Journal of Chromatography A, 1477 (2016) 1–10

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Simultaneous microextraction of inorganic iodine and iodinated amino acids by miniaturized matrix solid-phase dispersion with molecular sieves and ionic liquids☆

Jun Cao*, Li-Qing Peng, Jing-Jing Xu, Li-Jing Du, Qi-Dong Zhang

College of Material Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, China

ARTICLE INFO

Article history:
Received 22 August 2016
Received in revised form
23 November 2016
Accepted 25 November 2016
Available online 25 November 2016

Keywords:
Matrix solid phase dispersion
Molecular sieve
Ionic liquid
Iodine
Seaweed
Ultrahigh performance liquid chromatography

ABSTRACT

This study presents an effective method of using miniaturized matrix solid phase dispersion (MSPD) for the microextraction of inorganic iodine and iodinated amino acids from seaweed samples. Quantification of the target analytes was performed by ultrahigh performance liquid chromatography with UV detection. Molecular sieve (SBA-15) was chosen as the dispersing adsorbent with an ionic liquid (1-dodecyl-3-methylimidazolium bromide) as the elution solvent. The experimental conditions for the MSPD, such as the type of sorbent, ratio of sorbent to sample, type and concentration of the elution solvent, and grinding time were evaluated and optimized. Under the final working conditions, good recoveries were obtained in the range of 86.5–95.4%, with relative standard deviation values below 6.0% in all cases. The limits of detection and limits of quantitation were in the ranges of 3.7–16.7 ng/mL and 12.4 ng/mL, respectively. Compared with common ultrasound assisted extraction, the advantages of this green approach are low consumption of the sorbent and solvent, short extraction time and good selectivity, even in complicated matrices. The proposed SBA-15-based MSPD method was successfully applied to the microextraction of potassium iodide, 3-iodo-L-tyrosine, and 3,5-diiodo-L-tyrosine from kelp, nori and undaria pinnatifida, respectively.

1. Introduction

Natural products have attracted increasing interest in recent years due to their potential biological activities, such as anti-cancer, antioxidant, antiviral, anti-proliferative, antimutagenic, anti-inflammatory, antipyretic activities, among others [1–4]. Many classical extraction techniques have been used to extract various phytochemical compounds such as maceration [5], hydro-distillation [6], Soxhlet extraction [7], ultrasound-assisted extraction (UAE) [8], and microwave-assisted extraction (MAE) [9]. However, these techniques are time-consuming, costly and have poor selectivity. In addition, the classical extraction methods require large amounts of solvent and sample and haveionization, hydrolysis, and oxidation risks for thermolabile compounds due to the long operating times [10]. Although the UAE method can use green ionic liquids (ILs) solvents instead of organic solvents to reduce environmental pollution, the extraction volumes are generally too large [11]. Thus, it is necessary to develop a miniaturized green extraction method, which has been rarely reported in the literature.

Matrix solid-phase dispersion (MSPD), first introduced in 1989 by Barker, is an extraction procedure that combines aspects of several analytical techniques, allowing simultaneous sample (solid, semisolid or viscous) disruption, extraction, fractionation and purification within a single process [12]. The success of MSPD is due to its simplicity, feasibility, flexibility and ruggedness compared to other sample treatment methods. This method allows for simultaneous extraction and purification steps, thus greatly reducing the analysis time and consumption of organic solvents (especially when miniaturized) as well as increasing sample throughput. To date, MSPD has proven to be an efficient and versatile technique for the extraction and pre-concentration of several classes of substances, such as pesticides, drug residues, mycotoxins, contaminants and phytochemicals from a wide variety of animal and plant matrices [13]. However, no information is available in the literature about the application of miniaturized MSPD for the analysis of inorganic iodine and iodinated amino acids.

☆ Selected paper from 18th International Symposium on Advances in Extraction Technologies & 22nd International Symposium on Separation Sciences, 3–6 July 2016, Toruń, Poland.

* Corresponding author.
E-mail address: caojun91@163.com (J. Cao).

http://dx.doi.org/10.1016/j.chroma.2016.11.053
0021-9673/

Seaweed has been widely used since ancient times as a food, supplement, animal feed, fertilizer and medicine, especially in Asian countries [14]. Seaweed naturally contains iodine, dietary fiber, high levels of minerals, trace elements, vitamins, proteins and amino acids. A high concentration of iodine can accumulate in seaweeds. Iodine is an essential trace element for humans, and plays a vital role in basal metabolism, the function of the thyroid gland, cell development and differentiation [15,16]. In seaweed products, iodine can be retained in both inorganic and organic forms, and 9–99% of iodine is water soluble, with iodide being the major species (61–93%), accompanied by iodate (1.4–4.5%) and organic iodine compounds (such as monoiodotyrosine (MIT) and diiodotyrosine (DIT)) from 5% to 37% [17]. In recent years, many analytical methods have been developed for the analysis of different iodine species, including high performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS), capillary electrophoresis (CE), high performance liquid chromatography with UV detection (HPLC-UV), and atomic absorption spectrometry [8,18–20]. However, the most commonly applied extraction methods, such as ultrasound assisted extraction (UAE), are time-consuming, expensive, and consume large volumes of undesirable organic solvents, thus, violating the basic principles of green chemistry [21]. Hence, an eco-friendly and highly efficient method for the extraction of iodine species in seaweed is of great significance.

The object of this work is the development and validation of an effective, green, simple and fast MSPD method for the microextraction of iodine (including KI, MIT and DIT), and their determination by ultra-high performance liquid chromatography coupled to ultraviolet detector (UHPLC-UV). Santa Barbara Amorphous-15 (SBA-15), multi-walled carbon nanotubes (MWCNTs), carboxyl multi-walled carbon nanotubes (C-MWCNTs), mesoporous carbon (CMK-3), florisil and silica gel were used as dispersion sorbents to evaluate different types of seaweeds, with ILs as the elution solvents. The effects of various operating parameters, including the sorbent, the ratio of sorbent to sample, elution solvent, and grinding time on the MSPD extraction performance were thoroughly evaluated and optimized. Additionally, the sensitivity, precision and recovery of the developed method were also evaluated.

2. Materials and methods

2.1. Reagents and materials

MWCNTs (OD: 8–15 nm, length: 0.15–2 μm, SSA: >233 m^2/g), C-MWCNTs (OD: 10–20 nm, length: 10–30 μm, SSA: >200 m^2/g), SBA-15 (highly stable mesoporous silica, pore diameter: 7–9 nm, BET: 550–600 m^2/g) and CMK-3 (pore diameter: 3.9 nm, BET: 1201 m^2/g) were all purchased from XFnano Materials Tech Co., Ltd. (Nanjing, China). Florisil and N-hexadecyltrimethylammonium chloride (HDTA) were both obtained from ANPEL Scientific Instrument Co., Ltd. (Shanghai, China). Silica gel was supplied by Yantai Chemical Industry Research Institute (Shandong, China). Methanol (HPLC grade) was provided by Tedia Company Inc. (Fairfield, US). Acetic acid (HPLC grade) was supplied by Sigma-Aldrich Shanghai Trading Co., Ltd. (Shanghai, China). The ionic liquids, including 1-ethyl-3-methylimidazolium bromide ([Emim]Br), l-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4), 1-hexyl-3-methylimidazolium bromide ([Hmim]Br), 1-dodecyl-3-methylimidazolium bromide ([C_{12}mim]Br), 1-dodecyl-3-methylimidazolium chloride ([C_{12}mim]Cl), and 1-dodecyl-3-methylimidazolium hydrogen sulfate ([C_{12}mim]HSO_3) were purchased from Shanghai Cheng Jie Chemical Co., Ltd. (Shanghai, China). Double distilled water (Wahaha Group Co., Ltd., Hangzhou, China) was used in the experiments. The analytical standards, including potassium iodide (KI), 3-iodo-L-tyrosine (MIT), and 3,5-diiodo-L-tyrosine (DIT) were collected from Sigma-Aldrich Shanghai Trading Co., Ltd. (Shanghai, China). The stock standard solutions were prepared in 1 mM NaOH at the concentration level of 1000 μg/mL for KI, 200 μg/mL for MIT and DIT and stored in the dark at 4 °C before use. The seaweed samples including kelp, nori, undaria pinnatifida, shredded kelp and sea sedge were purchased from a local supermarket (Hangzhou, China). These samples were cleaned, cut, crushed and sieved before MSPD.

2.2. Instrumental configuration and chromatographic conditions

The materials were characterized by a scanning electron microscope (SEM) model HT7700 (Hitachi, Tokyo, Japan). Transmission electron microscopy (TEM) measurements were performed on a Zeiss Supra55 (Oberkochen, Germany) microscope with an accelerating voltage of 100 kV. Fourier transformation infrared (FT-IR) spectra were used qualitatively with a Thermo Scientific Nicolet iS5 spectrometer (Madison, WI, USA).

The UHPLC analysis was performed with an Agilent 1290 system (Santa Clara, CA, USA), equipped with a binary pump and an automatic injector. Separation of the analytes was achieved on an Eclipse XDB-C18 column (2.1 mm × 50 mm, 1.8 μm). The mobile phase consisted of 0.2% (v/v) acetic acid aqueous solution (A) and 0.2% acetic acid (v/v) in methanol (B) using the following gradient elution program for the separation: 0–1 min, 5–10% B; 1–2 min, 10–20% B; 2–3 min, 20–30% B; 3-3.5 min, 30–40% B; 3.5–4 min, 40–40% B; 4-4.5 min, 40–45% B; 4.5–5 min, 45–45% B; 5–6 min, 45–50% B (the separation of target analytes was completed); 6–7 min, 50–55% B; 7–7.5 min, 55–60% B; 7.5–8 min, 60–70% B; 8–8.5 min, 70–80% B; 8.5–9 min, 80–90% B; 9–9.5 min, 90–100% B; and 9.5–10 min, 100-5% B (elution of the impurities from 6 to 10 min). The wavelength of the ultraviolet detector was set at 226 nm. The column temperature was maintained at 22 °C, the flow rate was 0.4 mL/min, and the injection volume was 2 μL.

2.3. UAE and MSPD extraction

UAE procedure: 5.0 g of each milled seaweed sample (kelp, nori, or undaria pinnatifida) were weighed into a flask, and approximately 50 mL of double distilled water was added and mixed to thoroughly disperse the sample, and 5 mL of HDTA (25%, m/m) was added and the solution to bring it to volume. The process of UAE was conducted in a KQ-100 B ultrasonic cleaner (Kunshan, China) at 100 W (40 kHz) of output power for 30 min at 40 °C. Next, the extracting solution was centrifuged at 13,000 rpm for 5 min using a TG16A-WS centrifuge (Shanghai, China) to remove particles. Then, each sample filtered through a 0.22 μm disposable nylon-66 membrane filter into 2 mL sample vials prior to injection into the UHPLC system.

MSPD procedure: a 50 mg aliquot of seaweed sample (kelp, nori, or undaria pinnatifida) and 50 mg of sorbent (SBA-15, CMK-3, MWCNTs, COOH-MWCNTs, silica gel or florisil) (1:1) were placed into a small agate mortar and gently blended together using an agate pestle for 30 s to obtain a homogeneous mixture. The mixture was transferred into a 6 mL SPE cartridge that already contained a sieve plate, which was connected to a Visiprep™-DL solid phase extraction vacuum manifolds (SUPELCO, Bellefonte, PA, USA). Then, a second sieve plate was added to the top of the column and the cartridge was tightly compressed. Subsequently, the mixture was eluted with 0.4 mL of 200 mM IL ([C12mim]Br, [C12mim]Cl, [C12mim]HSO3, [Emim]Br, [Hmim]Br, or [Bmim]BF4) and the filtrate was collected in a 1.5 mL Eppendorf tube. Finally, the MSPD extracts collected were centrifuged at 13,000 rpm for 5 min before