showing the co-elution of cannabinoids with certain pesticides. Cannabinoids peaks elute at 28.932, 29.210, 32.368, 33.555, and 33.769 minutes. Details of the separation method for pesticides and cannabinoids can be found in section 2.2 of the Experimental.

Figure 2. Optimization of extraction conditions (salt content and temperature, pH, and extraction time) for pesticides using Fiber **3**. All extractions are at an analyte concentration of 200 µg/L and with a 10 mL sample volume. A) Extraction temperature (20-80°C). Extraction conditions: Salt, 30% (w/v) NaCl; pH, pH 5; extraction time, 60 min; fiber wash step, 1 min in water; desorption time, 15 min; desorption volume, 30 µL, desorption solvent, methanol. B) Effect of pH on the extraction of pesticides at 40°C with 30% (w/v) NaCl, a 60 min extraction time, a 1 min wash step in water, and a 15 min desorption time in methanol. C) Sorption-time profile for the pesticides at 40°C, 30% (w/v) NaCl, and pH 2 with a 1 min wash step in water followed by a 15 min desorption in methanol.

Figure 3. Optimization of the salt content, pH, and extraction time for cannabinoids using Fiber **3** with an analyte concentration of 200 µg/L and a sample volume of 10 mL. A) Effect of salt on the extraction of cannabinoids at pH 5, RT (20°C), a 60 min extraction time, a 1 min fiber wash step in water, and a 15 min desorption time in methanol. B) Effect of pH at RT conditions with no salt, a 60 min extraction time, and a 15 min desorption time in methanol. C) Sorption-time profile of cannabinoids at pH 8, RT sample conditions, no salt, and a 15 min desorption time in methanol. (▲) Cannabigerol, (●) Cannabidiol, (◆) Cannabinol, (●) Δ^9-THC, (-) Δ^8-THC, and (■) Cannabichromene.

Figure 4. Comparison of different PIL sorbents in extracting cannabinoids (A) and pesticides (B) under optimized conditions compared to commercial PDMS/DVB sorbent. Initial conditions: Concentration of analytes, 200 µg/L; Sample volume, 10 mL DI water; pH, pH 5; Salt content, 0% (w/v) NaCl; Temperature, 20°C; Extraction time, 60 min; Desorption time, 15 min; Desorption solvent, methanol; Desorption volume, 30 µL. Optimal conditions: Concentration of analytes, 200 µg/L; Sample volume, 10 mL DI water; pH, pH 2 (PIL), pH 8 (PDMS/DVB); Salt content, 30% (w/v) NaCl (PIL), 10% (w/v) NaCl (PDMS/DVB); Temperature, 40°C; Extraction time, 5 min (PIL), 30 min (PDMS/DVB); Fiber wash, 1 min with 30 µL of DI water; Desorption time, 30 s (PIL), 5 min (PDMS/DVB); Desorption solvent, methanol; Desorption volume, 30 µL.

Figure 5. Comparison of the affinity of the (■) PIL sorbent of Fiber **4** and (□) PDMS/DVB towards cannabinoids (A) and pesticides (B) when extracted under optimized conditions. Concentration of analytes, 200 µg/L; Sample volume, 10 mL DI water; pH, pH 2 (Fiber **4**), pH 8 (PDMS/DVB); Salt content, 30% (w/v) NaCl (Fiber **4**), 10% (w/v) NaCl (PDMS/DVB); Temperature, 40°C; Extraction time, 5 min (Fiber **4**), 30 min (PDMS/DVB); Fiber wash, 1 min with 30 µL of DI water; Desorption time, 30 s (Fiber **4**), 5 min (PDMS/DVB); Desorption solvent, methanol; Desorption volume, 30 µL. Responses were obtained using HPLC-UV.

Table 1. List of pesticides and cannabinoids monitored in this study along with their corresponding pKa values, retention times, UV absorbance wavelengths, and m/z values.

Analyte	Pesticides	pK_a[a]	Retention Time (min)[b]	Wavelength (nm)	m/z value (ion mode)[c]
1	Carbaryl	12.02 ± 0.46	11.3	215	219.1 (+)
2	Thiacloprid	0.01 ± 0.10	11.6	254	253.0 (+)
3	Fludioxonil	14.10 ± 0.50	13.5	254	247.0 (-)
4	Paclobutrazol	13.92 ± 0.20	14.3	230	294.1 (+)
5	Fipronil	-5.86 ± 0.20	15.2	230	454.0 (+)
6	Methiocarb	12.16 ± 0.46	15.5	230	243.1 (+)
7	Chlorantraniliprole	10.19 ± 0.70	17.2	230	490.0 (+)
8	Myclobutanil	2.30 ± 0.10	18.3	230	289.1 (+)
9	Boscalid	10.75 ± 0.70	19.5	230	343.0 (+)
10	Bifenazate	9.84 ± 0.43	24.1	230	301.2 (+)
11	Phosmet	-2.63 ± 0.20	25.3	230	340.0 (+)
12	Prallethrin	n/a	29.2	230	301.2 (+)
13	Azoxystrobin	-0.93 ± 0.18	27.3	254	404.1 (+)
14	Kresoxim-methyl	n/a	27.9	254	314.1 (+)
15	Clofentezine	-1.68 ± 0.31	29.5	280	303.0 (+)
16	Hexythiazox	12.77 ± 0.20	34.2	230	375.1 (+)
17	(E)-Fenpyroximate	1.58 ± 0.10	37.2	280	422.2 (+)
18	Pyridaben	-2.69 ± 0.20	37.8	280	365.1 (+)
19	Etofenprox	n/a	39.9	230	394.2 (+)
20	Acequinocyl	n/a	41.1	254	407.2 (+)
	Cannabinoids	pK_a[a]	Retention Time (min)[b]	Wavelength (nm)	
	Cannabigerol	9.71 ± 0.40	5.57	228	
	Cannabidiol	n/a	5.75	228	
	Cannabinol	9.40 ± 0.40	7.87	228	
	Δ^9-THC	9.81 ± 0.60	9.52	228	
	Δ^8-THC	9.83 ± 0.60	9.79	228	
	Cannabichromene	9.68 ± 0.40	11.7	228	

a. Values obtained from SciFinder and calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02.
b. Values correspond to the pesticide and cannabinoid separation methods using the UV detector listed in the experimental section.
c. Values represent the most abundant m/z value identified for each pesticide

Table 2. Chemical structures of IL monomers and IL crosslinkers examined in this study and used to prepare crosslinked PIL sorbent coatings.

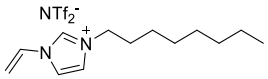
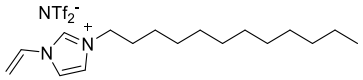
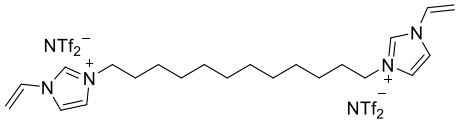
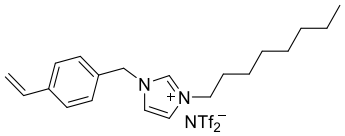
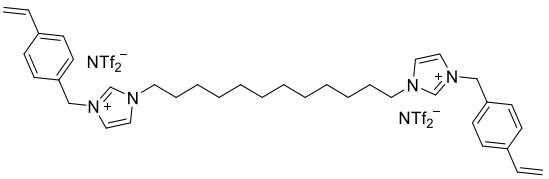
Name	Structure
1-vinyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide ([OVIM][NTf_2])	
1-vinyl-4-dodecylimidazolium bis(trifluoromethanesulfonyl)imide ([$VIMC_{12}$][NTf_2])	
1,12-di(3-vinylimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide ([$(VIM)_2C_{12}$]2[NTf_2])	
1-vinylbenzyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide ([$VBIMC_8$][NTf_2])	
1,12-di(3-vinylbenzylimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide ([$(VBIM)_2C_{12}$]2[NTf_2])	

Table 3. PIL sorbent coating composition for each fiber explored in this study and their approximate film thicknesses and sorbent volumes.

Fiber	Composition (Monomer + Crosslinker)	Film Thickness (µm)	Volume (µL)
Fiber **1**	$[OVIM^+][NTf_2^-]$ + $[(VIM)_2C_{12}^{+2}]2[NTf_2^-]$	82	0.18
Fiber **2**	$[VIMC_{12}^+][NTf_2^-]$ + $[(VIM)_2C_{12}^{+2}]2[NTf_2^-]$	118	0.36
Fiber **3**	$[VBIMC_8^+][NTf_2^-]$ + $[(VIM)_2C_{12}^{+2}]2[NTf_2^-]$	118	0.37
Fiber **4**	$[VBIMC_8^+][NTf_2^-]$ + $[(VBIM)_2C_{12}^{+2}]2[NTf_2^-]$	39	0.037

889 **Table 4.** Figures of merit for Fiber **4** and recovery results of pesticides using environmentally-
890 relevant concentrations. Eight calibration levels were used to construct the working ranges for
891 the pesticides.

Analyte	Linear Range (µg/L)	Slope ± SD	LOD (µg/L)	% Recovery (RSD)	
				Aqueous Sample[a]	Complex Sample[a]
1	200-900	3.9 ± 0.3	10	n.d.	n.d.
2	300-900	0.050 ± 0.004	200	n.d.	n.d.
3	20-900	1.33 ± 0.04	1	105 (4)	110 (5)
4	300-900	0.22 ± 0.02	200	n.d.	n.d.
5	20-900	1.01 ± 0.03	1	90 (8)	97 (4)
6	50-900	1.12 + 0.04	20	n.d.	n.d.
7	50-900	1.20 ± 0.04	20	n.d.	n.d.
8	200-900	0.47 ± 0.02	50	n.d.	n.d.
9	20-900	1.80 ± 0.05	1	109 (4)	130 (9)
10	10-900	2.38 ± 0.07	5	84 (9)	100 (4)
11	20-900	2.7 ± 0.1	1	120 (2)	138 (5)
12	20-900	1.91 ± 0.06	1	96 (9)	100 (15)
13	20-900	1.10 ± 0.03	5	111 (3)	141 (4)
14	20-900	0.52 ± 0.02	5	97 (7)	118 (4)
15	20-900	1.60 ± 0.05	1	103 (11)	120 (8)
16	20-900	1.25 ± 0.04	5	79 (15)	94 (10)
17	20-900	0.56 ± 0.01	5	104 (12)	119 (7)
18	20-900	0.57 ± 0.01	10	99 (13)	109 (6)
19	20-900	1.30 ± 0.04	10	82 (14)	102 (7)
20	20-900	0.88 ± 0.02	5	105 (9)	119 (6)

892 [a] n.d.: not detected

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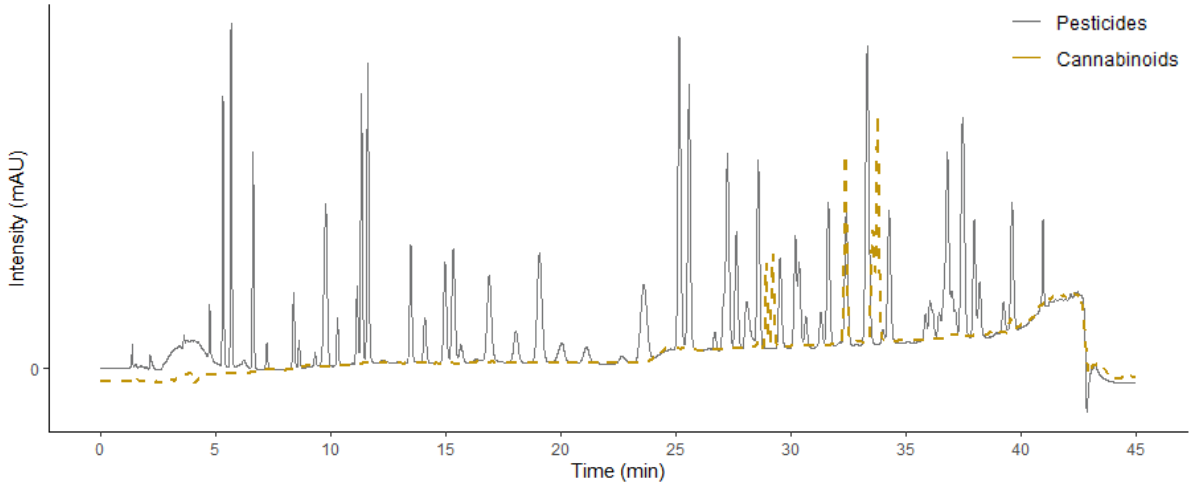

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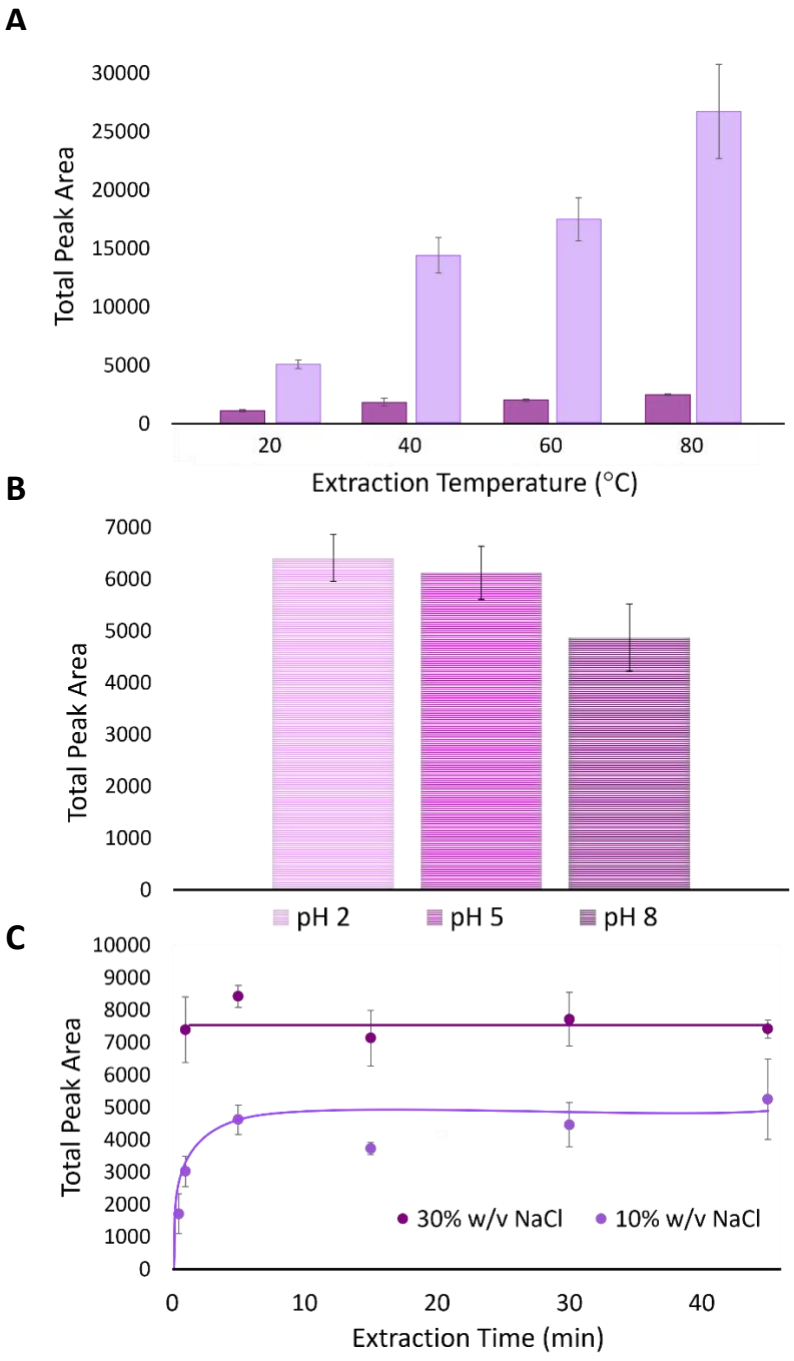

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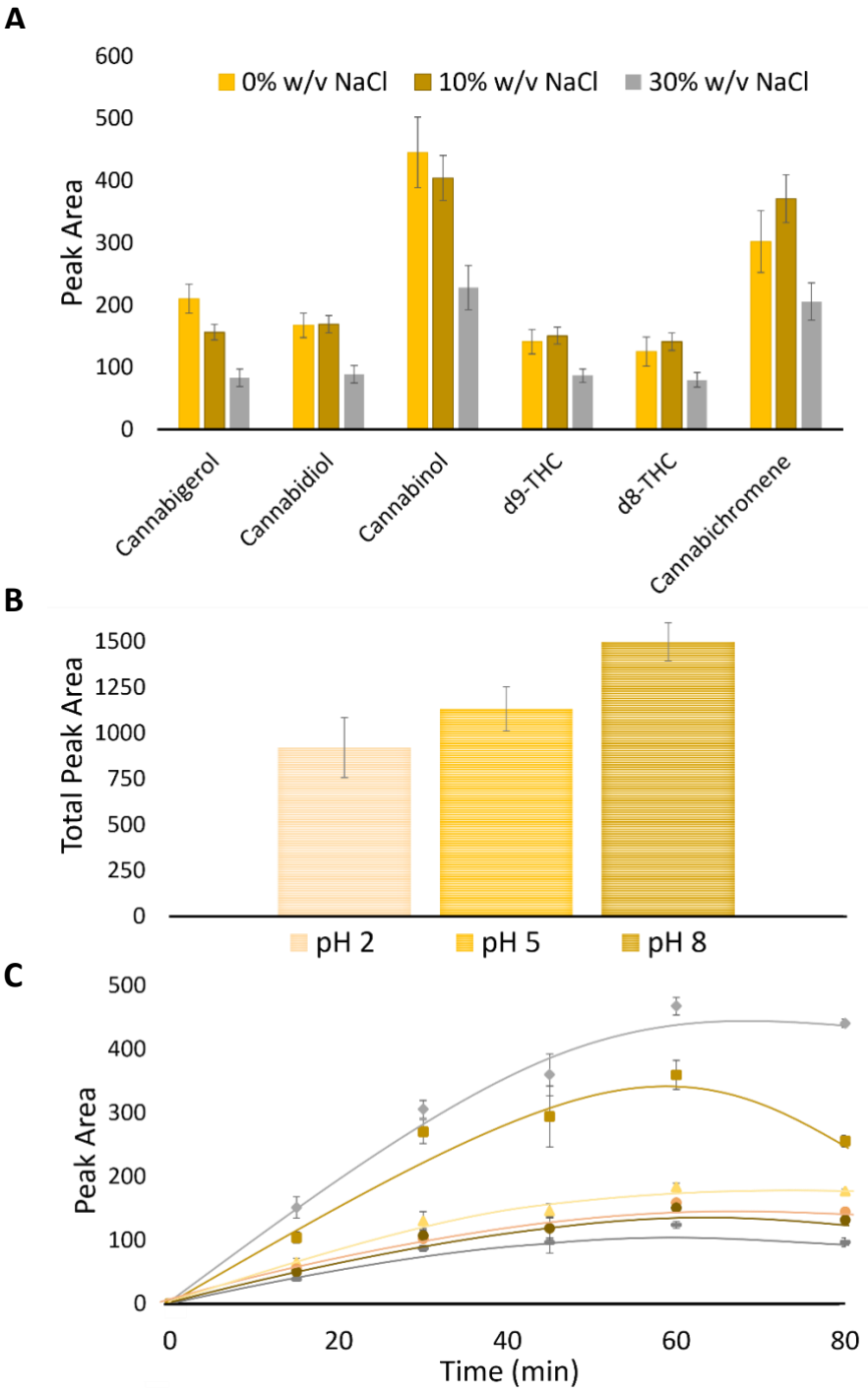
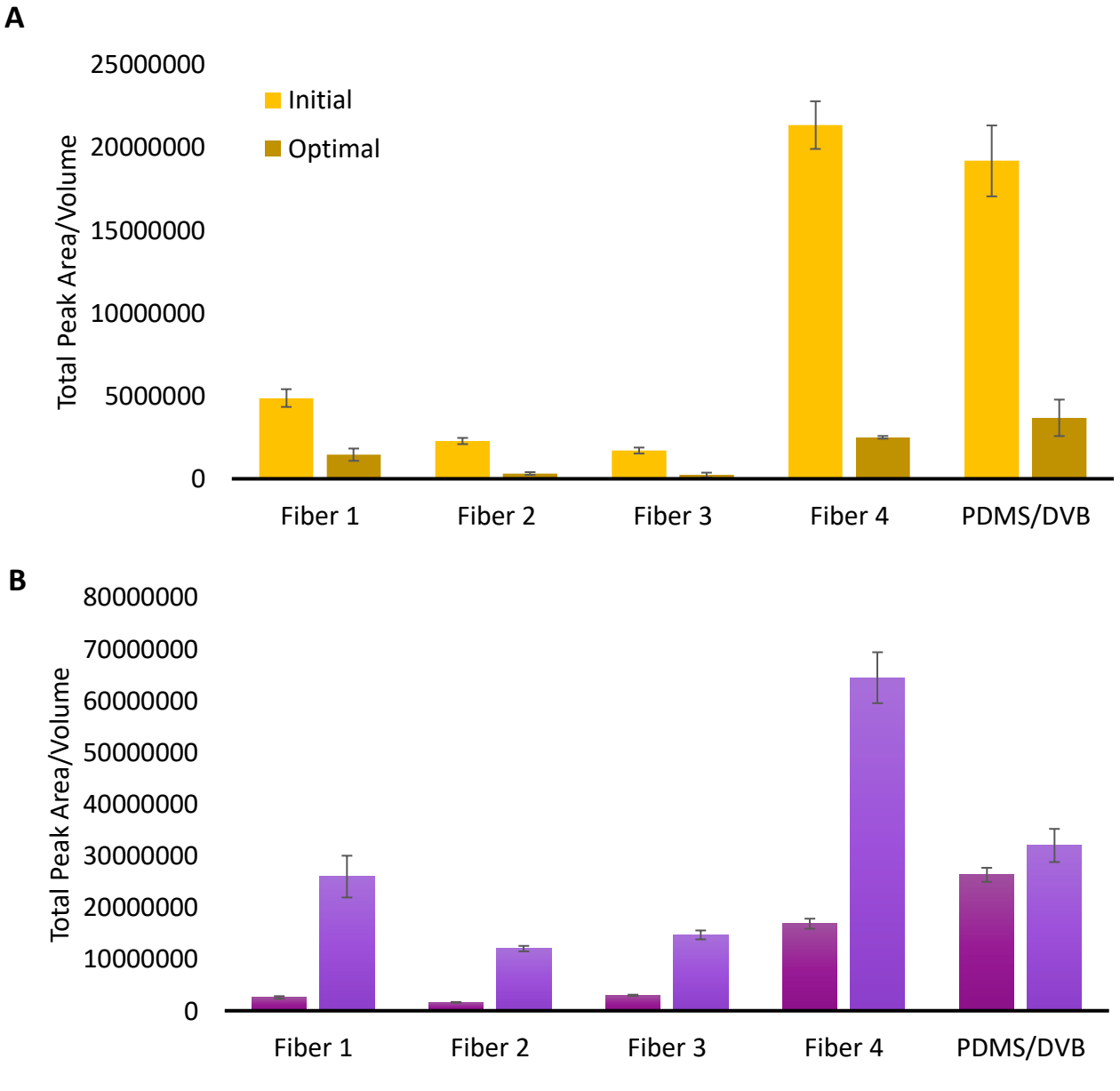


Figure 3. Optimization of the salt content, pH, and extraction time for cannabinoids using Fiber **3** with an analyte concentration of 200 µg/L and a sample volume of 10 mL. A) Effect of salt on the extraction of cannabinoids at pH 5, RT (20°C), a 60 min extraction time, a 1 min fiber wash step in water, and a 15 min desorption time in methanol. B) Effect of pH at RT conditions with no salt, a 60 min extraction time, and a 15 min desorption time in methanol. C) Sorption-time profile of cannabinoids at pH 8, RT sample conditions, no salt, and a 15 min desorption time in methanol. (▲) Cannabigerol, (●) Cannabidiol, (◆) Cannabinol, (●) Δ^9-THC, (-) Δ^8-THC, and (■) Cannabichromene.



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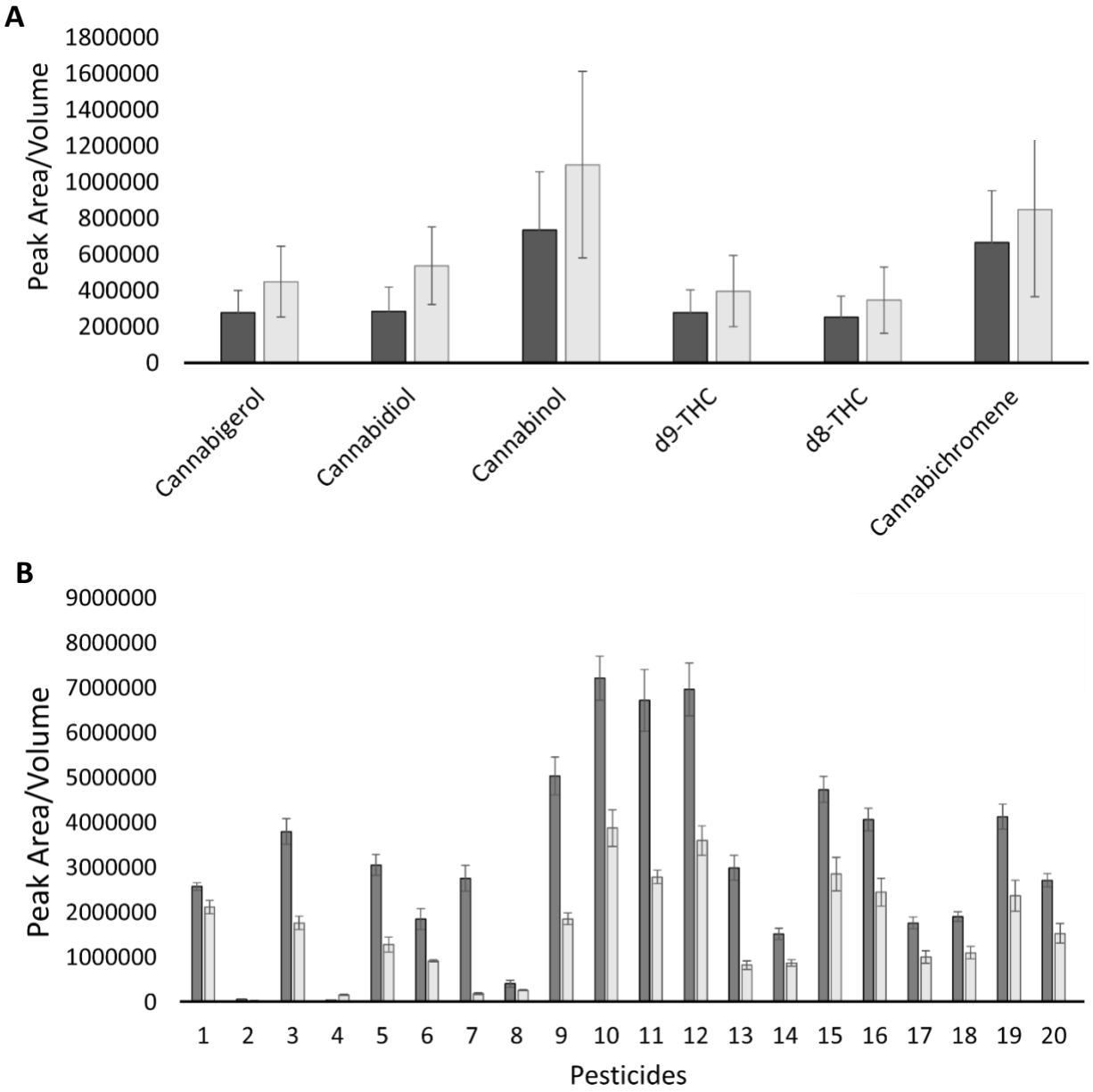

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933 **Figure 5.** Comparison of the affinity of the (■) PIL sorbent of Fiber **4** and (□) PDMS/DVB
934 towards cannabinoids (A) and pesticides (B) when extracted under optimized conditions.
935 Concentration of analytes, 200 µg/L; Sample volume, 10 mL DI water; pH, pH 2 (Fiber **4**), pH 8
936 (PDMS/DVB); Salt content, 30% (w/v) NaCl (Fiber **4**), 10% (w/v) NaCl (PDMS/DVB);
937 Temperature, 40°C; Extraction time, 5 min (Fiber **4**), 30 min (PDMS/DVB); Fiber wash, 1 min
938 with 30 µL of DI water; Desorption time, 30 s (Fiber **4**), 5 min (PDMS/DVB); Desorption
939 solvent, methanol; Desorption volume, 30 µL. Responses were obtained using HPLC-UV.
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