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Determination of acrylamide in brewed coffee and coffee powder using polymeric ionic liquid-based sorbent coatings in solid-phase microextraction coupled to gas chromatography–mass spectrometry

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ABSTRACT

This study describes a simple and rapid sampling method employing a polymeric ionic liquid (PIL) sorbent coating in direct immersion solid-phase microextraction (SPME) for the trace-level analysis of acrylamide in brewed coffee and coffee powder. The crosslinked PIL sorbent coating demonstrated superior sensitivity in the extraction of acrylamide compared to all commercially available SPME coatings. A spin coating method was developed to evenly distribute the PIL coating on the SPME support and reproducibly produce fibers with a large film thickness. Ninhydrin was employed as a quenching reagent during extraction to inhibit the production of interfering acrylamide. The PIL fiber produced a limit of quantitation for acrylamide of 10 $\mu g\,L^{-1}$ and achieved comparable results to the ISO method in the analysis of six coffee powder samples.

1. Introduction

Acrylamide is an unsaturated amide formed when carbohydrate-rich foods are subjected to high temperatures during cooking or thermal processing [1]. Initial studies on the mechanistic pathway of acrylamide formation in food proposed the Maillard reaction (non-enzymatic browning reaction) as the major chemical route [2,3]. Acrylamide has previously been observed in several food matrices such as potato crisps, French fries, crispy bread, breakfast cereals, pastries, and coffee. The concentration levels of acrylamide are high in coffee compared to other food products, although lower levels can be expected due to dilution within coffee beverages [4]. The toxicological properties of acrylamide have been well-studied and include neurotoxicity, genotoxicity, carcinogenicity, and reproductive toxicity [5,6]. For this reason, it is possible that maximum limits of acrylamide in food could be proposed in the future thereby requiring new analytical methods for its sensitive analysis.

Analytical methods employing high performance liquid chromatography (HPLC) coupled to mass spectrometry (MS) or tandem MS (MS/MS) for the analysis of acrylamide in food have been reported [7,8]. Gas chromatography-mass spectrometry (GC–MS) has also been demonstrated to be a viable alternative to HPLC–MS in the analysis of acrylamide [9–11]. Regardless if the method involves HPLC or GC, the analysis of acrylamide in complex food products such as coffee requires several pretreatment/cleanup steps before the sample can be subjected to analysis. Conventional extraction techniques using solid phase extraction (SPE) have been previously applied to purify crude sample extracts prior to the analysis of acrylamide [7–9]. However, due to the multiple steps inherent to SPE, these techniques are often cumbersome and can be time-consuming. Additionally, commercial SPE cartridges may lack the selectivity needed to discriminate the target analyte(s) from other matrix components, which can result in poor method accuracy and inadequate limits of detection (LOD).

Over the past few decades, solid-phase microextraction (SPME) has become a popular extraction technique in food analysis, due to its exceptional simplicity and ease-of-use [12]. SPME is an equilibrium-based extraction/pre-concentration technique that enables the consolidation of sample preparation, cleanup, and sampling into one simple step [13]. Compared to SPE, SPME is a non-exhaustive extraction technique that uses considerably smaller sample volumes and is not susceptible to analyte breakthrough. A number of studies have exploited SPME coupled to GC–MS for the determination of acrylamide using commercially available sorbent

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Table 1
Composition and abbreviations of all PIL-based SPME sorbent coatings examined in this study.

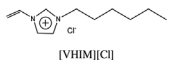
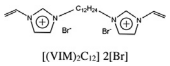
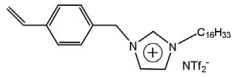
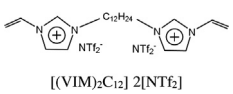
	IL monomer	IL-based crosslinker	Support	Coating method	Length of the sorbent coating	Approximate film thickness
Fiber **1**	 [VHIM][Cl]	 [(VIM)$_2$C$_{12}$] 2[Br]	Silica	Dip coating	1 cm	~10 μm
Fiber **2**	 [VBHDIM][NTf$_2$]	 [(VIM)$_2$C$_{12}$] 2[NTf$_2$]	Silica	Dip coating	1 cm	~10 μm
Fiber **3**			NiTi wire	Spin coating	1 cm	~35 μm
Fiber **4**			NiTi wire	Spin coating	1.3 cm	~35 μm
Fiber **5**			NiTi wire	Spin coating	1.3 cm	~35 μm
Fiber **6**			NiTi wire	Spin coating	1.3 cm	~35 μm

Table 2
Analytical performance of the 1.3 cm long spin coated 50% (w/w) [(VIM)$_2$C$_{12}$] 2[NTf$_2$] in [VBHDIM] [NTf$_2$] PIL-based fiber for the extraction of acrylamide.

LOQ	10 μg L^{-1}
Linearity	0.984
Analytical precision (% RSD 100 μg L^{-1})	10.9% (n = 5)
Fiber-to-fiber reproducibility (% RSD 100 μg L^{-1})	14.0% (n = 3)

coatings [8,14–17]. However, these approaches have been hindered by poor LODs when analyzing acrylamide at ultra trace-levels in complex matrices. Within the last few years, Anderson and co-workers have developed a contemporary class of SPME sorbent coating based on polymeric ionic liquids (PIL) [18]. PIL coatings are highly versatile as they can be custom designed to exhibit superior selectivity towards various classes of analyte(s) by altering the chemical structures of the cation and anion while also tailoring their unique combinations [18,19]. In addition, these coatings can be bonded and crosslinked to rugged supports, such as superelastic nitinol (NiTi) wires [20]. The physico-chemical properties (e.g., polarity and water solubility) of acrylamide are in-line with the sorbent characteristics of PIL-based SPME materials, particularly in terms of selectivity. Therefore, they can be exploited to improve the recovery of acrylamide from aqueous matrices such as coffee brew.

We report in this manuscript a crosslinked PIL-based SPME sorbent coating that exhibits superior sensitivity over commercially available coatings for the trace-level determination of acrylamide in brewed coffee and coffee powder when coupled to GC–MS. This report represents the first SPME method for the direct immersion analysis of acrylamide in brewed coffee and is a much faster method than the currently employed ISO SPE-HPLC–MS/MS method taken as a reference [21]. This method requires no derivatization steps, can be easily automated, and is rugged despite the complexity of the coffee matrix.

2. Experimental

2.1. Materials

Acrylamide (99.9%), ninhydrin, asparagine (98%), glucose (99.9%), menthol (99%), ethanol (99.9%) and DAROCUR 1173 (97%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Deionized water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Table 1 lists the crosslinked PIL-based SPME fiber coatings that were evaluated in this study. All IL monomers and crosslinkers were prepared according to previously published methods [19,20] and were fully characterized by ^{1}H NMR (see Supporting information). Two PIL SPME fibers possessing thin sorbent coatings (~10 μm) with varying chemical composition, namely, 50% (w/w) 1,12-di(3-vinylimidazolium)dodecane dibromide [(VIM)$_2$C$_{12}$] 2[Br] in 1-vinyl-3-hexylimidazolium chloride [VHIM][Cl] (Fiber **1**) and 50% [(VIM)$_2$C$_{12}$] 2[NTf$_2$] in 1-vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide [VBHDIM][NTf$_2$] (Fiber **2**) were fabricated on a 1 cm portion of etched and derivatized fused silica, according to previously reported methods [19]. Additional PIL-based fibers, composed of 50% (w/w) [(VIM)$_2$C$_{12}$] 2[NTf$_2$] in [VBHDIM] [NTf$_2$] and possessing larger film thicknesses (~30–45 μm), were prepared on derivatized NiTi wires as described previously [20]. Fiber **3** was crosslinked to a 1 cm portion of a derivatized NiTi wire and Fibers **4**–**6** were crosslinked to 1.3 cm portions of derivatized NiTi wires (Table 1).

Five commercially available SPME fibers, namely, DVB/Carboxen/PDMS (2 cm, ~30–50 μm), Carboxen/PDMS (1 cm, 75 μm), PA (1 cm, 85 μm), PDMS/DVB (1 cm, 65 μm), and PDMS (1 cm, 30 μm) were also employed in this study. These fibers were supplied by Supelco (Bellafonte, PA, USA) and were operated according the manufacturer instructions.

Commercial blends of roasted coffee and single-dose coffee capsules were kindly provided by Lavazza (Turin, Italy)

2.2. Standard and sample preparation

Individual stock solutions of acrylamide, asparagine, glucose, and menthol (used as an internal standard) were prepared in a 20 mL sealed vial by dissolving 2 mg of the pure standard in deionized water to obtain a concentration of 100 mg L^{-1}. A 200 mg L^{-1} solution of acrylamide was also prepared for preliminary studies. Working standards containing acrylamide, asparagine, and/or glucose were prepared by pipetting appropriate amounts of the stock standard(s) into a 20 mL sealed vial and further diluted with deionized water to obtain a final volume of 20 mL.

Brewed coffee samples were prepared from single-dose espresso capsules (7.6 g) using a Lavazza "A modo mio" espresso machine. Brewed coffee (19 mL) was mixed with 1 mL of 2% (w/v) ethanolic ninhydrin solution in a 20 mL sealed vial. Roasted coffee powder samples were prepared by transferring 2 g of roasted coffee powder into a 20 mL sealed vial containing 16.6 mL of deionized water. Subsequently, 44 μL of the menthol internal standard stock solution and 1 mL of 2% (w/v) ethanolic ninhydrin solution were added to the suspension. Reaction quenching by ninhydrin was carried out by placing the solution vial into a water bath thermostatted at 80 °C (with constant agitation at 1500 rpm) for 10 min. Sampling was performed immediately after the reaction.

2.3. Sampling and quantification of acrylamide in brewed coffee and coffee powder

Sampling was carried out by directly immersing the PIL and the commercial fibers into the sample solution under the following conditions: solution temperature: 25 °C, extraction time: 60 min; sample agitation: 1500 rpm. A temperature of 25 °C was selected to prevent the formation of new acrylamide in the sample at higher temperatures. The extraction time was optimized by sampling a solution of acrylamide at 5, 15, 30, 45, 60, 90 and 120 min with both the PIL and the commercial fibers. The analytes were then