Talanta 161 (2016) 143–150

Contents lists available at ScienceDirect

Talanta

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

A preconcentration method for indirect determination of acrylamide from chips, crackers and cereal-based baby foods using flame atomic absorption spectrometry

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ARTICLE INFO

Article history:
Received 4 June 2016
Received in revised form
11 August 2016
Accepted 16 August 2016
Available online 16 August 2016

Keywords:
Acrylamide
Baby foods
Fluorescein
Food safety
Preconcentration

ABSTRACT

Acrylamide is a toxic species for human health, and is a Maillard reaction product which forms spontaneously in heat treatment process of foods. Therefore, a simple, fast and cost-effective method was developed for the indirect determination of acrylamide in processed foods particularly consumed by children. The method is based on ion–pairing of acrylamide with fluorescein (F^{2-}) in presence of Ni(II) ions at pH 9.0, and then extraction of the formed ternary complex into micellar phase of poly(ethyleneglycol-mono-*p*-nonylphenylether) (PONPE 7.5) before analysis by flame atomic absorption spectrometry (FAAS). The ultrasonic-assisted cloud point extraction (UA-CPE) has been used for the preconcentration of acrylamide in the samples prior to its FAAS detection. The matrix matched calibration curve is linear in range of 0.3–150 μg kg^{-1} under optimal reagent conditions (1.75 mL of 0.1 mol L^{-1} ammonia buffer at pH 9.0, 2.2 mg L^{-1} Ni(II), 4.0×10^{-4} mol L^{-1} F^{2-}, 0.4% (w/v) NH_4Cl and 0.7% (v/v) PONPE 7.5) with sensitivity enhancement of 160-fold. The proposed method has been validated by assessment of the following parameters; the limits of detection (LOD) and quantification (LOQ) (0.08 μg kg^{-1} and 0.28 μg kg^{-1}, respectively) with a relative standard deviation (RSD%) lower than 6.3%, and extractive recovery higher than 95% for acrylamide spiked at levels of 5 and 25 μg kg^{-1}. The method was successfully applied to the indirect determination of acrylamide in the processed foods and two CRMs with satisfactory results.

1. Introduction

Acrylamide (AA) is a low-molecular-weight vinylic compound. It is a colorless and odorless crystalline substance and it is highly water soluble, easily reactive in air, and rapidly polymerizable. The AA is a Maillard reaction product, which forms spontaneously as frying or cooking heat treatment enforced in foods [1]. Though the mentioned chemical is widely found in the fried or oven-cooked foods, it can also exist in the grilled foods prepared at homes or at large restaurants [2]. The AA can be especially formed in high temperatures heating of carbohydrate-rich foods. However, no AA has been found in the raw or boiled foods. According to the research, neural destructions were observed in people exposed to this chemical [3]. The AA is also estimated to be a human carcinogen. Thus, the AA has been accepted as “probably carcinogenic to humans” (Group 2A) by International Agency for Research on Cancer [4]. According to Food and Agriculture Organization of the United Nations and World Health Organization (FAO/WHO), daily intake of the AA from the food can be in the range of 0.3–0.8 μg kg^{-1} body $weight^{-1}$ day^{-1} [5]. The daily intake of the AA from food (1–10 μg kg^{-1} bw^{-1} day^{-1}) higher than this value can cause toxic effects on humans. In conclusion, we can say that the AA creates a risk for human health only in the cases of long term exposure to it. Thus, the determination of trace AA residues in foods needs the development of new, easy to use, cost-effective, faster, and powerful analytical methods for control of the quality attributes.

Many analytical methods are developed from 2010 to the present to determine the AA in different foods using liquid chromatography–tandem mass spectrometry (LC–MS/MS) [6], headspace solid-phase microextraction (HS-SPME) followed by gas chromatography-flame ionization detection (GC-FID) [7], gas chromatography coupled with electron capture and ion trap mass spectrometry detectors (GC-ECD and GC-IT/MS) [8], dispersive liquid–liquid microextraction (DLLME) followed by gas chromatography–electron capture detection (GC–ECD) [9], high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) [10],

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http://dx.doi.org/10.1016/j.talanta.2016.08.053
0039-9140/

solid-phase extraction followed by high-performance liquid chromatography-tandem mass spectrometry (SPE-HPLC-MS/MS) [11], reversed-phase direct immersion single drop microextraction-gas chromatography (RP-DISDME-GC) [12], solid-phase microextraction (SPME) coupled to gas chromatography–positive chemical ionization tandem mass spectrometry (GC–PCI-MS–MS) [13], reversed phase-high performance liquid chromatography (RP-HPLC) coupled to a diode array detector (DAD) [14], catalytic square-wave voltammetric determination (CS-WV) [15] and liquid chromatography (LC) coupled with pulsed electrochemical detection [16]. In this study, ultrasonic-assisted cloud point extraction (UA-CPE) was used to reduce background noise and to enhance analytical signal after separation and preconcentration of target analyte from food matrices. The UA-CPE has come to the forefront to the other preconcentration techniques (liquid–liquid extraction and co-precipitation) due to the following advantages. This approach includes easy methodology, excellent sensitivity enhancement and preconcentration factors, lower cost, higher safety and simplicity, and it does not need to handle a great volume of organic solvent that is generally toxic [17]. However, while the most sensitive methods reported have to resort to sophisticated systems and procedures, others suffer from instabilities of the reagents used, high cost, tedious and lengthy analysis time or lack of accuracy and reproducibility especially at low concentrations. Because of its advantages such as simplicity, speedity, low operational cost, high accuracy and selectivity [18], flame atomic absorption spectrometric detection combined with micellar system could be a suitable detection strategy for indirect determination of the AA, due to its weak UV absorption and electrochemically inactive properties. In this context, it is important to note that the use of flame AAS with UA-CPE may offer interesting advantages over the other analytical methods.

To the best of our knowledges, there is no report on the use of FAAS for indirect determination of the AA. In this sense, the main objective of the current study is to develop a simple, easy to use, low cost, sensitive, accurate and precise UA-CPE procedure for separation and preconcentration of the AA from sample matrix as ternary complex of Ni(II) prior to indirect analysis by FAAS. To further improve detection sensitivity and selectivity of analysis by FAAS, another objective of the present work was efficiently to use fluorescein (F^{2-}) as ion-pairing reagent.

2. Experimental

2.1. Instrumentation

A flame atomic absorption spectrophotometer equipped with D2-background correction, a nickel hollow cathode lamp, an air-acetylene flame atomizer (AA-6300 Shimadzu, Kyoto, Japan) was used for the detection of Ni(II), which is linearly related to AA concentration in the samples. The instrumental parameters for analysis of Ni(II) by FAAS are as follows: wavelength, 232.0 nm; slit, 0.7 nm; lamp current, 6 mA; burner height, 7 mm; nebulizing flow rate, 6 mL min^{-1}; acetylene flow rate, 1.8 L min^{-1} and air flow rate, 15 L min^{-1}. An ultrasonic cleaner (UCP-10 model, Seoul, Korea) with variable temperature control for time in 0–80 °C (40 kHz, 300 W) was used for digestion of the samples. A vortex mixer (VM-96B model, Seoul, Korea) with variable speed control in 0–3200 rpm (50 Hz, 12 W) was used to fasten the extraction process and minimize the reagent consumption during experimental procedures. A Hettich universal 320 centrifuge was used to accelerate the phase separation. For measuring pH values in the aqueous phase, pH-2005 digital pH meter equipped with a glass-calomel was employed.

2.2. Reagents

All chemicals used were of analytical reagent grade, and ultrapure water with a resistivity of 18.2 MΩ cm was used in this study. Before starting the experiment, all the plastic and glassware were cleaned by 10% (v/v) HNO_3 solution, and were rinsed with the water. The stock solutions of 1000 mg L^{-1} the AA (Sigma, St. Louis, MO, USA) was prepared by dissolving the required amounts of the AA in the water. The calibration curve was established by stepwise dilution from stock solutions of the AA. A 1000 mg Ni(II) L^{-1} of stock solution was prepared by dissolving the suitable amount of solid, $Ni(NO_3)_2 \times 6H_2O$ (Merck, Darmstadt, Germany) in the water. The working standard solutions were prepared by stepwise dilution of stock solution and stored at 4 °C before analysis. An acidity of 0.1% (w/v) HNO_3 was maintained in all the solutions. Fluorescein solutions (Sigma) at 2.0×10^{-3} mol L^{-1} were prepared by dissolving its appropriate amount in 1:4 ratio of ethanol-water mixture. Electrolyte solutions (5.0%, w/v) including potassium nitrate, sodium chloride and sodium chloride as salting out agents were prepared by dissolving 5.0 g of salt in 100 mL volumetric flask while stirring. The solution of 1.0% (v/v) of PONPE 7.5 (Sigma) was prepared by mixing 1.0 mL of surfactant with 20 mL ethanol in a flask of 100 mL, and diluting 100 mL with the water. Ammonia buffer solutions at pH 7.5–11.0 were prepared by mixing appropriate volumes of 1.0 mol L^{-1} ammonia and ammonium chloride and adjusting to a suitable pH with diluted NaOH or HCl of 1.0 mol L^{-1} when necessary.

2.3. Sampling

Different food samples (potato chips, corn chips, cracker samples and cereal-based baby foods) were supplied from a local supermarket in the Sivas Province of Turkey. A 3.0 g of the food samples were homogenized in a blender, and were transferred into volumetric centrifuge tubes of 50 mL. Then, to the centrifuge tubes were added 4.0 g anhydrous $MgSO_4$, 0.5 g NaCl, 5 mL n-hexane, 10 mL ultra-pure water and 10 mL acetonitrile, respectively. Then, the mixture was digested for 5 min under ultrasonic power (300 W, 40 kHz) at 30 °C. In this process, the chemicals are used for the following purposes. The water was used to facilitate extraction of the AA. The n-hexane helps to remove fat and fat-soluble substances in the food samples. The NaCl salt provides a separation of water and acetonitrile layer. The mixture was then divided into three different phases by centrifugation for 5 min at 4000 rpm. The oil of the samples was extracted into the upper hexane phase. The solids and salts were extracted into the bottom aqueous phase. 2 mL of middle acetonitrile phase was transferred to a centrifuge tube containing 50 mg primary secondary amine (PSA) and 100 mg anhydrous $MgSO_4$. After inducing with vortex, it was divided into two phases by centrifugation for 2 min at 4000 rpm. Then, the digested samples were filtered using a membrane filter (0.45 μm pore size). A blank extraction process was carried out through the complete procedure. Then, the proposed UA-CPE method as described in Section 2.4 was applied to the selected food samples.

2.4. Procedure

For preconcentration procedure, 5.0 mL aliquots of the aqueous standard solutions containing the AA in the range of 0.2–210 μg L^{-1}, and the food samples were transferred in 50 mL volumetric centrifuge tubes. Then, 1.75 mL of 1.0 mol L^{-1} ammonia buffer solution at pH 9.0, 4.0×10^{-4} mol L^{-1} Fluorescein, 2.2 mg L^{-1} Ni(II), 0.4% (w/v) NH_4Cl and 0.7% (v/v) PONPE 7.5, respectively, were added. After these reagent additions, the extracted solution was placed in an ultrasonic bath (300 W, 40 kHz)