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Analytical Methods

Ultrasonic-assisted extraction and dispersive liquid-liquid microextraction combined with gas chromatography-mass spectrometry as an efficient and sensitive method for determining of acrylamide in potato chips samples

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ABSTRACT

In this research, for the first time, we successfully developed ultrasonic-assisted extraction and dispersive liquid-liquid microextraction combined with gas chromatography-mass spectrometry as a new, fast and highly sensitive method for determining of acrylamide in potato chips samples. Xanthydrol was used as a derivatization reagent and parameters affecting in the derivatization and microextraction steps were studied and optimized. Under optimum conditions, the calibration curves showed high levels of linearity ($R^2 > 0.9993$) for acrylamide in the range of 2–500 ng mL^{-1}. The relative standard deviation (RSD) for the seven analyses was 6.8%. The limit of detection (LOD) and limit of quantification (LOQ) were 0.6 ng g^{-1} and 2 ng g^{-1}, respectively. The UAE-DLLME-GC-MS method demonstrated high sensitivity, good linearity, recovery, and enrichment factor. The performance of the new proposed method was evaluated for the determination of acrylamide in various types of chips samples and satisfactory results were obtained.

1. Introduction

Acrylamide is a hydrophilic unsaturated amide with properties of white odorless, crystalline solid, low molecular weight, polar and low volatile. This compound is considered as the most actively investigated compound among heat-induced food contaminants (Krska et al., 2012) and forms as a by-product of cooking process in carbohydrate-rich foods at high temperatures and low moist conditions (Franek, Rubio, Diblikova, & Rubio, 2014). Maillard reaction of reducing sugars with asparagine at temperature higher than 120 °C is the most probable route to acrylamide formation during the browning process (Özer, Kola, Altan, Duran, & Zorlugenç, 2012). Acrylamide is a neurotoxic compound identified as a probable human carcinogen (group 2A) and genotoxicant (Liu, Zhao, Yuan, Chen, & Hu, 2008). Since November 2013, the European Commission (EC) proposed indicative value of acrylamide between 50 and 4000 μg kg^{-1} in various foodstuff (Boushey, Beresford, Omenn, & Motulsky, 1995).

Many method have been used for measuring acrylamide in different samples, including planer chromatography (Alpmann & Morlock, 2008), high-performance liquid chromatography (HPLC) (Kaplan, Kaya, Ozcan, Ince, & Yaman, 2009; Wenzl et al., 2006), gas chromatography-mass spectrometry (GC–MS) (Fernandes & Soares, 2007; Hoenicke & Gatermann, 2005; Oracz, Nebesny, & Żyżelewicz, 2011; Zhang, Zhang, & Zhang, 2005), and bioanalytical methods, such as immune enzymatic tests and biosensors (Tekkeli, Önal, & Önal, 2012). Among this method instrumental analysis method especially gas chromatography-mass spectrometry (GC–MS) was used as a powerful technique for the determination of acrylamide in various food samples. Prior to GC–MS analysis, derivatization of acrylamide is necessary to increase of vapor pressure and decrease of interaction with GC column. Recently, some studies have been employed xanthydrol as a novel acrylamide-derivatization reagent. This method was applied to aqueous sample and it is claimed to be more environmentally friendly, requires mild reaction conditions at low temperature, and proceeds in aqueous solution (Tsukakoshi et al., 2012; Yamazaki, Isagawa, Kibune, & Urushiyama, 2012).

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The isolation of acrylamide from carbohydrate-rich samples such as potato needs primary extraction procedures and multi-step sample-preparation techniques (Gökmen, Şenyuva, Acar, & Sarıoğlu, 2005; Twaddle et al., 2004). Ultrasonic assisted extraction (UAE) due to its high extraction efficiency and rapid sample preparation has attracted much attention in recent years as a successful and well developed method (Sharma et al., 2006). UAE is fast and easy to operate with high enrichment factor. (Jia et al., 2010). Therefore this method can be applied as an effectively sample preparation technique for the release of acrylamide from sample matrix prior to GC–MS analysis.

Microextraction techniques have been characterized as a promising basis for a new generation of sample preparation techniques and have recently received a great deal of attention (Abedi, Mohammadi, Azadniya, Mortazavian, & Khaksar, 2014; Asadi, Dadfarnia, Shabani, & Abbasi, 2015; Ghobadi, Yamini, & Ebrahimpour, 2015; Kamankesh, Mohammadi, Hosseini, & Tehrani, 2015; Kamankesh, Mohammadi, Tehrani, Ferdowsi, & Hosseini, 2013; Kim, Hwang, & Lee, 2007; Madani-Tonekaboni, Kamankesh, & Mohammadi, 2015; Mollahosseini, Toghroli, & Kamankesh, 2015; Reboredo-Rodríguez et al., 2014; Song, Shi, & Chen, 2013; Wu et al., 2013).

One of the techniques attracting special attention is the dispersive liquid-liquid microextraction (DLLME), which was introduced in 2006 by Rezaee and co-workers (Rezaee et al., 2006). DLLME, which is based on the use of a ternary mixture of solvent systems, involves the rapid injection of an appropriate mixture of an extraction solvent and a disperser solvent into the sample solution. The disperser solvent must be fully miscible with both the aqueous sample and the extraction phase. But the extraction solvent must be miscible only with the dispersing phase, and must be insoluble in water. The main advantages of DLLME include its simplicity, requirement of very small volumes of extraction solvents, and the presence of very large surface area between the extraction solvent and the aqueous sample which rapidly reaches a state of equilibrium between the organic and aqueous phases. High enrichment factor, high speed and high recovery are other advantage of this technique. In addition, this microextraction method has been successfully employed for the determination of many compounds in various food samples (Aeenehvand et al., 2015; Bashiry et al., 2016; Mohammadi, Ghasemzadeh-Mohammadi, Haratian, Khaksar, & Chaichi, 2013; Mohammadi et al., 2013; Nojavan, Kamankesh, Shahraz, Hashemi, & Mohammadi, 2015; Pirsaheb & Fattahi, 2015; Ramezani, Hosseini, Kamankesh, Ghasemzadeh-Mohammadi, & Mohammadi, 2014).

In this work, for the first attempt, UAE-DLLME-GC-MS after derivatization with xanthydrol was applied as a fast, sensitive and accurate method for the determination of acrylamide in potato chips samples. Experimental variables of derivatization and microextraction process, such as type and volume of extraction and disperser solvents, derivatization reagent amount, sample pH, time and temperature of derivatization were optimized. The merit figures of the new proposed method compare with other previous methods. Finally, the newly developed method was used in the determination of acrylamide in potato chips samples and suitable results were obtained.

2. Experimental

2.1. Chemicals and reagent

Chemicals standards of acrylamide (99%) and acetamide were purchased from Merck (Darmstadt, Germany). Hydrochloric acid, sodium chloride, ethanol, methanol, acetone, acetonitrile tetrachloroethylene, chloroform, carbon tetrachloride, dichloromethane, hydroxide potassium, xanthydrol, di-potassium hydrogen phosphate (K_2HPO_4), potassium hexacyanoferrate (II) and zinc acetate were obtained from Merck (Darmstadt, Germany).

The derivatization reagent was prepared by dissolving 5 g of xanthydrol in 100 mL methanol. For preparation of carrez solution I, 10.6 g of potassiumhexacyanoferrate (II) was dissolved in 100 mL distilled water. Carrez solution II was prepared by mixing 21.9 g of zinc acetate with 3 mL of acetic acid, then adjusting the volume to 100 mL with distilled water. All solvents were analytical reagent grade or HPLC grade.

2.2. Standard

Stock standard solution (2000 $\mu g\ mL^{-1}$) was prepared in methanol. To obtain a working solution, the upper standard solution was diluted with methanol; this working solution was applied to evaluate extraction performance under different conditions (2–500 $ng\ g^{-1}$). Acetamide was used as an internal standard, and prepared in methanol at a concentration of 1000 $\mu g\ mL^{-1}$. Stock and working solutions were stored at 4 °C in a refrigerator and were used daily in proper concentrations or directly.

2.3. Instrumentation

Chromatographic separations and detections of the target analytes were performed using a 7890A GC system from Agilent Technologies (Palo Alto, CA, USA) with a triple-axis detector fitted with a split/splitless injector and coupled with a 5975C inert MSD network mass selective detector. An HP-5 MS capillary column (5% phenyl siloxane/95% methyl polyorganosiloxane; 30 m × 0.25 mm I.D., 0.25 μm film thickness) was used for the separation of chemical compounds. The oven temperature was programmed as follows: 100 °C held for 1 min, ramped to 300 °C at 20 °C min^{-1}, held for 10 min. Helium was used as a carrier gas in a constant flow of 0.8 mL min^{-1}. The injector temperature and auxiliary temperature were set at 290 °C and 280 °C, respectively. 2 μL of the sample was injected in a split mode with split ratio of 1:50. The selected ion monitoring (SIM) acquisition mode was used for the quantification of acrylamide, and the ions monitored were as follows: m/z 251 for acrylamide and m/z 239 for acetamide (IS). Also retention time for acetamide and acrylamide is 14.35 and 16.88 min, respectively.

An ultrasonic water bath, working at 50–60 kHz with maximum output power of 350 W (Euronda company, Vicenza, Italy) was used for ultrasonication of the samples.

2.4. Procedures

2.4.1. Preparation of real sample

Potato chips samples were purchased from main supermarkets and stored at a temperature of 4 °C. 1 g of potato chips sample was weighted, thoroughly grinded and transferred to a conical flask. Then this sample was spiked with acetamide (internal standard) at a concentration of 50 $ng\ g^{-1}$ and this mixture was thoroughly stirred to obtain a very homogeneous sample. 3 mL of hexane was added to remove the fat of sample. Then hexane was separated and the residual of solvent was evaporated. This sample was placed into the glass test tube and 5 mL deionized water was added. In order to accelerated extraction of acrylamide from sample matrix to aqueous phase the container of sample was immersed into an ultrasonic water bath for 5 min at 40 kHz of ultrasound frequency and 0.138 kW of power at 25 °C. After this stage, 0.5 mL carrez solution I and 0.5 mL carrez solution II were added to the sample solution to precipitate protein and soluble carbohydrate. This sample was thoroughly agitated and was centrifuged for 5 min in 4000 rpm. Then the supernatant was separated and filtered using