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Exploiting the tunable selectivity features of polymeric ionic liquid-based SPME sorbents in food analysis

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Abstract

In this work, the performances of polymeric ionic liquid (PIL) based solid-phase microextraction (SPME) coatings were assessed for applications concerning food safety and quality. Two different polymeric ionic liquid coatings, namely poly(1-4-vinylbenzyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl] imide (poly([VBHDIM][NTf2]), PIL **1**, and N,N-didecyl-N-methyl-d-glucaminium poly(2-methyl-acrylic acid 2-[1-(3-{2-[2-(3-trifluoromethanesulfonylamino-propoxy)-ethoxy]-ethoxy}-propylamino)-vinylamino]-ethyl ester) (poly([DDMGlu][MTFSI]), PIL **2,** were evaluated. The PIL-based coatings were compared to commercially available SPME coatings in terms of their performance toward extraction of pesticides and fruit metabolites. The partition coefficients (K_{fs}) of the tested coatings were calculated, with PIL **1** demonstrating similar or better performance compared to the commercial coatings. Design of experiment (DoE) was applied to optimize the parameters that most influenced

[1] Equal contribution of both authors

SPME extraction, and a quantitative method for determination of 5 organophosphorus pesticides was developed by using PIL-based coatings and commercial SPME fibers. Despite the thin layer of the sorbent coating, PIL **1** achieved limits of quantitation at the low part-per-billion level. Moreover, in a comparative investigation of analyte coverage carried out via HS-SPME-GCxGC-ToF/MS with grape homogenate as model matrix, excellent performances were observed for the PIL-based coatings toward the determination of fruit metabolites, demonstrating their capability towards broad extractive coverage of analytes characterized by various physicochemical properties.

Keywords: Polymeric Ionic Liquids (PIL), Solid-phase Microextraction (SPME), Food analysis, Pesticides, Fruit metabolites

1. Introduction

The denomination 'food' encompasses an enormous, diverse group of matrices characterized by widely different compositions. Within this context, determinations of matrix components and external contaminants lie amongst the main objectives of food analysis research. However, food analysis is often encumbered by various challenges, which pertain not only to the constitution of a given matrix, but to the particular physical-chemical properties of the analytes to be investigated within said matrix. In view of this, regardless of the final objective of the research being carried out within this field, special attention should always be paid in the selection of an appropriate sample preparation method [1]. Undoubtedly, for analyses of volatiles of aroma and flavor composition, from both qualitative and quantitative perspectives, solid-phase microextraction (SPME) distinguishes itself as the sample preparation method of choice [2–4]. Indeed, the implementation of SPME methods for isolation and determination of aroma and flavour compounds from complex food matrices is well established, with several headspace (HS)-SPME methods,

which take advantage of the volatility of such compounds, available to date [1,5]. However, with respect to food quality and safety analysis, the most commonly performed analysis of food commodities pertains to the determination of pesticides. In this regard, available methods for the determination of pesticides in food have significantly evolved within the last few years, advancing from laborious and environmentally unfriendly methods to simpler methods covering a broader range of analytes. In the continuous search for greener, yet accurate protocols for determination of pesticides in food, SPME certainly stands out as an analytical method capable of fulfilling the aforementioned requirements by integrating sampling, extraction, concentration, and sample introduction into a single solvent-free step [6]. Yet, despite the advantages offered by SPME, some critical limitations have hindered its application in food analysis, such as the limited chemistry of commercially available extraction phases. In this sense, research towards the development of new materials as extraction phases is a "hot topic" of investigation [7]. In recent years, ionic liquids (ILs) have drawn increased attention in the analytical chemistry community due to their unique physical and chemical properties. ILs are a new class of non-molecular solvents consisting largely of organic cations paired with organic or inorganic anions [8]. Within the analytical context, the main attraction of ILs lies in their structure, which can be controlled to produce desired chemical properties. Typically, ILs tend to have negligible vapor pressure, elevated thermal stability, tunable viscosity, and miscibility with other solvents, as well as the capability of undergoing numerous solvation interactions. In particular, as extraction phases, the selectivity of ILs can be improved by introducing functional groups that impart specific chemical functionalities, and thus enhance specific extraction capabilities. Modifications to the composition of ILs (i.e. structural tuning of the cation as well as combination of cations and anions) enable tuning of IL coatings for selective extraction of either a specific group of analytes, or towards a broader range of analytes [9]. With

respect to the development of new SPME coatings, attention has been focused on the development and application of polymeric ionic liquids (PILs). Due to their tunable physical and chemical properties, in addition to their versatility and ruggedness, PILs have been successfully employed as sorbent coatings for SPME, affording advantageous analytical results in comparison to those achievable by commercially available coatings [10,11]. Furthermore, given their successful performance as extraction phases, PIL-based coatings continue to attract significant interest in the area of food analysis [12–17].

The present work builds upon the utility of PILs by presenting an evaluation of two different PIL sorbent coatings, namely poly(1-4-vinylbenzyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl] imide (poly([ViBHDIM][NTf2]), PIL **1**, and N,N-didecyl-N-methyl-d-glucaminium poly(2-methyl-acrylic acid 2-[1-(3-{2-[2-(3-trifluoromethanesulfonylamino-propoxy)-ethoxy]-ethoxy}-propylamino)-vinylamino]-ethyl ester) (Poly([DDMGlu][MTFSI]), PIL **2**, via an extraction performance comparison with two commercially available SPME coatings (PA and PDMS) for the determination of food metabolites and pesticides. The study is divided in two parts: (1) A determination of organosphophorous pesticides in grapes, which involves the implementation of the abovementioned PIL coatings in a safety evaluation of this foodstuff, and; (2) extraction of selected analytes representing different chemical classes of metabolites commonly found in fruit, which accounts for the implementation of PILs in metabolomics studies associated with the quality of foodstuff.

2. Materials and Methods

2.1. *Reagents and Materials*

Analytical standards (purity > 97 %) and HPLC grade methanol were obtained from Supelco (Oakville, Canada). A list of targeted analytes and their physico-chemical properties can be

found in Table S1 (Supplementary Information). Commercial SPME fiber assemblies in 23-gauge needle sizes and automated formats, 100 µm PDMS, 7 µm PDMS, 85 µm PA, an automated SPME holder, and 20 mL screw cap vials were also purchased from Supelco (Oakville, Canada).

2.2. *Instrumentation*

The currently presented work employed a Hewlett Packard 6890/5973 GC-MS equipped with a split/splitless injector as well as a CTC Combipal® autosampler (CTC Analytics, Zwingen, Switzerland), which was used in the automation of the SPME method. The capillary column used for chromatographic separation was a J&W DB5-MS UI (30 m, 0.25 mm i.d., 0.25 µm film thickness). For the determination of organophosphorus pesticides (OPPs), the column oven was programmed as follows: temperature was set at 40 ºC for 3 min, ramped at 20 ºC/min to 180 ºC, then ramped at 10 ºC/min to 230 ºC, and finally ramped at 30 ºC/min to 280 ºC, for a total run time of 16.7 min. The injector was kept at the appropriate desorption temperature for each coating type, in splitless mode. Helium (99.999% purity) was used as carrier gas at 1 mL min^{-1}. For the metabolites study, the column temperature program was initially set at 35 °C for 6 min, ramped at 20 °C/min to 140 °C, then ramped at 40 ºC/min to 260ºC, where it was held for 2 min, for a total run time of 16.3 min. Helium was used as carrier gas, with a flow rate set at 1.2 mL/min. The same mass spectrometer working conditions were employed for both classes of analytes: ion source temperature: 230 °C; quadrupole temperature: 150 °C; transfer line temperature: 280 ºC; electron ionization (EI) 70 eV. For the metabolites study, the quadrupole was operated in full scan mode in the mass range of 35-350 m/z, while it was operated in SIM mode for the OPPs study. Untargeted analysis was carried out with a GCxGC-ToF/MS Pegasus 4D (LECO Corp., St Joseph, MI, USA) equipped with an Agilent 7890 GC oven as a chromatographic system. The column configuration included an Rtx®-5SilMS (30 m x 0.25 mm x 0.25 µm) (Restek Corp., Bellefonte, PA, USA)

capillary column in the first dimension (1D) and a BP-20 (1 m x 0.1 mm x 0.1 µm) (SGE, Austin, TX, USA) in the second dimension (2D). The trapping and refocusing of compounds eluting from the first dimension (1D) column and to the second dimension (2D) column was performed by a quad-jet modulator consisting of two cold nitrogen jets and two hot-air jets. Liquid nitrogen was used to create the cold jets. The two columns were connected with the use of a universal glass press tight connector (Restek Corporation, Bellefonte, PA, USA). A modulation period of 5 s was used, with a hot pulse duration of 0.8 s and a cooling period of 1.70 s. Ultra high purity helium (99.999%) was used as carrier gas, with a constant flow rate of 1.5 ml/min. Desorption of analytes from SPME coatings were performed in splittless mode at 270 °C for 15 min. An evaluation of carryover of analytes onto the coating was performed by re-desorbing the same coating immediately after analysis at 270 °C for 15 min . Chromatographic separation of analytes was achieved using the following temperature program in the primary oven: an initial temperature of 35 °C was held for 5 min; a ramp of 6°C/min was then used to reach a temperature of 250 °C, which was then held for 10 min — for a total run time of 50.8 min. The offset for the secondary oven temperature was set at +10 °C above the primary oven temperature. The modulator offset was set at 30 °C. The transfer line and ion source temperatures were 250 °C and 200 °C, respectively. A solvent delay of 60 s was used. Electron impact ionization was performed at 70 eV with an acquired mass range from 35-600 m/z.

2.3. *Data processing*

MSD Chemstation (Agilent Technologies) software was used for GC-MS data processing. Library searches were performed using the commercial NIST library. Data was further processed using Microsoft Excel (2010) and GraphPad Prism 5 (Version 5.01, 2007, GraphPad Softwate, San Diego, CA, USA). Microsoft Excel was also used to design the experiments and evaluate results

from the Plackett-Burman Design. The Statistica 8.0 (2007, StatSoft, Tulsa, OK, USA) software was used to construct Central Composite Design experiments, as well as to evaluate the associated results.

2.4. *Ionic Liquid Coating Preparation*

The chemical structures of PIL-based coatings are shown in Table S2. The synthesis of Poly([VBHDIM][NTf_2]) was carried out as previously published in the literature[18] . The synthesis of the poly([DDMGlu][MTFSI]) PIL was performed by combining two previously reported synthetic procedures [19,20], with complete synthesis conditions and schemes shown in a report by Ho, et al. [21]. Further details regarding the synthesis and preparation of employed PILs can be found in extensive detail elsewhere [22,23].

2.5. *SPME Procedure*

2.5.1. *Determination of Pesticides*

Twelve grams of grape pulp was weighed into a 20 mL headspace vial. Prior to extraction, vials containing samples were pre-incubated for 5 min at 65ºC (with the exception of experiments carried out with the PIL **2** coating, wherein the temperature was set at 30ºC due to coating degradation). Extractions were performed for 45 min at a stirring rate of 250 rpm. Coatings were desorbed in the GC-MS injection port for 5 min at 260 ºC (PDMS), 280 ºC (PA), and 175 ºC (PIL coatings), in splitless mode. Carryover tests, carried out to evaluate the desorption efficiency of the coatings, were performed by further desorbing coatings after analysis.

2.5.2. *Determination of Metabolites*

100 µL of a stock working mixture of target analytes was spiked into a 9 mL solution of ultrapure water with 20% (w/w) NaCl, inside a 20 mL headspace vial. Since the targeted analytes are susceptible to degradation, all samples were freshly prepared prior to analysis. Extraction

temperature, stirring rate, and incubation time were kept at 30 ºC, 500 rpm, and 20 min, respectively, for the entire sample set. Coatings were desorbed in the GC-MS injection port for 10 min at 250 ºC (commercial coatings) and 175 ºC (PIL coatings) in splitless mode. Desorption efficiency was evaluated by carrying out subsequent injections of the same coatings immediately after analysis. HS-SPME-GC-MS calibration curves, constructed to investigate the concentration ranges reported in Table S3, were acquired following the experimental procedure described above, using an extraction timeframe of 60 min.

3. Results and discussion

3.1. *Part I – Safety evaluation: Determination of Organosphosphorous Pesticides in Grapes*

In the current work, the two PILs SPME coatings were selected in light of their enhanced ability to extract polar analytes compared to commercially available SPME coatings [10,21,24]. Thus, this characteristic of PILs can represent an enormous advantage in food analysis, where the effective extraction of both polar and non-polar analytes is of utmost importance.

SPME coatings that extract via an absorption mechanism were considered for comparison with the PIL coatings. Based on their physical-chemical properties and previous applications, the commercial PDMS 100 µm and PA 85 µm coatings were selected as suitable candidates for comparison [25–27]; PDMS is a nonpolar extraction phase, while PA is a moderately polar coating.

3.1.1. Special Considerations – Moisture Effect & Coating Lifetime

Whenever applicable, headspace SPME is the mode of choice for analysis of complex food matrices, since the risk of coating deterioration is drastically minimized in relation to applications involving direct immersion SPME. Yet, according to the physical-chemical properties of the OPPs targeted in this study (see **Error! Reference source not found.**), it can be reasonably presumed that relatively high extraction temperatures would be required to ensure effective transfer of

analytes from the sample matrix and into the headspace of vials for analysis. While increasing sample temperature may significantly reduce equilibration times, the application of such high temperatures to an aqueous-based matrix such as grape pulp may lead to a build-up of pressure inside the vial, as well as the accumulation of high water vapour content in the vial headspace, all of which may pose additional challenges to method precision. To verify the durability of the PIL coatings under such conditions, each fiber was submitted to 20 successive extractions of grape pulp at 60ºC for 30 min. As seen in **Error! Reference source not found.Error! Reference source not found.**, the PIL **1** fiber was demonstrated to be quite durable, providing excellent repeatability throughout the study. Conversely, the PIL **2** fiber exhibited a decreasing trend in extraction efficiency, indicating deterioration of the coating at the aforementioned extraction and desorption conditions. Considering that the PIL **2** fiber is a highly polar coating fabricated without chemical crosslinking, it is understandable that deterioration of the coating would occur under such strenuous extraction conditions (e.g. high temperature and humidity in the headspace). Based on the obtained results, further experiments were conducted only with the PIL **1** fiber.

3.1.2. Multivariate Experimental Design for Optimization of HS-SPME Conditions

In most SPME studies, optimization of extraction conditions is carried out by conducting one variable-at-a-time (OVAT) experiments. However, the results of these types of experiments fail to account for interactions concurrently occurring between factors. In the present work, design of experiment (DoE) was employed to identify and optimize factors that are most influential on overall extraction efficiency.

The most significant variables influencing the SPME process were identified by Plackett-Burman Design (Supplementary Information -Section S2). This was followed by an optimization of these variables aimed at the establishment of optimal values that yield maximum signal response.

For this purpose, a Central Composite Design (CCD) was employed for optimization of (1) dilution ratio (% of water added), (2) extraction time (in min), (3) extraction temperature (in ºC), and (4) sample mass (in g). All other parameters were kept constant, as follows: no salt addition; stirring rate at 250 rpm; pre-incubation time of 5 min; and no pH modification (natural pH of ~ 3.8), according to results obtained in previous studies[28]. In the present study, the CCD consisted of four factors, with rotability $\alpha = 2$ (the choice of α value will determine the predictability of the model), and 5 central points. To summarize, all four factors were evaluated at 5 levels ($-\alpha$, -1, 0, +1, $+\alpha$), resulting in 29 experiments. A summary of all conditions utilized for each experiment is presented in Table S5, which can be found in Supplementary Information.

An investigation of the Pareto charts of effects in relation to the profiles of predicted values and desirability (Supplementary Information, Figures S2 and S3) revealed that the most important factor impacting extraction efficiencies is sample mass. Optimal results were obtained at masses higher than 9.9 g for the PDMS coating, and 11.6 g for the PA coating. Increasing the sample temperature was also noted to improve extraction efficiencies: optimized temperature values were 65.0 ºC for PDMS, and 57.5 ºC for the PA coating. This was expected, since increasing the extraction temperature can reduce sample viscosity, decrease analyte interactions with the sample matrix, and improve their transfer to the headspace.

In SPME, when additional phases are present in the sample, the partitioning of analytes in complex matrices occurs among all phases present in the system. Therefore, in the case of complex matrices such as grapes, sample dilution may improve the partitioning of analytes between the sample and the coating as analyte competition between the other phases is diminished [6]. However, a closer inspection at surface responses generated between extraction time and sample dilution (**Error! Reference source not found.**) shows that maximum extraction efficiencies could

be obtained without sample dilution. With regard to extraction time, optimum extraction efficiencies were obtained at extraction times longer than 42.0 min and 44.3 min for the PA and PDMS coatings, respectively.

Taking into account the optimal conditions obtained for the studied parameters, the working conditions employed to carry out further experiments were then set as follows: sample temperature, 65.0 ºC; pre-incubation time, 5.0 min; sample mass, 12.0 g; stirring rate, 250 rpm; desorption time, 5.0 min; and desorption temperatures of 250.0 ºC, 280.0 ºC, and 170.0 ºC for PA, PDMS, and PIL fibers, respectively. Salt addition and sample dilution were not performed. Also, the pH was kept at its natural value of ~3.8 for grape pulp samples.

According to the CCD results, optimal results were obtained at extraction times longer than 42.0 min and 44.3 min for PA and PDMS coatings, respectively. To verify whether equilibrium is being reached at 45.0 min of extraction, extraction time profiles were attained for PDMS, PA, and PIL **1** fiber, covering a time interval spanning from 15.0 to 120.0 min. Extraction time profiles are presented in Section S3 of Supplementary information alongside a succinct discussion. Briefly, only diazinon and methyl parathion were observed to reach equilibrium for extractions carried out with PIL **1** at the optimized extraction time (45 min). For instance, for extractions carried out with the PIL **1** fiber, the attained profile for chlorpyrifos shows that extraction occurs under the pre-equilibrium regime at 45.0 min. Malathion and parathion exhibit a linear relationship between amount extracted and extraction time. Therefore, at 45.0 min, these OPPs are being extracted under the linear regime (i.e., amount extracted is less than 50 % of amount extracted at equilibrium) [29].

3.1.3. Analytical Performance of the Method

Following the establishment of optimal extraction conditions, the developed method was validated in fortified grape pulp via an evaluation of method linearity, sensitivity, precision, and

accuracy. Method linearity was studied by means of matrix-matched calibration curves, using the detector response of the quantifier ion at seven concentration levels, varying from 0.001-0.5 mg kg^{-1}. Results pertaining to the validation of the method are summarized in **Error! Reference source not found.**.

Owing to the pre-concentration capabilities of this method, admirably low limits of quantitation could be attained. It is worth highlighting the excellent sensitivity, seen as the slope of the calibration curve, obtained by the PIL **1** fiber, despite this fiber being 10-times thinner than the commercial PDMS coating. It has been previously reported in the literature that the PIL **1** coating exhibited superior sensitivity over the PDMS fiber due to enhanced π-π interactions [21].

In the present study, limits of quantitation are presented as objective limits of quantitation or lowest limits of quantitation (LLOQ). LLOQ is defined as the lowest concentration of an analyte assessed through the calibration curve that gives a reproducible response that is both accurate and precise (according to SANCO/12495/2011 and FDA directives) [30,31]. LLOQs obtained for the commercial fibers ranged from 0.001 to 0.01 $mg.kg^{-1}$. For the PIL **1** fiber, LLOQs were: 0.001 $mg.kg^{-1}$ for diazinon; 0.025 $mg.kg^{-1}$ for methyl parathion; and 0.01 $mg.kg^{-1}$ for malathion, chlorpyrifos, and parathion. It is worth noting that despite its thickness, the fiber PIL **1** was capable of achieving LLOQs at low part-per-billion levels. A comparison of the method performance to other data published in literature, related to the determination of OPPs in food commodities by SPME, is showed in Table S6 (Supplementary Information). The precision (repeatability) of the method was determined for grape samples spiked at two concentrations: 0.05 and 0.5 $mg.kg^{-1}$. Data from three analyses at each concentration level, performed within the same day, were used for calculations and expressed as relative standard deviations (RSD, %). As presented in **Error! Reference source not found.**, good results were obtained for all pesticides (RSD < 15%).

Importantly, no significant differences were found between precision values obtained for the commercial fibers and the PIL **1** fiber.

In order to check the accuracy of the method in our study, recovery by means of "estimated concentration values" [32] was assessed by fortifying blank grape pulp with known concentrations of each analyte. Two concentration levels (0.05 and 0.5 $mg.kg^{-1}$) were assessed. As presented in Table 2, the recoveries were within an acceptable range (70 – 130 %) for nearly all analytes.

To ascertain its applicability, the validated HS-SPME GC-MS method was applied in the analysis of real grapes. Four grape samples, cultivated according to conventional agricultural procedures, were purchased from different retailers in Waterloo, Ontario, Canada, and immediately processed according to the procedure described in *Section 2.5.1*. However, none of the analyzed samples presented OPPs above their respective LLOQ levels.

3.1.4. Calculation of partition coefficients (K_{fs}) and comparison of extraction efficiencies as normalized calibration slopes

The extraction time profile study showed that OPPs were unable to reach equilibrium in the studied coatings under the range of extraction times studied (Supplementary Information, Section S3); thus, amounts extracted at two different time points were utilized to calculate amounts extracted at equilibrium (n_e) [33]. Employment of this method allowed for more accurate calculations of Kfs values, rather than simply considering amounts extracted under pre-equilibrium conditions. As shown in **Error! Reference source not found.**-A, the Log K_{fs} values calculated for the PIL **1** coating are similar or higher than those calculated for the PA and PDMS coatings. The experimental results indicate that better sensitivity and faster equilibration times could be achieved with the PIL **1** coating, even with a relatively thinner film compared to commercial coatings. Moreover, a previously proposed normalization method, in which the

slopes obtained by the calibration curves are divided by the thickness of the fiber coating used, was employed as a simple and efficient way of comparing extraction efficiencies amongst different SPME coatings [12,13,34,35]. Figure 3-B depicts a comparison between the commercial fibers (PDMS 100 µm and PA 85 µm) and the PIL **1** fiber (~ 10 µm). As can be seen, the comparison corroborates that PIL **1** displays superior performance towards the extraction of the selected OPPs in grape pulp under the experimental conditions employed.

It is important to note that such normalized slopes account for the normalized sensitivity at a given extraction time. In fact, according to the values of Log K_{fs} presented in Figure 3A, the PIL **1** fiber exhibits higher affinity towards the studied OPPs compared to the commercial fibers. Between the commercial fibers, PA fiber exhibits higher K_{fs} values for OPPs compared to the PDMS fiber. Therefore, it can be assumed that the smaller values of the normalized slopes obtained for the PA fiber (Figure 3B) are related to the fact that, for this fiber, extractions at 45 min were occurring under the pre-equilibrium regime. Nonetheless, taking into consideration both results (Log K_{fs} and normalized slopes), the superior extraction efficiency achieved by the PIL **1** fiber is remarkable, despite its smaller film thickness.

3.2. *Part II - Quality: Determination of Selected Metabolites*

The compounds used for this investigation belong to different chemical classes and range from low to medium polarity, as well as low to medium-high molecular weight. The selection of compounds was based on their presence as metabolites in fruits [36]. This investigation allowed for an assessment of the suitability of these coatings for determinations of food aroma and metabolome. To ensure an effective comparison between the PILs and commercially available coatings in terms of their extraction efficiencies, both their compositions and thicknesses were

considered. Considering that the thickness of the PIL coatings was approximately 10 µm, the commercially available PDMS (7 µm) coating was selected for evaluation. Since PILs are generally polar, a relatively polar commercial fiber, polyacrylate, 85 µm (PA), was also included in the evaluation.

3.2.1. Analytical Performance

Linear dynamic range determinations can yield information that can be useful in both targeted and discovery-based untargeted studies, considering the wide range of metabolite concentrations present in complex matrices. Bearing this in mind, the analytical performance of the coatings were tested to investigate their linear dynamic range for the selected metabolites, and the reproducibility of the method at different concentration levels (Table S3). As a necessary step towards future employment of PIL coatings in other applications, this investigation imparted valuable findings regarding the capability of PIL coatings to extract from multicomponent systems with broad concentration ranges. As shown in Table 3, the PIL coatings yielded satisfactory linearity as compared to commercial fibers. The obtained values ranged from 0.9955 to 0.9998 for PIL **1,** and 0.9908 to 0.9913 for PIL **2**.

Moreover, PIL **1** achieved better LLOQs for all extracted analytes as compared to PIL **2** and PDMS, as well as LLOQs comparable to those of PA. In terms of reproducibility (expressed as RSD%), these values ranged from 0.3 to 13.6% for PIL **1,** while PIL **2** yielded relatively values, ranging from 7.6 to 38.4%. It is worth noting that PIL-based coatings generally provided broader linear ranges compared to the tested commercial coatings, particularly for 2-undecanone, 1-undecanol, and ethyl nonanoate.

3.1.1. Comparison of coatings in terms of extraction sensitivity

A better understanding of the characteristic selectivity of each functionalized PIL-based fiber can be ascertained by comparing the extraction efficiencies of the coatings, which can be done by taking into account their respective sensitivities towards the targeted analytes. For this comparison, coating sensitivities were expressed by normalizing the calibration slopes obtained by SPME sampling according to the coating's thickness [12,13,34,35].

Taking into account the normalized extraction efficiencies shown in Figure 4, PIL **1** showed better performance compared to the other coatings for 2-hexanone, benzene, ethyl nonanoate, and 1-undecanol. In addition, the PIL **1** coating yielded efficiencies comparable to PA for benzaldehyde, 1-pentanol, and acetophenone, as well as efficiencies comparable to PDMS for ethyl butanoate, eucalyptol, 2-undeanoate, and α-pinene. The higher selectivity of the PIL-based coating for benzene is in agreement with previously reported studies, corroborating that this fiber coating is highly selective for large polyaromatic molecules due to enhanced π-π stacking and high dispersion interactions [21]. The results obtained for acetophenone and benzaldehyde may be attributed to the inductive effect of aromatic ring substituents that partially deactivate π electrons, reducing these analytes affinity for the sorbent coating. While PIL 1 was demonstrated to yield extraction efficiencies for the compounds under study that were comparable or greater than the PDMS and PA coatings, the PIL 2 fiber the PIL **2** fiber generally exhibited lower efficiencies for all analytes, with the notable exception of 2-undecanoate, for which it yielded an extraction efficiency comparable to that of PA. When the extraction efficiencies of the coatings are expressed through K_{fs} (obtained by NT method, described in Supplementary Information – Section S4), the attained results fall in line with the general trends observed in the normalized calibration slopes investigation; the higher extraction efficiency of PIL **1** for most of the targeted analytes is confirmed, as well as the lower performance of PIL **2** (Figure S5).

3.2.5 Applicability to untargeted analysis

In this investigation, the analyte coverage capabilities of the tested coatings were compared in order to assess their suitability for untargeted analysis. In view of its diversified volatile composition, green grape homogenate was selected as model, and sampled in headspace mode with each coating under study. Analyses were carried out by GCxGC-ToF/MS in order to separate and detect a greater number of extracted features compared to conventional one dimensional chromatographic approaches. The peak apex plots presented in Supplementary Information Figure S6 depict the distribution of the analytes extracted according to their retention times in the first and second dimension of the GCxGC system. Under the employed column configuration (see Section 2.2), the first dimension retention time (RT^1) provided information regarding their volatility, while the second dimension retention time (RT^2) provided insight into their polarity. As summarized in Figure S6, the PIL **1** fiber (~10 μm) extracted a total of 255 features, which eluted from 280 to 4485 sec in the first dimension, and from 0.365 and 4.475 sec on the second dimension. On the other hand, the PA fiber (85 μm) extracted a total of 154 features, which eluted from 380 to 3370 sec in the first dimension, and from 0.085 to 4.430 sec in the second dimension. The PDMS fiber (7 μm) could only extract 21 features, which eluted from 255 to 2365 sec and 0.520 and 3.735 sec in the first and second dimensions, respectively.

The results attained in this investigation certainly provide significant insight regarding the potential of the PIL **1** coating in the extraction of a broad range of analytes, presenting the PIL 1 coating as a potential candidate for untargeted food analysis.

4. Conclusions

In this work, the performances of two PIL-based SPME coatings were assessed in order to explore their applicability for food analysis. The new coatings were tested and compared to commercial SPME fibers for the determination of organophosphorus pesticides and fruit metabolites, providing excellent performance in terms of linearity, and achieving LODs in the sub part-per-billion level in the case of determination of pesticides in grape homogenate. The extraction capability of the PIL-based coatings were assessed by calculating the partition coefficients K_{fs}, wherein the PIL 1 coating was shown to yield higher or comparable values with respect to commercial SPME coatings for most of the analytes studied. An attentive investigation of coating lifetime revealed the effect of moisture on both PIL-based coatings, confirming the higher robustness of the PIL **1** coating. Studies aimed at verify coating extraction coverage showed that PIL **1** provided broader extraction capability for analytes constituting the headspace of grape homogenate as compared to the PA and PDMS 7 μm coatings, regardless of its thin film. The potential of these PIL-based SPME coatings for both determination of targeted contaminants and untargeted screening of food commodities was demonstrated. Given the tunable properties of this class of sorbent coatings, the authors of this study foresee their future employment towards a range of applications in food analysis.

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Figure 1 – PIL coating lifetime over 20 extractions at 60 ºC for 30 min.

Figure 2 – Response surface plots for desirability versus extraction time (min) and sample dilution (%) for PA and PDMS fibers.

Figure 3 – Calculated partition coefficients (K_{fs}) (A) and normalized slopes (B) for selected OPPs in grape pulp, for all studied SPME fibers.

Figure 4 – Comparison of calibration slopes. Calibration slopes were normalized by coating thickness and calculated for all analytes under study. All analyses were carried out by HS-SPME-GC-MS.

Table 1 - Analytical performance of calibration curves obtained in grape pulp by HS-SPME-GC-MS (SIM) with PDMS (100 µm), PA (85 µm), and PIL **1** (~ 10 µm) fiber.

Analyte	Calibration range ($mg.kg^{-1}$)	Slope ± SD x 10^3	Y-intercept ± SD	R^2	LLOQ ($mg.kg^{-1}$)
		PDMS 100 µm			
Diazinon	0.001-0.5	6534 ± 78	-18220 ± 16810	0.998	0.001
Methyl Parathion	0.01-0.5	658.9 ± 35.5	-23270 ± 8272	0.972	0.01
Malathion	0.01-0.5	443.8 ± 17.8	-13720 ± 4144	0.984	0.01
Chlorpyrifos	0.001-0.5	2877 ± 53	2711 ± 11530	0.996	0.001
Parathion	0.01-0.5	1101 ± 35	-31620 ± 8073	0.990	0.01
		PA 85 µm			
Diazinon	0.001-0.5	2084 ± 41	-7763 ± 8939	0.995	0.001
Methyl Parathion	0.025-0.5	155.7 ± 7.0	-2256 ± 1776	0.984	0.025
Malathion	0.01-0.5	154.1 ± 5.9	-1681 ± 1374	0.986	0.01
Chlorpyrifos	0.01-0.5	1187 ± 21	-7291 ± 4784	0.997	0.01
Parathion	0.01-0.25	482.7 ± 21.2	-4729 ± 2610	0.985	0.01
		PIL 1 (~ 10 µm)			
Diazinon	0.001-0.5	2084 ± 41	-7763 ± 8939	0.995	0.001
Methyl Parathion	0.025-0.5	155.7 ± 7.0	-2256 ± 1776	0.984	0.025
Malathion	0.01-0.5	154.1 ± 5.9	-1681 ± 1374	0.986	0.01
Chlorpyrifos	0.01-0.5	1187 ± 20	-7291 ± 4784	0.997	0.01
Parathion	0.01-0.25	482.7 ± 21.2	-4729 ± 2610	0.985	0.01

Table 2 - Repeatability and accuracy for commercial fibers and PIL **1** fiber.

Analyte	PDMS (100 µm) Accuracy [a] (Precision[b])		PA (85 µm) Accuracy [a] (Precision[b])		PIL#1 (10 µm) Accuracy [a] (Precision[b])	
	0.05 $mg.kg^{-1}$	*0.5* $mg.kg^{-1}$	*0.05* $mg.kg^{-1}$	*0.5* $mg.kg^{-1}$	*0.05* $mg.kg^{-1}$	*0.5* $mg.kg^{-1}$
Diazinon	116 (5)	108 (2)	82 (3)	107 (4)	74 (10)	90 (1)
Methyl Parathion	118 (1)	116 (5)	105 (3)	75 (10)	80 (14)	89 (11)
Malathion	120 (2)	110 (10)	60 (2)	71 (10)	66 (13)	70 (12)
Chlorpyrifos	107 (5)	105 (0.4)	96 (11)	136 (10)	72 (3)	107 (5)
Parathion	112 (4)	120 (6)	95 (15)	97 (7)	75 (8)	106 (1)

[a] expressed as % relative recovery (n= 3, each)
[b] expressed in % RSD (n= 3, each)

Table 3: Summary of analytical performances and reproducibility values (% RSD) for all tested coatings

Analyte	Linear range ($\mu g\ L^{-1}$)	Correlation coefficient (R^2)	Slope ± SD	Y-intercept ± SD	%RDS*(1)	% RSD*(2)	% RSD*(3)
			PIL **1**				
benzene	0.5-500	0.9998	16.2 ± 0.1	9.2 ± 13.8	5.4	6.0	1.6
1-pentanol	10-10000	0.9997	1.20 ± 0.01	-50.3 ± 23.4	13.2	0.4	0.4
2-hexanone	2-2000	0.9996	5.03 ± 0.03	196.0 ± 24.3	10.0	0.4	0.3
ethyl butanoate	2-2000	0.9996	12.02 ± 0.09	255.9 ± 64.8	8.4	0.7	0.3
α-pinene	0.5-250	0.9996	155.5 ± 1.23	120 ± 132	4.4	3.9	2.9
benzaldehyde	2-1000	0.9997	6.92± 0.04	-49.2 ± 19.0	5.7	1.6	0.6
eucalyptol	2-400	0.9997	47.7 ± 0.4	-145.9 ± 53.8	4.3	5.3	0.3
acetophenone	2-2000	0.9998	7.63 ± 0.04	138.4 ± 29.5	4.4	2.0	0.9
2-undecanoate	0.5-10	0.9977	2799 ± 78	283 ± 398	5.7	1.2	5.2
ethyl nonanoate	0.5-10	0.9957	2500 ± 95	76.9 ± 48.9	13.6	1.1	1.2
1-undecanol	0.5-25	0.9955	2542 ± 75	602 ± 97	10.1	1.4	7.5
			*Obtained from triplicate extractions at calibration levels 3(1), 6(2), 10(3) (Table S3)				
			PA				
benzene	0.5-100	0.9998	108.2 ± 0.8	81.9 ± 33.1	3.8	0.9	2.2
1-pentanol	10-2000	0.9999	15.1 ± 0.1	22.6 ± 60.6	1.2	1.4	5.7
2-hexanone	2-400	0.9998	25.7 ± 0.2	233.3 ± 26.5	1.6	2.0	2.3
ethyl butanoate	2-400	0.9998	64.5 ± 0.4	318.0 ± 58.8	0.5	4.3	7.6
α-pinene	0.5-100	0.9991	561.2 ± 7.6	578 ± 297	5.3	8.4	6.5
benzaldehyde	2-400	0.9997	87.2 ± 0.6	400 ± 101	4.4	5.7	7.2
eucalyptol	2-400	0.9992	163.2 ± 2.4	902 ± 400	5.4	8.9	3.5
acetophenone	2-400	0.9996	85.6 ± 0.8	498 ± 125	4.6	1.4	6.1
2-undecanoate	0.5-5	0.9994	10730 ± 192	-1077 ± 528	3.5	4.0	3.8
ethyl nonanoate	0.5-5	0.9992	10550 ± 211	-1276 ± 580	0.9	9.8	3.3
1-undecanol	0.5-5	0.9935	13880 ± 798	-2671 ± 2195	3.3	14.4	4.1
			*Obtained from triplicate extractions at calibration levels 3(1), 6(2), 8(3) (Table S3)				
			PIL **2**				
benzene	1-500	0.9993	0.586 ± 0.002	3.7 ± 0.5	7.3	5.2	2.3
1-pentanol	20-10000	0.9953	0.1603 ± 0.002	-8.9 ± 7.1	26.5	2.3	4.0
2-hexanone	20-2000	0.9972	0.77 ± 0.09	42.5 ± 27.8	13.9	3.3	4.4
ethyl butanoate	4-2000	0.9969	0.68 ± 0.01	6.0 ± 7.5	5.7	2.7	9.8
α-pinene	1-500	0.9961	7.98 ± 0.12	-48.7 ± 24.4	13.6	3.4	4.7
benzaldehyde	40-1000	0.9908	2.5 ± 0.2	62.5 ± 37.2	<LOQ	5.4	4.0

eucalyptol	4-2000	0.9962	2.69 ± 0.04	-65.2 ± 34.1	38.4	6.4	2.4
acetophenone	20-1000	0.9982	1.5 ± 0.4	77.6 ± 65.1	<LOQ	3.4	4.4
2-undecanoate	1-250	0.9993	109.7 ± 1.5	-205 ± 179	22.6	0.7	4.1
ethyl nonanoate	1-250	0.9979	113.1 ± 3.0	-492 ± 362	22.4	1.2	6.2
1-undecanol	1-200	0.9993	142.4 ± 2.6	-19.7 ± 2.1	33.6	4.2	0.9
*Obtained from triplicate extractions at calibration levels 3(1), 6(2), 10(3)(Table S3)							
			PDMS 7 µm				
benzene	1-500	0.9998	7.84 ± 0.04	26.5 ± 8.3	2.0	2.1	3.5
1-pentanol	20-10000	0.9942	0.48 ± 0.02	-34.3 ± 60.2	4.5	5.9	4.2
2-hexanone	4-2000	0.9972	2.31 ± 0.07	158.1 ± 56.3	2.6	4.0	3.1
ethyl butanoate	4-2000	0.9913	8.46 ± 0.32	21.0 ± 25.9	1.1	2.8	2.6
α-pinene	1-250	0.9990	137.4 ± 1.9	77.1 ± 20.4	2.2	6.6	2.3
benzaldehyde	4-1000	0.9983	3.12 ± 0.06	140.4 ± 23.7	2.7	3.0	4.0
eucalyptol	4-1000	0.9929	33.3 ± 1.3	-838 ± 111	5.5	4.1	3.6
acetophenone	4-1000	0.9978	1.92 ± 0.09	332.9 ± 40.2	5.7	3.0	2.7
2-undecanoate	1-20	0.9984	893.4 ± 20.6	428 ± 212	3.1	1.8	3.7
ethyl nonanoate	1-20	0.9997	1277 ± 11	63.9 ± 11.6	3.1	5.0	9.5
1-undecanol	1-25	0.9980	566.4 ± 76.5	983.2 ± 1061	11.9	4.1	0.1
*Obtained from triplicate extractions at calibration level 3(1), 6(2), 10(3) (Table S3)							

Highlights:

- Two different polymeric ionic liquid-based SPME coatings, namely poly([VBHDIM][NTf2]) and poly([DDMGlu][MTFSI]) were evaluated for analysis of pesticides and fruit metabolites.
- The PIL-based coatings were compared to commercially available SPME coatings in terms of their performance toward extraction efficiency and coverage.
- The partition coefficients (K_{fs}) of the tested coatings were calculated, with poly([VBHDIM][NTf2] demonstrating similar or better performance compared to the commercial coatings.
- PIL-based coatings demonstrated their capability towards broad extractive coverage of analytes characterized by various physico-chemical properties.