



# Determination of imidazole derivatives by micellar electrokinetic chromatography combined with solid-phase microextraction using activated carbon-polymer monolith as adsorbent



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## ABSTRACT

In this study, an effective method for the separation of imidazole derivatives 2-methylimidazole (2-MEI), 4-methylimidazole (4-MEI) and 2-acetyl-4-tetrahydroxybutylimidazole (THI) in caramel colors using cation-selective exhaustive injection and sweeping micellar electrokinetic chromatography (CSEI-sweeping-MEKC) was developed. The limits of detection (LOD) and quantitation (LOQ) for the CSEI-sweeping-MEKC method were in the range of 4.3–80  $\mu\text{g L}^{-1}$  and 14–270  $\mu\text{g L}^{-1}$ , respectively. Meanwhile, a rapid fabrication activated carbon-polymer (AC-polymer) monolithic column as adsorbent for solid-phase microextraction (SPME) of imidazole colors was developed. Under the optimized SPME condition, the extraction recoveries for intra-day, inter-day and column-to-column were in the range of 84.5–95.1% (<6.3% RSDs), 85.6–96.1% (<4.9% RSDs), and 81.3–96.1% (<7.1% RSDs), respectively. The LODs and LOQs of AC-polymer monolithic column combined with CSEI-sweeping-MEKC method were in the range of 33.4–60.4  $\mu\text{g L}^{-1}$  and 111.7–201.2  $\mu\text{g L}^{-1}$ , respectively. The use of AC-polymer as SPME adsorbent demonstrated the reduction of matrix effect in food samples such as soft drink and alcoholic beverage thereby benefiting successful determination of trace-level caramel colors residues using CSEI-sweeping-MEKC method. The developed AC-polymer monolithic column can be reused for more than 30 times without any significant loss in the extraction recovery for imidazole derivatives.

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## 1. Introduction

Over the past decades, carbonaceous materials such as activated carbon (AC) has been considered as one of the first materials applied as sorbent in the removal of contaminants in biological, environmental, and food samples due to its high surface area (500–1000  $\text{m}^2 \text{g}^{-1}$ ), nanoporosity, and low cost [1–7]. AC comprises of six-membered rings with  $\text{sp}^2$ -hybridized carbon together with five- and seven-membered non-aromatic carbon rings with varying sizes of micropores that provide sites for adsorption [8,9]. Despite the success of AC as adsorbent, several problems associated to it has been encountered such as high cost of reusability, stability in nature, and inability to adsorb inorganic compounds at trace or ultra-trace levels [10]. To improve the stability and adsorbing capacity of AC, modifications on its functional surface have been proposed such as oxidative and non-oxidative approach [1]; however, functionalization on its surface requires additional

steps and also time consuming. In previous studies, deposition of polypyrrole (Ppy) into the pores and surface of AC with via in situ chemical oxidative polymerization in the presence of  $\text{FeCl}_3$  [11] or electrochemical polymerization [12] have been used as alternative method for surface functionalization of AC. The incorporation of PPy into the AC (PPy-AC) has facilitated in the removal of sulfates in aqueous solution [11,12].

Solid-phase microextraction (SPME), first introduced by Arthur and Pawlizyn [13], is a miniaturized form of solid-phase extraction (SPE) that offers several advantages such as short extraction time, less consumption of organic solvents, ease of operation, and can be automated to reduce the cost and time consuming sample preparation [14]. Among the proposed SPME techniques, porous monolithic materials for in-tube SPME (IT-SPME) has attracted considerable attention due to its chemical and mechanical stability, high surface area and rapid mass transfer under dynamic condition [14]. Typically, IT-SPME utilizes organic polymer [9,15], silica [16] and organic-silica hybrid monoliths [17] as adsorbent. However, drawbacks on their lack of interaction sites may lead to low adsorption efficiency [18]. Recently, several reports showed that by embedding nanoparticles [19], such as metal organic framework (MOF) [20–22] or graphene [23], into the monolithic polymer may

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increase the interaction sites and surface area. In particular, a rapid and novel synthetic method of incorporating MOF nanoparticles into polymer-based monolith was introduced using ionic liquid (IL) as reaction medium via microwave-assisted polymerization. These MOF-polymer hybrid monoliths were successfully applied as stationary phases in capillary electrochromatography (CEC) system [24–26] and SPME [20].

Food colorants like caramel colors are normally associated with food taste and to improve the visual perception of a product. Caramel colors are commonly present in food and beverages under Millard reaction system where carbohydrates like glucose, sucrose and inverted sugars are reacted in the presence of ammonium salts under controlled heat treatment [27]. Previous reports have suggested that during caramelization, undesired compounds such as 2-methylimidazole (2-MEI), 4-methylimidazole (4-MEI) and 2-acetyl-4-tetrahydroxybutyl imidazole (THI) are formed. These side products are deemed as carcinogenic compounds, which can inhibit enzyme (cytochrome P450) [28] at high levels of 2-MEI and 4-MEI; and proven to cause acute hyperexcitation in animals basis [29]. Meanwhile, THI was reported as an immunosuppressive compound [30,31]. Consequently, the European commission and Taiwan set a monitoring standard to 250 mg kg<sup>-1</sup> for 2-MEI and 4-MEI while 25 mg kg<sup>-1</sup> for THI to protect humans from these hazardous chemicals [32]. Several analytical methods such as gas chromatography (GC) and high performance liquid chromatography (HPLC) coupled to mass spectrometry (MS) detection have been used successfully in the determination of caramel colors in food samples with good limit of detections (LODs) ranging from 0.10 to 5.0 µg L<sup>-1</sup> or µg kg<sup>-1</sup> [33–41]. Similarly, capillary electrophoresis (CE) has been reported as alternative tool in the separation of imidazole derivatives due to its good separation efficiency, low solvent consumption and low cost. However, the CE methods, capillary isotachopheresis [42] and capillary zone electrophoresis [43,44], used to analyze the 2-MEI and 4-MEI have LODs as low as 0.16 mg L<sup>-1</sup>, which was poorer than the LC-MS or GC-MS method. To improve the sensitivity of CE, on-line pre-concentration methods such as cation-selective exhaustive injection (CSEI) sweeping (CSEI-sweeping) micellar electrokinetic chromatography (MEKC) [45–47] and anion-selective exhaustive injection (ASEI-sweeping) MEKC [48,49] have been developed to capable of further increasing its sensitivity up to a thousand- to million-folds [45].

Herein, we propose a new method of separating the imidazole derivatives using CSEI-sweeping-MEKC technique to further improve its detection limit. Despite the early studies about the utilization of AC as adsorbent for the removal of contaminants in environmental, biological and food samples, however, no attempt has been reported using AC as adsorbent for in-tube SPME without surface modification. In this work, AC was incorporated into the poly(butyl methacrylate-co-ethylene dimethacrylate) (poly(BMA-EDMA)) monolithic column (referred to AC-polymer) via room temperature ionic liquids (RTIL) as reaction media coupled with microwave-assisted heating and then was used as SPME adsorbent to extract caramel colors in food samples. Using the optimized condition, the AC-polymer monolithic column was applied in SPME of caramel colors in soft drink and alcoholic beverage. The extracted imidazole residues were analyzed using the proposed CSEI-MEKC method.

## 2. Experimental

### 2.1. Chemicals and reagents

All chemicals and reagents were at least of analytical grade. 2-Methylimidazole (2-MEI), 4-methylimidazole (4-MEI), 2-acetyl-4-tetrahydroxybutylimidazole (THI) and activated carbon

(AC) were purchased from Sigma-Aldrich (St. Louis, MO, USA). 2-Acrylamido-2-methylpropane sulfonic acid (AMPS), butyl methacrylate (BMA) (Lancaster, Ward Hill, MA, USA), ethylene dimethacrylate (EDMA) (ACROS, New Jersey, USA) and azobisisobutyronitrile (AIBN) (Showa, Tokyo, Japan) were used for the polymerization while 3-trimethoxysilylpropyl methacrylate (MSMA, 98%) were purchased from ACROS (Geel, Belgium) for pre-treatment of column. Methanol (MeOH), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and sodium dodecyl sulfate (SDS) were purchased from Merk (Darmstadt, Germany). The acetonitrile (ACN) and sodium hydroxide (NaOH) were purchased from J.T. Baker (Phillipsburg, NJ, USA). The ionic liquid, 1-hexyl-3-methylimidazolium tetrafluoroborate ([C<sub>6</sub>mim][BF<sub>4</sub>]), was synthesized in our laboratory and the identity was confirmed by <sup>1</sup>H NMR spectroscopy. The uncoated fused-silica capillary with 0.8 mm I.D. and 1.1 mm O.D. was purchased from Kimble Chase (Mexico). The 2- and 4-MEI were dissolved in methanol (MeOH) while THI was in dimethyl sulfoxide (DMSO) at a stock concentration of 1000 µg L<sup>-1</sup>.

### 2.2. Instrumentation

An LC pump (Model 260D, ISCO, Lincoln, NE, USA) was used for washing the monolithic columns. A scanning electron microscope model JSM-7600F (JEOL, Japan) was used for morphology observation. A FTIR spectroscopy model vertex 70v (Bruker, Billerica, MA, USA) was used for infrared spectrum measurement. A nitrogen adsorption/desorption equipment model Micromeritics Tri-star 3000 (Norcross, GA, USA) was employed for surface area and pore size measurement. Raman spectrometer model iHR 320 (Horiba Jobin Yvon, France) was used to probe the polymer, AC and AC-polymer.

### 2.3. Apparatus and operating conditions for CE

All experiments were performed using Beckman Coulter MDQ capillary electrophoresis system equipped with a photo diode array detector (Fullerton, CA, USA). Beckman Coulter MDQ 32 Karat software was used for instrumental control and data analysis. Separations were performed in uncoated fused-silica capillaries of 50.2 cm total length (40 cm to detector) and 50 µm I.D. (Polymicro Technologies, Phoenix, AZ, USA). The carrier electrolyte composed of pH 2 phosphoric acid (20 mM) and 140 mM SDS was used as the running buffer for (normal mode) MEKC and CSEI-sweeping MEKC separation.

#### 2.3.1. Normal mode MEKC

The capillaries were conditioned prior to separation by washing with 0.1 M sodium hydroxide (NaOH) solution (10 min, 20 psi), deionized water (10 min, 20 psi) and carrier electrolyte (i.e. running buffer) (5 min, 20 psi). Samples or standard solutions were pressure-injected into the capillary for conventional MEKC (0.5 psi, 3 s). Subsequently, a -20 kV voltage was applied for MEKC separation. The temperature of the capillary was maintained at 30 °C and the detection wavelengths were set at 214 nm and 280 nm for 2-(4)-MEI and THI, respectively.

#### 2.3.2. On-line concentration mode MEKC

The on-line concentration procedure of CSEI-sweeping MEKC used in this study (Scheme S1) was described briefly as below. The capillaries were conditioned prior to separation by washing with 0.1 M NaOH solution (10 min, 20 psi), deionized water (10 min, 20 psi) and carrier electrolyte (5 min, 20 psi). A high conductivity zone was pressured-injected into the capillary (acid plug: pH 2, 50 mM H<sub>3</sub>PO<sub>4</sub>, 0.5 psi, 420 s) followed by water plug (D.I. water, 0.5 psi, 20 s). The sample or standard solutions were mixed with 0.05 mM H<sub>3</sub>PO<sub>4</sub> to convert the imidazole derivatives into cationic

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