Analytica Chimica Acta 690 (2011) 221–227

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

A novel method of ultrasound-assisted dispersive liquid–liquid microextraction coupled to liquid chromatography–mass spectrometry for the determination of trace organoarsenic compounds in edible oil

Wei-Xun Wang[a], Tzung-Jie Yang[a], Zu-Guang Li[a,b], Ting-Ting Jong[a], Maw-Rong Lee[a,*]

[a] Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan
[b] College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, Zhejiang, PR China

ARTICLE INFO

Article history:
Received 11 November 2010
Received in revised form 8 February 2011
Accepted 13 February 2011
Available online 19 February 2011

Keywords:
Ultrasound-assisted dispersive liquid–liquid microextraction
Organoarsenicals
Edible oil
Liquid chromatography–mass spectrometry

ABSTRACT

A novel approach, ultrasound-assisted dispersive liquid–liquid microextraction combined with liquid chromatography–mass spectrometry (UA-DLLME with LC–MS) is demonstrated to be quite useful for the determination of trace amounts of organoarsenic compounds in edible oil. The organoarsenic compounds studied include dimethylarsinic acid (DMA), monomethylarsonic acid (MMA) and 3-nitro-4-hydroxyphenyl arsenic acid (Roxarsone). Orthogonal array experimental design (OAD) was utilized to investigate the parameter space of conditions for UA-DLLME. The optimum conditions were found to be 4 min of ultrasonic extraction using 1.25 mL of mixed solvent with 50 μL of buffer solution. Under these optimal conditions, the linear range was from 10 ng g^{-1} to 500 ng g^{-1} for DMA and Roxarsone, from 25 ng g^{-1} to 500 ng g^{-1} for MMA. Limits of detection of DMA, MMA and Roxarsone were 1.0 ng g^{-1}, 3.0 ng g^{-1} and 5.8 ng g^{-1}, respectively. The precisions and recoveries also were investigated by spiking 3-level concentrations in edible oil. The recoveries obtained were over 89.9% with relative standard deviation (RSD) of 9.6%. The new approach was utilized to successfully detect trace amounts of organoarsenic compounds in various edible oil samples.

1. Introduction

The widespread use of inorganic and organic arsenic compounds in agriculture and industry results in significant anthropogenic contamination in the environment [1]. The determination of the chemical forms of arsenic in the environment [2,3] and food [4] is critical because of the varying toxicity of different arsenic species. Although the toxicity of the organoarsenicals is less than that of the inorganic As compounds [5,6], the toxicity of organoarsenic species is of concern because of bioaccumulation in the organism [7]. To distinguish speciation of arsenic compounds, chromatographic separation coupled to element-specific spectrometric detection has been utilized. High performance liquid chromatography (HPLC) with inductively-coupled plasma mass spectrometry (ICP-MS) [8,6,9,10], liquid chromatography–mass spectrometry (LC–MS) [11–13], atomic absorption spectrophotometry (AAS) [14,15], inductively-coupled plasma atomic emission spectrometry (ICP-AES) [16], and atomic fluorescence spectrometry (AFS) [17,18] have played important roles in previous arsenic speciation studies.

Sample preparation is a critical part of analysis, because it provides isolation of the components of interest from the sample matrix and from some potential interferences. Recently, research on sampling approaches has been focused on the development of simple, efficient techniques requiring less organic solvents. Such methods include solid-phase microextraction (SPME) [19], liquid-phase microextraction (LPME) [20,21], single-drop microextraction (SDME) [22,23] and liquid–liquid microextraction (LLME). The development of microextraction resolved some drawbacks of the previous methods, particularly liquid–liquid extraction (LLE) [10,24] and solid-phase extraction (SPE). The drawbacks included complex equipment, solvent losses, excessive times and unsatisfactory enrichment (low preconcentration ratios) [25].

To enable sample extraction and preconcentration to be done in a single step, dispersive liquid–liquid microextraction (DLLME) was demonstrated by Assadi and coworkers [26]. This novel method is based on a mixed component solvent system like homogenous liquid–liquid extraction and cloud point extraction. An appropriate mixture of extraction solvent and disperser solvent is injected into the aqueous sample with a syringe and a cloudy solution is formed. The resulting fine droplets of extraction solvent provide very efficient extraction due in part to their extreme surface area. Thus, the analytes of interest in the sample solution are quickly transferred into the fine droplets of extraction solvent. During centrifugation,

* Corresponding author. Tel.: +886 4 2285 1716; fax: +886 4 2286 2547.
E-mail address: mrlee@dragon.nchu.edu.tw (M.-R. Lee).

0003-2670/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2011.02.033

the fine droplets accumulate and coalesce at the bottom of a conical vial. The sediment phase of solution is removed and analyzed conventionally. The advantages of the DLLME approach are simplicity of operation, rapidity, low cost, high recovery and high enrichment factor. This method has been applied successfully for the determination of organic pollutants [27–30] and metallic ion compounds [31–34] in environmental samples.

The application of ultrasonic excitation is a powerful aid in the acceleration of analytical processes. Ultrasound-assisted liquid–liquid extraction (LLE) was developed by Cocito's group [35] and has been used as an alternative to conventional LLE. Ultrasound-assisted emulsification (USAE) was also demonstrated [36] and has been applied to determinate the polar and non-polar compounds in solid plant samples. Other ultrasound-assisted methods were used to extract toxic elements in contaminated soil [37], seafood [38], animal feed [39] and meat [40,41] prior to determination. One advantage of this approach is offered high extraction efficiency in a short time preparation.

The analysis of organoarsenic compounds in edible oil had less been done in the past research. In this project, UA-DLLME combined with liquid chromatography–mass spectrometry was developed and applied to the determination of trace amounts of organoarsenicals in edible oil. The use of this technique for oil samples is significantly different from the application to aqueous samples. The buffer solution mixed with hexane was used to extract trace amounts of organoarsenicals in oil. The optimum conditions for UA-DLLME were investigated by using an orthogonal array of parameters. The feasibility of UA-DLLME combined with liquid chromatography–mass spectrometry was evaluated on the basis of linearity, precision, enrichment factor and extraction recovery. The proposed method was demonstrated for the determination of organoarsenicals in various edible oil samples.

2. Experimental

2.1. Chemicals and reagents

Monomethylarsonic acid (MMA) was obtained from Chem Service, Inc. (West Chester, PA, USA). Dimethylarsinic acid (DMA) and 4-hydroxy-3-nitrophenyl arsonic acid (Roxarsone) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Trimethylamine *N*-oxide was used as the internal standard and obtained from Sigma–Aldrich (St. Louis, MO, USA). All organic solvents used in this study were purchased from Merck (Darmstadt, Germany). All chemicals used were analytical-reagent grade. The ultrapure water was prepared by RiOs^{TM} 3 Water Purification Systems from Millipore (Billerica, MA, USA). Stock solutions of MMA, DMA and Roxarsone at a concentration of 1000 μg mL^{-1} were prepared using ultrapure water and stored at 4 °C prior to performing the experiment. The working standard solutions were prepared by diluted stock solution with 1-octanol to the required concentration.

2.2. Apparatus

A Surveyor liquid chromatograph (Thermo Finnigan, San Jose, CA, USA) with two LC pumps was used for separation. The three organoarsenic compounds were separated on a Hypersil Gold C18 column (2.1 × 150 mm, 5 μm) from Thermo Fisher Scientific (Waltham, MA, USA). Mobile phases A and B were water solutions with 0.1% formic acid and acetonitrile, respectively. The analysis program used was as follows: initially 10% B was held 1 min and then increased linearly to 95% B over 9 min. Finally, isocratic elution was held for 1 min at the component of mobile phase of 95% B. The column temperature was maintained at ambient.

A Finnigan LCQ ion trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA), equipped with an electrospray ionization (ESI) source, was used for the determination of organoarsenic compounds. The optimum MS conditions were obtained by tuning with an automated procedure that maximized the signal for the ions of organoarsenicals. The instrument conditions were set as follows: capillary temperature, 200 °C; sheath gas pressure, 90 (arbitrary units); capillary voltage, 23 V and spray voltage, 5 kV. The selected ion monitoring (SIM) mode was used for the quantification of the trace amount of organoarsenicals. The mass peak width was set at 1.0 Th.

Power sonic 410 sonicator (Hwashin Technology Co., Seoul, Korea) was used in sonication. EASY SPIN centrifuge (Sorvall Instruments, Stevenage, UK) was utilized for the centrifugation of the sample tube.

2.3. Ultrasound-assisted dispersive liquid–liquid microextraction (UA-DLLME) procedure

3.0 g aliquots of edible oil containing MMA, DMA, Roxarsone and 30 μL of 10 μg mL^{-1} Trimethylamine *N*-oxide (I.S.) were placed in a 15 mL screw cap PTFE test tube with conical bottom. Then 1.25 mL portions of hexane (disperser solvent) containing 50 μL of pH 7 ammonium formate buffer solution (extraction solvent) were injected rapidly into each sample solution using a 5 mL syringe. The mixed solution was bathed in the sonicator for 5 min resulting in the formation of a cloudy mixture in the test tube. During this process, the organoaresenicals were extracted into the fine droplets of pH 7 buffer solution. The solution was centrifuged at 10,000 rpm for 5 min. The fine droplets of pH 7 ammonium formate buffer solution were coalesced and deposited at the bottom of conical test tube. Samples of 25 μL of the sediment phase were removed using a 100 μL pipette. 5 μL portions were injected into the LC–MS system for analysis. The overall analysis time was 30 min containing LC system analysis.

Calibration was implemented by measuring the concentration of organoaresenicals spiked in edible oil blanks under the optimum conditions described. The enrichment factor was calculated as the ratio of the signals of organoaresenicals obtained after and before extraction. Extraction recovery was obtained from the percentage of C_x-to-C_{std}; where C_x is the concentration measured from the linear equation and C_{std} is the concentration of organoarsenicals spiked in the oil.

2.4. Sample analysis

Six kinds of oil samples were collected from the traditional market (Taichung, Taiwan). Included were sunflower oil, olive oil, grapeseed oil, soybean oil, palm oil and frying oil of restaurant. 3.0 g oil samples were pipetted into PTFE test tubes and subjected to the UA-DLLME procedure described above.

3. Results and discussion

In this study, UA-DLLME coupled to liquid chromatography–mass spectrometry was developed for the determination of trace amounts of organoarsenicals in oils. To improve the extraction efficiency from oils, the effects of different parameters affecting the formation of emulsion and extraction conditions, such as ultrasound-assist, disperser solvent, disperser volume, extraction solvent, extraction volume and extraction time were optimized.

3.1. Comparison of ultrasound-assisted and shake-assisted liquid–liquid microextraction

In oil phases, it is very difficult to effect homogenous dispersion of extraction solvent by using disperser solvent. To improve the homogeneity, ultrasound- and shaking-assisted methods were