Talanta 125 (2014) 72–77

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Ternary composites of nanocellulose, carbonanotubes and ionic liquids as new extractants for direct immersion single drop microextraction

Celia Ruiz-Palomero, M. Laura Soriano, Miguel Valcárcel *

Department of Analytical Chemistry, Marie Curie Building, Campus de Rabanales, University of Córdoba, E-14071 Córdoba, Spain

ARTICLE INFO

Article history:
Received 15 October 2013
Received in revised form
18 February 2014
Accepted 22 February 2014
Available online 2 March 2014

Keywords:
Nanocellulose
Carbonanotubes
Ionic liquid
Composites
Single drop microextraction
Heterocyclic amine

ABSTRACT

We proposed for the first time the use of Nanocellulose (NC) into a single drop for extracting and preconcentrating a heterocyclic amine (HCA) in fried food. In conventional single-drop microextraction (SDME) techniques, ionic liquids (IL) or other organic solvents cannot extract HCAs due to its polarity. The advantageous combination of nanomaterials and nanohybrids based on NC and multiwalled carbonanotubes (MWCNT) with IL allows the preparation of a stable droplet with an excellent and selective ability for the preconcentration of the mutagenic 2-amino-3,8-dimethylimidazo[4,5-f]quinoxaline (MeIQx) by the simple direct immersion SDME technique. The main variables involved in the extraction and preconcentration steps have been evaluated and optimized. The developed method was found to achieve a linear calibration curve in the concentration range of 0.1–10 mg L^{-1} (r^2=0.998), with a detection limit (LOD) of 0.29 mg L^{-1}. Recovery of the method, which was studied in quintuplicate in sausage samples, varied from 90.1% to 95.3% for MeIQx.

1. Introduction

The employment of nanomaterials in different areas has increased exponentially in the last decade because of their unusual advantages such as unique thermal, mechanical, electronic and biological properties not found in conventional materials [1–4].

Within the group of nanomaterials we can find the nanocellulose (single individual fibers with nanometric size), which is a natural biopolymer renewable, cheap and abundantly available in nature with fascinating properties such as high specific surface area, high chemical or biological reactivity, and occasionally even high porosity. Their applications in the field of nanocomposites can be summarized as non-caloric food thickeners, emulsion/dispersion, oil recovery and cosmetic/pharmaceutical applications in the electronics sector [5]. However, there is no record of the application of nanocellulose in analytical chemistry. The preparation of nanocellulose can be performed by oxidation and defibrillation of microcellulose with strong acids or 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical [6]. Other methodologies for preparing nanofibers involve the use of high-intensity ultrasonication and deacytilation and cationization reactions of cellulose [7,8].

Carbonanotubes (CNTs) are well-known type of nanomaterials characterized for their unusual strength and physical properties that make them very unique and promising sorbent materials for analytical purposes [9]. However, CNTs are highly prone to aggregate, which limits their excellent properties. Last decade ionic liquids have emerged as a green alternative to those common toxic organic solvents (dimethyl formamide and N-methyl pyrrolidone) for the dispersion effectiveness of nanotubes. Fukushima et al. [10] used imidazolium ion-based ILs as a new class of CNT dispersants for the first time. The employment of CNTs in combination with ILs has been described in our group for the determination of pesticides [11], in which the soft material was immobilized on cotton fibers to perform the preconcentration of polycyclic aromatic hydrocarbons (PAHs) from river water.

Heterocyclic aromatic amines are one family of compounds that were shown to be potent geno-toxins. The group of amino-imidazo-azaarenes is formed under mild heating conditions (150–300 °C) during the cooking of food, in particular red meat, but also fish. Imidazoquinoxaline derivatives such as 2-amino-3,8-dimethylimidazo[4,5-f]quinoxaline (MeIQx) and 2-amino-3,4,8-dimethylimidazo[4,5-f]quinoxaline (DiMeIQx) were found to be much more mutagenic than imidazopyridine 2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP) [12], which is most prevalent in cooked food [13]. The determination of this family is

Abbreviations: CNTs, carbon nanotubes; c-MWCNTs, carboxylated multiwalled carbonanotubes; ILs, ionic liquids; BMIM · PF_6, 1-butyl-3-methylimidazolium hexafluorophosphate; NC, nanocellulose; SDME, single-drop microextraction; DI, direct immersion; HS, head space; TEMPO, 2,2,6,6-tetramethyl-1-piperidinyloxy; PAHs, polycyclic aromatic hydrocarbon; HCAs, heterocyclic amines; MeIQx, 2-amino-3,8-dimethylimidazo[4,5-f]quinoxaline; PHiP, 2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine; 4,8-DiMeIQx, 2-amino-3,4-8-trimethylimidazo[4,5-f]quinoxaline; Fa, adhesion force; LQ, limit of quantification; LOD, limit of detection; RSD, relative standard deviation

* Corresponding author. Tel./fax: +34 957 218616.
E-mail address: qa1meobj@uco.es (M. Valcárcel).

http://dx.doi.org/10.1016/j.talanta.2014.02.055
0039-9140

mainly carried out by chromathographic techniques but also using capillary electrophoresis (CE) [14,15]. Since CE has LOD higher than liquid chromatography–mass spectrometry, it is important to preconcentrate analytes. Preconcentration of HCAs has been carried out by using solid phase extraction techniques [16]; however, no record for the preconcentration of HCAs using SDME has to date been reported.

The use of ILs in SDME [17,18] has been extensively described for being a simple and low cost method of preconcentration analytes from different matrices. Previously, our group has described the innovative combination of quantum dots (QDs) and ILs for the first time in Head Space Single Drop Microextraction [19], with the aims of preconcentrating aliphatic amines into ILs and detecting them *in-situ* using luminescence QDs as nanosensor.

This paper proposes the first introduction of NC and/or CNTs into IL for selectively preconcentrating 2-amino-3,8-dimethylimidazo[4,5-f]quinoxaline in fried-sausages using the direct immersion SDME technique, owing to the enhancement of the adsorption ability and the stability of the single drop and being possible the introduction of a highly stirring step.

For better comprehension of the paper, we will introduce the terms "hybrid" to name the combination of NC and c-MWCNTs, and "composite" to talk about nanomaterials combined with 1-butyl-3-methylimidazolium hexafluorophophate ($BMIM \cdot PF_6$).

2. Experimental section

2.1. Reagents and materials

Avicel PH-101 cellulose microcrystalline (50 μm of particle size), 2,2,6,6-tetramethylpiperidine-1-oxyl radical (98%), sodium hypochlorite solution (10–15%), sodium chloride (BioXtra, ≥99.5%), sodium bromide (>99%), phosphoric acid (85%), potassium hydroxide (85%), potassium bromide (FTIR grade, ≥99%), ethanol (anhydrous) and immersion oil were purchased from Sigma-Aldrich; nitric acid (69%), hydrochloric acid (37%), sodium hydroxide and methanol from PANREAC; MWCNTs from Baytubes (C150F, Lot no. Z0010AAD07, Drum-no. 040); 1-butyl-3-methylimidazolium hexafluorophophate (99%) from MERK; 2-amino-3,8-dimethylimidazo [4,5-f]quinoxaline (MeIQx), 2-amino-1-methyl-6-phenylimidazo [4,5-b]pyridine (PHiP), and 2-amino-3,4-8-trimethylimidazo[4,5-f] quinoxaline (4,8-DiMeIQx) from Toronto Research Chemicals Inc. All cartridge-type filters were purchased from Análisis Vínicos.

Ultrapure water used throughout all experiments was purified through a Millipore system.

All reagents were used as received without further purification.

2.2. Instrumentation

A P/ACE MDQ Capillary Electrophoresis System from Beckman (Palo Alto, CA, USA) equipped with a DAD and using a fused silica capillary (Beckman Coulter) of 75 μm inner diameter, 70.2 cm total length, and 40 cm effective separation length was used. The applied voltage was 20 kV and the working temperature was 25 °C. The samples were injected into the capillary by hydrodynamic injection for 10 s at 0.5 psi. All buffer solutions were filtered through a nylon membrane of 0.45 μm of pore size before analysis. Prior to first use, the capillary was conditioned by rinsing with 1 M HCl for 5 min, 0.1 M NaOH for 10 min, and water for 5 min using a pressure of 20 psi in all cases. The capillary was prepared for daily use by rinsing with 0.1 M KOH in methanol for 2 min, methanol for 5 min, water for 5 min and separation buffer for 15 min, with a pressure of 20 psi.

Raman spectra were obtained using a frequency doubled Nd-YAG laser with 532 nm excitation with a WITec UHTS 300 spectrometer. Nanomaterials and composite were placed onto a glass and objectives of Eplan 100 × /0.9 EPI and 100 × /1.25 oil 160/0.17 WDO.14 applying oil immersion were used, respectively.

Infrared spectra were recorded with a Tensor 27 FT-MIR spectrophotometer equipped with a Hyperion 2000 microscope, using KBr pellets prepared from the samples.

Using a Q 50 TGA instrument thermogravimetric measurements were performed. Temperature programs for dynamic tests were run from 100 °C to 900 °C at a heating rate of 10 °C/min. These tests were carried out under nitrogen atmosphere (20 ml/min) in order to prevent any thermoxidative degradation.

2.3. Preparation of nanomaterials and composites

In this subsection, the carboxylation of pristine-MWCNTs, the oxidation and defibrillation of microcellulose and the preparation of composites are described.

2.3.1. Preparation of carboxylated MWCNTs (c-MWCNTs)

Pristine MWCNTs (80 mg) were oxidized with HNO_3 3 N (70 ml) under refluxed conditions. Prior to the process, MWCNTs were sonicated in nitric acid for 2 h to avoid agglomeration of nanotubes and anchoring acid solution uniformly on the carbon surface. Thereafter, homogenized carbon solution was oxidized under reflux at 120 °C for 72 h to introduce functional groups. Stirring and decantation were consecutively conducted for five times and finally c-MWCNTs were filtered and washed with plenty of deionized water till the water pH reach approximately 7. A yield of 90.5% was obtained after drying the resulted nanotubes under vacuum. The final product was characterized using TGA and Raman spectroscopy.

2.3.2. Functionalization and defibrillation of microcellulose

Dry microcellulose (2 g) is suspended in water (80 ml) and stirred. Then, NaBr (12.2 mmol, 1.25 g) and TEMPO (0.125 g prepared in 10 ml of water) were added. A pH-probe was used to maintain the pH at 10 with NaOH 1 M during all the reaction period. Next, NaClO (2.5 mmol, 23 ml) was added dropwise from a plastic syringe mounted on a syringe pump to keep constant pH = 10. The end of the reaction is reached when no further changes in pH are observed. Finally, quenching is performed with 15 ml of ethanol and filtration and washing steps with water were followed afterwards. A yield of 80% was obtained after drying under vacuum. This material was characterized using TGA, IR and Raman spectroscopy.

2.3.3. Preparation of the composites

Preparation of the composites based on CNTs, NC and NC–CNT hybrid in $BMIM \cdot PF_6$ follows the same procedure; all components were well mixed manually in different proportions (see Table 1) during 15–20 min in an agate mortar to assure the homogeneity of the resulting material. The final mixtures were stable and homogeneous and were subsequently stored at room temperature for the posterior evaluation of their preconcentration abilities. The selected composite was characterized by IR and Raman spectroscopy with an oil immersion lens.

2.4. Proposed method to determine 2-amino-3, 8-dimethylimidazo [4,5-f]quinoxaline

2.4.1. Extraction procedure

A single drop fixed in a syringe-needle came into direct contact with 3 ml of stock solutions containing different concentrations of analyte. Each vial contains a 7 mm × 2 mm magnetic stirring bar. All vials were tightly sealed with a silicone septum, placed in