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Yunjing Meng, *University of Toledo*

Veronica Pino, *University of Toledo*

Jared L. Anderson, *University of Toledo*



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Exploiting the Versatility of Ionic Liquids in Separation Science: Determination of Low-Volatility Aliphatic Hydrocarbons and Fatty Acid Methyl Esters Using Headspace Solid-Phase Microextraction Coupled to Gas Chromatography

Yunjing Meng, Verónica Pino,[†] and Jared L. Anderson*

Department of Chemistry, The University of Toledo, Toledo, Ohio 43606

The determination of high-molecular weight aliphatic hydrocarbons and fatty acid methyl esters possessing high boiling points and low vapor pressures was performed using a headspace solid-phase microextraction gas chromatography (HS-SPME-GC) method comprised entirely of ionic liquids (ILs). The method utilizes three independently structurally engineered ILs in which the imparted physical and chemical properties make them compatible with the requirements of each component of the method. Component one is composed of a thermally stable IL solvent used to increase the equilibrium concentration of analytes in the HS, component two is a SPME sorbent coating based on a polymeric ionic liquid (PIL) for the selective HS extraction of analytes, and component three is an IL-based low-bleed GC stationary phase that performs the selective separation of the analytes. The method demonstrates the versatility of ILs within separation science in addition to determining these analytes, for the first time, using HS extraction at elevated temperatures with detection limits ranging from 0.3 to 0.6 mg kg⁻¹, relative recoveries from 69.9% to 106%, and precision (relative standard deviation for the overall method) from 6.9% to 16%.

Static headspace-gas chromatography (HS-GC) is a common approach used for the analysis of analytes in the vapor phase that are in equilibrium with a solid or liquid phase. In the sampling of less volatile analytes, it is often necessary to thermostat the liquid or solid phase at elevated temperatures, thereby increasing the equilibrium amount of analyte present in the headspace.¹ However, heating of the sample often causes partial vaporization of the solvent, resulting in increased pressure build-up within the sample vial. For that reason, it has been stated that the vapor

pressure of the extracting solvent dramatically affects the enrichment factor achieved in HS-GC.²

We are particularly interested in utilizing the unique properties of ionic liquids (ILs) to address challenges in separation science. ILs are an interesting class of nonmolecular solvents due to their tunable physicochemical properties, making them versatile solvents in a variety of applications.^{3,4} Important properties of ILs include their low vapor pressure, high thermal stability, variable viscosity, and the ability to interact with dissolved molecules through a multitude of solvation interactions. The application of ILs as a sample solvent in HS-GC has been previously reported.^{5–7} In these studies, the low vapor pressure of the ILs was exploited to avoid pressure build-up in the sample vial as well as to enhance the sensitivity when determining analytes possessing high boiling points. Once present in the headspace, a method is required to sample the analytes for subsequent analysis. Various approaches, such as headspace solid-phase microextraction (HS-SPME), can be used to preconcentrate volatile analytes from the headspace of a sample. SPME is a solvent free sampling technique first introduced by Pawliszyn and co-workers.⁸ The success of SPME is due to its simplicity, speed, and sensitivity. SPME utilizes a fused silica fiber coated with a small volume of stationary phase into which analytes from the sample partition. Analytes are then thermally desorbed from the fiber coating in the injector of the GC. The utilization of HS-SPME can be problematic if a sample needs to be heated as the vaporized solvent may compete with target analytes for sorption sites within the SPME coating and thus may decrease the sensitivity and selectivity of the extraction.

In this technical note, we demonstrate the versatility of ILs in separation science by introducing a HS-SPME-GC extraction/separation method in which carefully designed ILs are used as (1) a sample solvent for hydrocarbons and fatty acid methyl esters (FAMES) possessing high boiling points (higher than 380 °C) and

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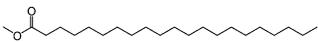
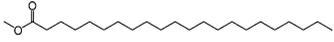
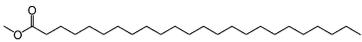
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* To whom correspondence should be addressed. Jared L. Anderson, Department of Chemistry, The University of Toledo, 2801 W. Bancroft Street, MS 602, Toledo, OH 43606. Phone: (419) 530-1508. Fax: (419) 530-4033. E-mail: Jared.Anderson@UToledo.edu.

[†] On leave from the Department of Analytical Chemistry, Universidad de La Laguna, Spain.

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Table 1. Structures, Boiling Points, and Vapor Pressures of the Hydrocarbons and Fatty Acid Methyl Esters Evaluated in This Study

Analyte	Structure and Molecular Formula	Boiling Point (at 760 torr) ^a	Vapor Pressure (at 25°C) ^a
Tricosane	 (C ₂₃ H ₄₈)	380°C	1.24 × 10 ⁻⁵ torr
Hexacosane	 (C ₂₆ H ₅₄)	412°C	1.26 × 10 ⁻⁶ torr
Triacontane	 (C ₃₀ H ₆₂)	450°C	7.37 × 10 ⁻⁸ torr
Methyl heneicosanoate	 (CH ₃ (CH ₂) ₁₉ COOCH ₃)	387°C	3.47 × 10 ⁻⁶ torr
Methyl behenate	 (CH ₃ (CH ₂) ₂₀ COOCH ₃)	398°C	1.52 × 10 ⁻⁶ torr
Methyl tetracosanoate	 (CH ₃ (CH ₂) ₂₂ COOCH ₃)	420°C	3.03 × 10 ⁻⁷ torr

^a Calculated using Advanced Chemistry Development (ACD/Laboratories) Software version 9.04 for Solaris.

low vapor pressures, (2) a high selectivity SPME sorbent coating for the HS extraction of analytes, and (3) a low-bleed, high-selectivity stationary phase for GC. Each IL has been independently structurally engineered so that the imparted physical and chemical properties are compatible with the requirements of each component of the method thereby producing a robust method in terms of overall analytical performance. To our knowledge, this is the first report in which these analytes have been successfully quantified by HS-GC.

EXPERIMENTAL SECTION

Materials. The six analytes determined in this work were purchased from Sigma-Aldrich (Milwaukee, WI). Their molecular structures, boiling points, and vapor pressures are shown in Table 1. PTFE stir bars (6 mm long) and silicone oil were obtained from Fisher Scientific (Fair Lawn, NJ). Untreated fused silica capillary tubing (0.25 mm i.d.) and glass vials (2 mL) with PTFE septa caps were purchased from Supelco (Bellefonte, PA). A model 324 direct immersion heater was purchased from Cole Parmer (Vernon Hills, IL), and a model Arrow 6000 overhead stirrer was obtained from Arrow Engineering Co., Inc. (Hillside, NJ). A Cimarec magnetic stirrer was acquired from Barnstead Thermolyne (Dubuque, IA). The IL 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [HMIM] [FAP] was provided by Merck KGaA (Darmstadt, Germany). The molecular structure of this IL is shown in Figure 1.

Methods. The coating of the GC column with the high stability IL was performed using the static method on a 15 m capillary column (0.25 mm i.d.). The coating method utilized a 0.25% (w/v) solution of the dicationic IL 1,12-di-(3-butylimidazolium)-dodecane bis[(trifluoromethyl)sulfonyl]imide [C₁₂(BIM)₂] [NTf₂]

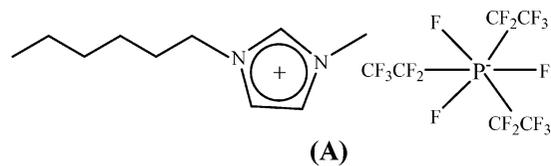
(shown in Figure 1) in methylene chloride at 40 °C, following a previously published procedure.⁹ The synthesis of this dicationic IL was carried out as previously reported.¹⁰ Coated capillaries were conditioned overnight from 40 to 100 °C at 1 °C min⁻¹ using a constant flow of helium at a flow rate of 1.0 mL min⁻¹. Column efficiency was tested with naphthalene at 120 °C. The column possessed an efficiency of 1554 plates m⁻¹ at 120 °C and was tested weekly to ensure that the efficiency remained constant throughout the study.

All GC experiments were conducted using an Agilent Technologies 6890N gas chromatograph (Palo Alto, CA). The gas chromatograph was equipped with thermal conductivity (TCD) and flame ionization (FID) detectors coupled in series. Helium was used as the carrier gas with a flow rate of 1 mL min⁻¹. The inlet and detector temperatures were operated at 250 °C. Splitless injection was used during all experiments. The makeup flow of helium was maintained at 45 mL min⁻¹, the hydrogen flow at 40 mL min⁻¹, and the air flow at 450 mL min⁻¹. The following temperature program was used in the separation of the analytes: the initial temperature of 150 °C was held for 4 min, then raised to 160 °C at a ramp of 10 °C min⁻¹ and held for 2 min, and then raised to 170 °C at a speed of 10 °C min⁻¹ and held for 5 min. Afterward, a 10 °C min⁻¹ ramp was used to increase the oven temperature to 180 °C and was held for another 5 min. Finally, the temperature of the oven was raised to 195 °C using a ramp of 15 °C min⁻¹ and was held for 15 min. Agilent ChemStation software was used for data acquisition.

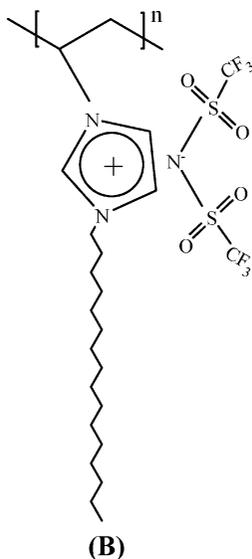
The preparation of the polymeric ionic liquid (PIL)-based SPME coating involved the synthesis of the poly[ViHDIM] [NTf₂]

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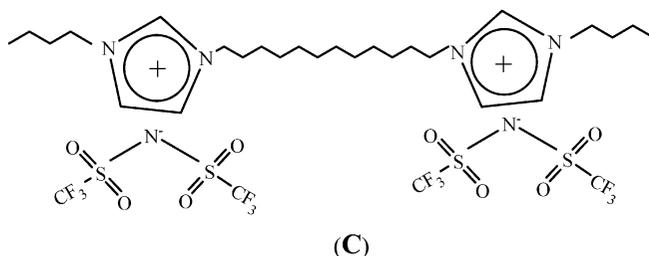
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(A)
1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [HMIM] [FAP]



(B)
poly(1-vinyl-3-hexadecylimidazolium bis((trifluoromethyl)sulfonyl)imide) (poly[ViHDIM] [NTf₂])



(C)
1,12-Di-(3-butylimidazolium)dodecane bis((trifluoromethyl)sulfonyl)imide [C₁₂(BIM)₂] [NTf₂]

Figure 1. Structures of the ILs and PIL used in the HS-SPME-GC method: IL (A) was used as the high-temperature solvent to solubilize the analytes in the study, PIL (B) was used as a SPME sorbent coating, and IL (C) was used as a low-bleed, highly selective stationary phase in GC.

PIL (see structure in Figure 1) followed by the preparation of fibers using recently published procedures.¹¹ The film thickness of the coating was in the range of 10–15 μm , as estimated by optical microscopy. The desorption time for the fiber in the GC injector was fixed at 5 min in all experiments.

A stock solution was prepared by dissolving 2 mg of each of the analytes into 40 g of the [HMIM] [FAP] IL, which was dried in a vacuum oven at 70 °C overnight before use. The stock solution was maintained at approximately 60 °C in order to ensure a homogeneous mixture. The working solution was prepared by diluting different amounts of the stock solution with pure [HMIM] [FAP] to various concentrations. The total mass of the working solution was maintained at 400 mg in the sample vial, and the volume of the headspace was 1.5 mL for all extractions. The

sorption-time profiles were obtained by immersion of the PIL coated fiber into the headspace of the working standard solution containing the studied analytes at a concentration of 25 mg of analyte per kg of [HMIM] [FAP], using different extraction times (from 15 to 150 min) while stirring at 170 \pm 10 °C.

Figure 2 shows a detailed schematic of the extraction and separation system utilized in this work. Static headspace extractions were performed by first piercing the sampling vial containing the IL/analyte mixture and stir bar with the syringe housing the SPME fiber. The sampling vial was then positioned in the heated silicone oil bath followed by stirring of the IL/analyte mixture using a magnetic stirrer. The SPME fiber was then exposed to the headspace of the sampling mixture. In order to minimize large temperature variations throughout the extraction, an overhead mechanical stirrer was used to stir the oil bath. Following the

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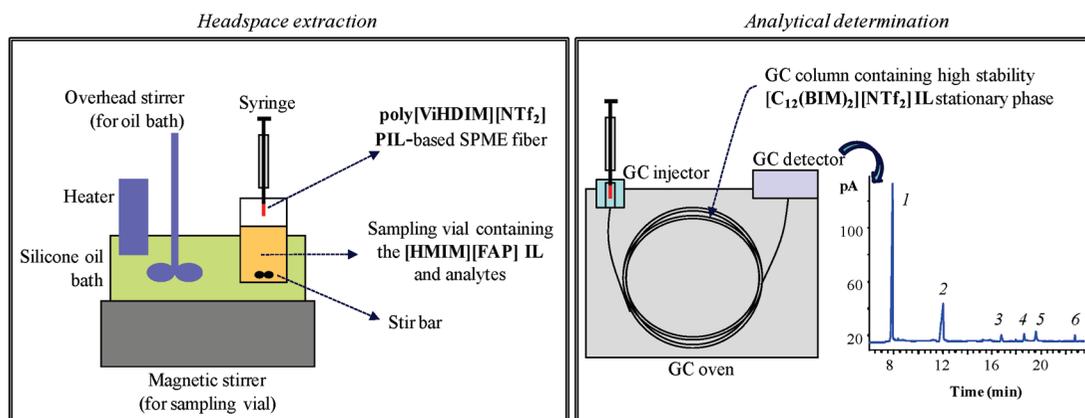


Figure 2. Schematic diagram demonstrating the use of [HMIM][FAP] as a headspace solvent, the poly[ViHDIM][NTf₂] PIL as the SPME sorbent coating, and the [C₁₂(BIM)₂][NTf₂] IL as a high stability GC stationary phase. The analytes are (1) tricosane, (2) hexacosane, (3) methyl heneicosanoate, (4) methyl behenate, (5) triacontane, and (6) methyl tetracosanoate.

extraction, the SPME fiber was withdrawn into the syringe, the syringe removed from the vial, and the fiber thermally desorbed in the GC injector thereby subjecting the analytes to the IL-based stationary phase for separation.

RESULTS AND DISCUSSION

Component 1: [HMIM][FAP] IL as Thermally Stable Solvent for High-Temperature Extraction. To function as an effective solvent in headspace extraction studies, an IL should possess the following features: (1) be chemically unreactive with analytes being examined, (2) exhibit high thermal stability, (3) ability to dissolve the analytes in the concentration range needed for making adequate calibration curves, and (4) exhibit reasonably low viscosity to facilitate the preparation of samples and standards as well as to ensure efficient sample agitation during extraction. Merck KGaA has recently developed a class of hydrophobic ILs that exhibit much lower water uptake than commonly studied NTf₂⁻ and hexafluorophosphate-based ILs.^{12–14} ILs containing this unique anion exhibit viscosities comparable to the NTf₂⁻ anions. Thermal gravimetric analysis of this class of ILs has revealed that imidazolium-based ILs decompose at temperatures above 280 °C. The solubility of the analytes in the [HMIM][FAP] IL was found to be acceptable in the range up to 50 mg of analyte per kg of IL.

Component 2: Poly[ViHDIM][NTf₂] PIL as SPME Sorbent Coating for Selective Headspace Extraction of Analytes. Recently, a new class of sorbent coatings for SPME based on PILs was introduced.¹¹ The polymeric nature of these compounds provides them additional thermal stability as well as exceptional film stability, thereby producing high extraction-to-extraction reproducibility and lifetimes comparable to commercially coated fibers. The selectivity of PIL-based coatings can be modulated by introducing functional groups to the cationic portion of the IL or by incorporating different anions to impart desired solvent characteristics. In this study, the poly[ViHDIM][NTf₂] PIL was chosen as it undergoes stronger dispersion-type interactions with the analytes thus producing high extraction efficiencies.

Component 3: [C₁₂(BIM)₂][NTf₂] IL as Highly Selective and Low-Bleed GC Stationary Phase. ILs have been shown to be highly selective stationary phases for GC.⁹ To fulfill the requirements of this component for this study, a relatively nonpolar stationary phase possessing low bleed at elevated temperatures was required. The dicationic IL [C₁₂(BIM)₂][NTf₂] was chosen as it has been shown previously to exhibit high thermal stability, a wide liquid range, and broader selectivities compared to many traditional classes of monocationic ILs.¹⁰

Synergy of Three IL-Based Components in Extraction/Separation System. The analytes extracted in this work include three hydrocarbons, tricosane, hexacosane, and triacontane, and three fatty acid methyl esters, methyl behenate, methyl heneicosanoate, and methyl tetracosanoate. These analytes were dissolved in the [HMIM][FAP] IL and then extracted by HS-SPME-GC. In order to achieve adequate extraction efficiencies using the HS-SPME method, high temperature is required for these less volatile analytes. However, the sorption of the analytes to the SPME coating is an exothermic process, and as the temperature increases, the analyte to coating partition coefficient decreases. Therefore, the temperature must be optimized so that the decrease of the partition coefficient is offset by the increase in the equilibrium concentration of the analytes in the headspace to achieve reasonable extraction efficiencies. The optimized extraction temperature was 170 ± 10 °C. The extraction time and temperature in several previously reported studies involving headspace applications for less volatile analytes (with boiling points ranging from 152 to 228 °C) are 10 min at 110 °C,⁶ 15 min at 100 °C,⁷ and 15 min at 150 or 180 °C, depending on the analyte.⁵

Sorption-time profiles were generated by performing the extraction at various time intervals to identify the equilibration time using the optimum temperature. Figure 3 shows the sorption-time profiles obtained by plotting the analyte peak area versus the extraction time. Tricosane and hexacosane reach equilibrium at around 60 min whereas the remaining analytes reach equilibrium in around 100 min. An extraction time of 100 min was considered as the optimum extraction time. The comparison of the extraction efficiencies for the hydrocarbons and FAMES can also be observed in Figure 3. With respect to the hydrocarbons, the lightest hydrocarbon (tricosane) exhibits the highest extraction efficiency whereas the lowest extraction efficiency

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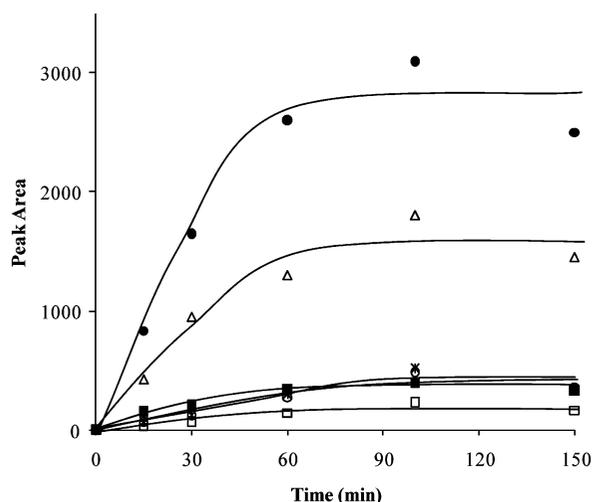


Figure 3. Sorption-time profiles obtained for the PIL fiber poly-[ViHDIM][NTf₂] when performing headspace extraction at 170 ± 10 °C using a concentration of 25 mg of analyte per kg of [HMIM][FAP] IL. The studied analytes are (●) tricosane, (Δ) hexacosane, (*) methyl heneicosanoate, (○) methyl behenate, (■) triacontane, and (□) methyl tetracosanoate.

is seen with the heaviest hydrocarbon, triacontane. The same trend is observed with the three FAMES, although their extraction efficiencies are much lower compared to the studied hydrocarbons. The trend in the extraction efficiency is consistent with the vapor pressures and boiling points of these analytes (see Table 1).

Analytical Performance of the Method. Calibration curves were obtained using working standard solutions of analytes in the [HMIM][FAP] IL at different concentrations while performing the extraction at the optimum extraction time and temperature. The figures of merit for the entire method, shown in Table 2, include the sensitivity, calibration range, correlation coefficients, error of the estimate, and limits of detection. The obtained linearity of the overall method was found to be acceptable, with correlation coefficients (R) ranging from 0.990 to 0.998. The sensitivity, which can be evaluated by the slope, is higher for the hydrocarbons, particularly for tricosane, than for the FAMES. It can be clearly observed that the sensitivity decreased with increasing carbon chain length of the hydrocarbons and FAMES. The limits of detection varied from 0.1 mg kg^{-1} for tricosane to 0.6 mg kg^{-1} for methyl tetracosanoate. This constitutes the first report of a headspace extraction approach for these particular analytes. However, other analytes possessing high boiling points have been determined previously by headspace extraction. They include *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone

Table 3. Precision and Extraction Efficiency at Different Spiking Levels for the Overall Method

analyte	spiking level: 4 mg kg^{-1}		spiking level: 20 mg kg^{-1}	
	RSD ^a (%)	RR ^b (%)	RSD ^a (%)	RR ^b (%)
tricosane	15	99.1	10	75.9
hexacosane	18	78.5	5.9	69.9
triacontane	21	114	16	103
methyl behenate	22	121	15	98.3
methyl heneicosanoate	21	115	16	78.3
methyl tetracosanoate	11	122	6.9	106

^a RSD: relative standard deviation for $n = 4$. ^b RR: relative recovery for $n = 4$.

(NPM), propylene glycol (PG), formamide, tri-*n*-butylamine (tBA), and 2-ethylhexanoic acid (2EHA). The boiling points for these analytes are in the range $152\text{--}228$ °C, and the reported detection limits for these analytes are 53 mg L^{-1} (ref 6) or $1\text{--}90 \text{ mg L}^{-1}$ depending on the IL solvent⁷ for DMF; 2.5 mg L^{-1} (ref 6) or $1\text{--}100 \text{ mg L}^{-1}$ depending on IL solvent⁷ for NMP; 13 mg L^{-1} for formamide;⁵ 8 mg L^{-1} for tBA;⁵ and 22 mg L^{-1} for 2EHA.⁵ For comparison, the analytes determined in this method possess boiling points in the range $380\text{--}450$ °C with detection limits less than 0.6 mg kg^{-1} .

The reproducibility of the method was evaluated by carrying out a series of extractions using working standard solutions of the analytes at two different concentration levels, namely, 4 and 20 mg of analyte per kg of [HMIM][FAP] IL. The obtained results can be observed in Table 3. The relative standard deviation ranged from 11 to 22% for the lower spiking level (4 mg kg^{-1}) and from 5.9 to 16% for the higher spiking level (20 mg kg^{-1}). This precision reflects all of the errors in the overall method, including the temperature fluctuations that occur during SPME. The extraction efficiency, expressed as relative recoveries, varied from 78.5 to 122% at the lower spiking level and from 69.9 to 106% at the higher spiking level. Under the extreme extraction temperatures and times used in this study, the fiber lifetime dropped to approximately 30 extractions before the extraction-to-extraction reproducibility decreased dramatically. Finally, the performance of the GC column comprised of the [C₁₂(BIM)₂][NTf₂] IL stationary phase was evaluated. A sample chromatogram of the six analytes separated on this stationary phase is shown as Supporting Information. The reproducibility of the analyte retention times during the study produced RSD values ranging from 0.9 to 2.6% ($n = 60$).

Table 2. Figures of Merit of the Calibration Curves for the Overall Method Using a Three Component Extraction and Separation System Comprised of Ionic Liquids

analyte	calibration range (mg kg^{-1})	slope \pm SD ^a	error of the estimate	R	LOD ^b (mg kg^{-1})
tricosane	1–45	137.7 ± 3.4	164	0.998	0.1
hexacosane	1–35	123.4 ± 4.6	151	0.996	0.2
triacontane	1–30	36.8 ± 2.2	36.3	0.993	0.3
methyl behenate	2–30	25.9 ± 0.5	28.3	0.998	0.4
methyl heneicosanoate	1–45	13.4 ± 0.7	14.7	0.994	0.4
methyl tetracosanoate	2–45	12.6 ± 0.7	29.6	0.990	0.6

^a SD: error of the slope for $n = 8$ calibration levels. ^b LOD: limits of detections calculated as 3 times the signal-to-noise ratio.

CONCLUSIONS

One of the most interesting and useful characteristics of ILs lies with their vast structural tuneability which provides a wealth of opportunities in adapting the physical and chemical properties of the material for applications in separation science. Herein, an analytical method utilizing three distinct and separate IL components was used to perform high-temperature headspace extraction and separation of six analytes possessing high boiling points and low vapor pressures. The [HMIM] [FAP] IL has been shown to be an excellent solvent in that the hydrophobic and refractory nature of the IL promotes dissolution of the apolar analytes while avoiding pressure build-up within the sample vial under extreme temperatures. As a selective sorbent coating for SPME, the PIL component exhibits acceptable extraction efficiency of the studied analytes under the extreme experimental conditions. Finally, the structural design of the IL-based GC stationary phase produces a thermally stable material that exhibits high separation selectivity of the analytes while producing minimal column bleed. The overall method nicely demonstrates the versatility of ILs within separation science for the determination of low volatility analytes using the headspace extraction mode with detection limits ranging from 0.3 to 0.6 mg kg⁻¹, relative recoveries ranging from 69.9% to 106%, and precision values between 5.9 and 22% as relative standard deviation. This method may be particularly useful for monitor-

ing reaction products formed during catalysis experiments when ILs are used as the reaction solvent. Future work will involve the use of blended ILs and task-specific ILs to further improve the sensitivity and reproducibility of the overall method.

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SUPPORTING INFORMATION AVAILABLE

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