Food Chemistry 192 (2016) 9–14

Contents lists available at ScienceDirect

Food Chemistry

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

Analytical Methods

An efficient method for the simultaneous determination of furan, 2-methylfuran and 2-pentylfuran in fruit juices by headspace solid phase microextraction and gas chromatography–flame ionisation detector

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ARTICLE INFO

Article history:
Received 26 March 2015
Received in revised form 25 June 2015
Accepted 28 June 2015
Available online 30 June 2015

Chemical compounds studied in this article:
Furan (PubChem CID: 8029)
2-Methylfuran (PubChem CID: 10797)
2-Pentylfuran (PubChem CID: 19602)

Keywords:
2-Alkylfrans
Furan
2-Methylfuran
2-Pentylfuran
Headspace solid phase microextraction
GC–FID

ABSTRACT

A headspace solid phase microextraction (HS-SPME) procedure followed by gas chromatography–flame ionisation detector (GC–FID) analysis was developed and validated for the simultaneous analysis of furan, 2-methylfuran and 2-pentylfuran from juice samples. Extraction at 32 °C for 20 min with stirring at 600 rpm and NaCl concentration 15% (W/V) was the optimal HS-SPME condition for all the three compounds by using a carboxen/polydimethylsiloxane fused silica fibre (75 μm). The extracted compounds were base line separated on a SPB-1 GC column within 12 min. The relative standard deviations of all analytes were less than 6.7%. The recovery rates were between 90.2% and 110.1%. The limits of detection and limits of quantification were 0.056–0.23 ng/mL and 0.14–0.76 ng/mL, respectively. The results showed that the developed method was sensitive, precise, accurate and robust for the determination of furan, 2-methylfuran and 2-pentylfuran in complex matrices without interferences from other components.

1. Introduction

Furan is a five-membered heterocyclic compound with four carbon atoms and one oxygen atom. It has been classified as a possibly carcinogenic chemical to humans (Group 2B) (IARC, 1995). Except for its presence in industrial products, furan could be formed in a variety of food and its formation in food usually involves complex steps, mostly involving thermal degradation. For example, furan could be formed in carbohydrate system and ascorbic acid solution under elevated temperature (Huang, Duan, & Barringer, 2011; Mogol & Gökmen, 2013; Owczarek-Fendor et al., 2010a) and fat oxidation products also have an important role in furan formation (Owczarek-Fendor et al., 2010b, 2012). In the 176 food samples including 17 samples of baby food, Becalski et al. found furan present in all the samples above 1 ng/g (Becalski et al., 2010). In addition to thermal treatment, novel technology has also been found to be able to induce furan in food, e.g. up to 60 ng/mL of furan was detected in UV light treated apple cider (Fan & Geveke, 2007). Besides furan, methylfuran has also been found in different food, Becalski et al. found 96% of the 176 samples they analysed contained 2-methylfuran above 1 ng/g including reconstituted apple juice and cranberry cocktail drink (Becalski et al., 2010). That implied a similar concern for 2-methylfuran in processed food, since 2-methylfuran was found to be a potent hepatotoxin (Ravindranath, McMenamin, Dees, & Boyd, 1986). There have been a few reports on the formation of furan during UVC treatment of fruit juices (Bule et al., 2010) and UV light treatment has been rapidly gaining acceptance across the whole spectrum of food and beverage industries. Therefore it is necessary to examine if other 2-alkylfurans were induced in fruit juices after UV light treatment. As a first step we chose 2-pentylfuran to start due to its medium chain length.

Due to their low concentration, the analysis of furan and its analogues in food matrices has been a challenge. Furan and methyl analogues of furan in food samples have been analysed via an isotope dilution method, in which the target furan compounds were extracted together with the addition of the isotope-labelled

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http://dx.doi.org/10.1016/j.foodchem.2015.06.100
0308-8146/

standards and then analysed using headspace-gas chromatography/mass spectroscopy (HS-GC/MS) (Becalski et al., 2005, 2010). This method possesses high sensitivity and wide linear range, but the use of isotopic standards made it less favoured. Solid phase microextraction (SPME) has gained popularity due to the advantage of being fast, simple and solvent free, and at the same time offering high sensitivity. SPME has been used for the extraction of volatile and nonvolatile compounds from different matrices, such as volatile compounds from fruit (Iiario et al., 2013), and pesticides from environmental samples (Sampedro et al., 2000), and there are many other literatures relating to this techniques. SPME has also been applied in the extraction of furan and 2-alkylfurans from juice and water solutions. For instance, Fan et al. used SPME (85 μm carboxen–PDMS fibre) to extract furan from apple juice (Fan & Geveke, 2007), Adam et al. used a divinyl benzene/carboxen/polydimethylsiloxane (DVB/carboxen/PDMS) fibre for the extraction of 2-alkylfurans in water solution (Adams, Bouckaert, Van Lancker, Meulenaer, & Kimpe, 2011). However, none of the groups reported the extraction efficiency of their methods. Since experimental parameters such as sample temperature, volume, extraction time, sample matrix, addition of salt and particularly the SPME fibre will substantially affect the analysis results, each of them needs to be examined. Therefore the objective of this study is to develop and evaluate an SPME method for the simultaneous extraction of furan, 2-methyl furan and 2-pentyl furan in juices and apply it to UV light treated juices.

2. Materials and methods

2.1. Reagents and materials

Furan (⩾99%), 2-methylfuran (99%, 2-MF), 2-pentylfuran (99%, 2-PF) were from Sigma–Aldrich (St. Louis, USA). High purity water was made by a Barnstead Nanopure purification system (Thermo Scientific, Dubuque, USA). Stock solutions of each standard were prepared by adding around 12 μL of the standard via a syringe through the septum of a 15-mL headspace vial (Supelco, Bellafonte, USA) containing 10 mL of HPLC grade methanol (Caledon Laboratories Ltd., Georgetown, Canada). The weight increase was measured to determine the exact concentration of each standard (at 1000 mg/L level). Stock solution of mixed standards was prepared by mixing each individual standard stock solution in equal volume (1.0 mL) in water (7.0 mL) with a final concentration at 100 mg/L level. Stock solutions were stored at 4 °C for less than two weeks. Sodium chloride (NaCl, AR) was from Sigma–Aldrich (St. Louis, USA). Apple juice and orange juice were purchased in a local store and stored at 4 °C. Apple cider was obtained from a local farm market (without addition of ascorbic acid and pasteurisation, no furan was found in it, Fig. 1B) and stored at −20 °C. Spiked apple cider (1.0, 5.0, 10.0, 50.0 100.00 ng/mL) was made freshly by adding the stock solution of mixed standards to apple cider before use.

The SPME device and carboxen/polydimethylsiloxane (CAR/PDMS) fused silica fibres (75 μm) were supplied by Supelco (Bellafonte, PA, USA). All the fibres were conditioned as recommended by the manufacturer prior to use. The 15-mL headspace glass vials with open top screw-caps (phenolic) and septa (PTFE/Silicone) were also from Supelco (Bellafonte, PA, USA).

2.2. UV light treatment of fruit juices

UV light treatment on fruit juices was carried out by using a model R-52G Mineralight lamp (UVP, Upland, CA, USA) at 254 nm (UVC). The fruit juice samples were exposed to UVC radiation in a quartz demountable cuvette of 2.0 mm path length

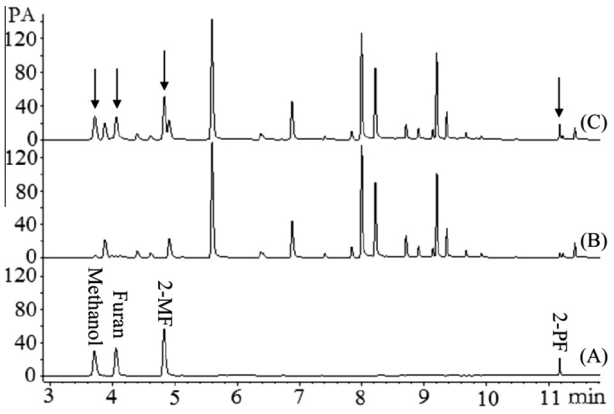

Fig. 1. Chromatograms of apple cider and standard solution. (A) 100 ng/mL mix standards of furan, 2-methylfuran (2-MF) and 2-pentylfuran (2-PF) (methanol is the solvent), (B) apple cider control, (C) apple cider spiked at 100 ng/mL of mix standards.

(model 20ES2, Precision Cell Inc., Farmingdale, NY, USA). Each sample (about 750 μL) was pipetted into the quartz cuvette (full of sample) containing a mini magnetic stirrer bar (coated with PTFE), and then the cuvette was properly sealed using a demountable quartz lid without generation of bubbles. All samples were kept in fridge (4 °C) before being exposed to UVC light. During UV light treatment, quartz cuvettes containing the samples were set straight down of the UV lamp and on the stirrer plate in the marked area, and the samples were stirred to achieve equal UV distribution. The distance between the UV lamp and the cuvette can be adjusted according to the required UVC intensity which was measured using a digital ILT 1700 radiometer (International Light Technologies, Peabody, MA, USA). In this study, the distance was fixed at around 8.0 cm to attain the corresponding UVC (254 nm) intensity at the cuvette position as expected to be 5.0 mW/cm^2. Different doses (0.3, 1.5, 3.0, 6.0 and 9.0 J/cm^2) of UVC light were applied to the juices by varying the time of exposure (1, 5, 10, 20 and 30 min, respectively).

2.3. HS-SPME optimisation

In the optimisation of SPME procedure, the CAR/PDMS fibre was selected preferentially according to previous reports (Bicchi et al., 2011; Fratini, Lois, Pazos, Parisi, & Medina, 2012; Goncalves et al., 2014; Lorenzo, 2014), where it has been demonstrated much superior for the analysis of small molecules and successfully used for furan analysis. With the CAR/PDMS fibre, major parameters for SPME such as extraction temperature, extraction time, stirring speed and salt addition effect were evaluated on the extraction efficiency. For the extraction temperature, three temperatures were selected: 23, 32 and 40 °C. For the extraction time, five extraction times were selected: 5, 10, 15, 20, 30 min. For the stirring speed, four stirring speeds were selected: 200, 400, 600 and 800 rpm. For the salt effect, five concentrations of NaCl in the sample were examined: 0%, 5%, 10%, 15%, 20% (W/V).

2.4. HS-SPME procedure

The HS-SPME was carried out by applying the optimised conditions. Five millilitre of mixed standard solution or diluted fruit juice (1:4) sample was taken from fridge (4 °C) and transferred into a 15-mL glass vial (21 × 70 mm) containing a magnetic stirrer bar and 15% (W/V) NaCl. The vial was sealed with a PTFE-lined septum and screw cap, and then was incubated at 32 °C for 10 min in a 15-mL vial holder sitting on a Corning heat/stir plate (Corning