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On-fiber furan formation from volatile precursors: A critical example of artefact formation during Solid-Phase Microextraction

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ABSTRACT

For the analysis of furan, a possible carcinogen formed during thermal treatment of food, Solid-Phase Microextraction (SPME) is a preferred and validated sampling method. However, when volatile furan precursors are adsorbed on the carboxen/PDMS fiber, additional amounts of furan can be formed on the fiber during thermal desorption, as shown here for 2-butenal and furfural. No significant increase in furan amounts was found upon heating the furan precursor 2-butenal, indicating that the furan amounts formed during precursor heating experiments are negligible as compared to the additional amounts of furan formed during fiber desorption. This artefactual furan formation increased with increasing desorption time, but especially with increasing desorption temperature. Although this effect was most pronounced on the Carboxen/PDMS SPME-fiber, it was also noted on two other SPME-fibers tested (PDMS and DVB/Carboxen/PDMS). The general impact on furan data from food and model systems in literature will depend on the amounts of volatile precursors present, but will probably remain limited. However, considering the importance of this worldwide food contaminant, special care has to be taken during SPME-analysis of furan. Especially when performing precursor studies, static headspace sampling should preferably be applied for furan analysis.

1. Introduction

As furan is classified as 'possibly carcinogenic to humans' by the International Agency for Research on Cancer [1], its presence in food products is of concern. Following publication of a survey of furan in food by the FDA in 2004 [2], numerous foods have been analyzed focusing mainly on food products that have been heat-treated in closed containers, in particular baby food and coffee. Moreover, the European Commission requested in the Commission Regulation 2007/196/EC to monitor the presence of furan in food and to collect data on furan concentration in commercial heated foodstuffs, and several reports have been published since then by the European Food Safety Authority [3,4]. Over the last five years, research on furan has focused mainly on its presence in diverse food products [5–7], its origin and formation pathways from various precursors [8–10] and other aspects relevant for furan exposure [11–13]. Crucial to all studies in this field is the use of reliable quantitative analytical methods. Because of the high volatility of furan, its extraction from the matrix can be based on headspace sampling and, accordingly, static headspace [14,15] as well as headspace Solid-Phase Microextraction (SPME) [16,17] analytical methods have been proposed and validated. When combined with GC–MS-analysis, these techniques both offer a simple approach to determine low concentrations of furan in basically any food sample. Quantification is based on the use of D_4-furan in a stable isotope dilution assay. The main advantage of SPME sampling as compared to static headspace sampling is the higher sensitivity that can be obtained: whereas the limit of detection (LOD) reported for static headspace sampling is around 2 ng g^{-1} [18], LOD-values as low as 25.7 ng kg^{-1} have been reported for SPME [17]. Therefore, headspace SPME-GC–MS has been proposed as an alternative for the static headspace method of the US Food and Drug Administration (FDA) for routine analysis of furan in foods [19].

However, when performing trace analysis of thermally generated volatiles, special care must be taken to avoid artefactual analyte formation during the analytical procedure. Careful examination of literature on the subject showed quite some difficulties in avoiding furan carry-over between samples and in obtaining 'blank chromatograms'. Heat is a crucial factor in furan formation and must be avoided as much as possible. As a consequence, the temperature should be kept as low as possible during sample equilibration and extraction. The equilibration temperature used in the

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official FDA method has been decreased from 80 to 60 °C to avoid furan formation during analysis [14]. However, even at an equilibration temperature of 40 °C, Şenyuva and Gökmen reported the formation of furan during analysis, depending on the food composition [20]. For SPME extraction of furan the superiority of the carboxen/polydimethylsiloxane fiber (CAR/PDMS) has been repeatedly reported [16,17] and this fiber has always been selected for furan extraction. However, quite high temperatures are required for its desorption, and it has been shown to be prone to artefact formation during the desorption step, specifically for amines and thiols [21–23]. Because of some unexpected results in our own experiments on furan analysis and driven by the importance of obtaining correct results on this worldwide food contaminant, we decided to investigate artefactual furan formation during SPME desorption further.

The main precursors of furan in food are Maillard reaction systems [24], vitamin C [9,25] and oxidized lipids [8,26], for which 2-butenal was identified as a crucial intermediate [27]. Formation of furan out of the volatile precursor 2-butenal was selected as a model system to investigate on-fiber formation of furan during SPME desorption, as it was during such experiments that artefactual furan formation became clear. In addition, artefactual furan formation from furfural was evaluated as well.

2. Materials and methods

2.1. Chemicals

2-Butenal (crotonaldehyde, >99%, Acroseal), L-alanine (>99%) and D_4-furan (99%) were obtained from Acros Organics (Geel, Belgium). Furan (>99%), furfural (2-furaldehyde, >99%) and glucose (99.5%) were purchased from Sigma–Aldrich (Bornem, Belgium).

2.2. Sample preparation

Twenty milliliter SPME-vials (Gerstel, Mülheim a/d Ruhr, Germany) were subsequently filled with 0.25 mmol of furan precursor (2-butenal or furfural) and 2 g of sand (50–70 mesh, Sigma–Aldrich) or 1 ml of water. The vials were hermetically closed with a magnetic crimp cap with a septum (silicone/PTFE; 55 Shore A; 1.5 mm, Gerstel) and mixed well by means of vortex. All samples were prepared at least in duplicate. Heating was performed in a preheated oven at 180 °C for 20 min.

For the alanine/glucose model reactions representing dry-roasting conditions, 0.25 mmol glucose and 0.5 mmol alanine in 1 g of purified sea sand were mixed in a 20-ml headspace vial. The samples were heated at 180 °C for 20 min in a stirred oil bath. For pressure cooking conditions, 0.25 mmol glucose and 0.5 mmol alanine were weighed in a 1 ml volumetric flask. Water was added to obtain the final volume of 1 ml. The reaction mixtures (1 ml) were transferred in a 20 ml headspace vial, which was sealed with a magnetic crimp cap. The samples were heated at 121 °C for 25 min in a stirred oil bath.

2.3. Furan quantification

Stock solutions of furan and D_4-furan were prepared by adding 10 μL of (D_4-)furan via a gastight syringe through the septum of a 20-mL headspace vial (Gerstel) containing 20 mL methanol. The weight increase was measured to determine the exact concentration of furan. The working solutions were prepared by adding 50 μL of stock solution to a 20-mL headspace vial containing 20 mL of water. After heating, reaction mixtures were spiked with 50 μL of D_4-furan working solution by means of a gastight syringe. All samples were kept in ice during spiking and were closed as fast as possible after spiking to minimize losses of furan. For calibration, exact amounts of furan working solutions were added to 2 g of sand, which was spiked with 50 μL of D_4-furan working solution. All samples were analyzed at least in duplicate.

2.4. SPME parameters

SPME extraction and desorption were performed automatically by means of an MPS-2 autosampler (Gerstel). SPME extraction was performed for 25 min at 35 °C. Time and temperature of desorption varied as specified in the tables or figures, but standard conditions were 5 min at 300 °C. Three different fibers were compared: carboxen/polydimethylsiloxane (Car/PDMS), divinylbenzene/carboxen/polydimethylsiloxane (DVB/Car/PDMS) and polydimethylsiloxane (PDMS) (Supelco, Bornem, Belgium). After each sample, a blank fiber analysis was performed to correct for furan carry-over in between samples.

2.5. GC–MS analysis

For furan determination, a Hewlett-Packard 6890 GC Plus coupled with a HP 5973 MSD (Mass Selective Detector-Quadrupole type), equipped with a CIS-4 PTV (Programmed Temperature Vaporization) Injector (Gerstel), and a Varian CP-PoraBOND Q capillary column (25 m × 0.32 mm i.d.; coating thickness 5 μm) was used. Working conditions were: transfer line to MSD: 260 °C, oven temperature: start at 35 °C, hold 1 min; from 35 to 100 °C at 10 °C min^{-1}, hold 5 min; and from 100 °C to 260 °C at 30 °C min^{-1}, hold 6 min; splitless mode; carrier gas (He) 1.7 ml min^{-1}; ionization EI 70 eV. Analyses were performed in selective ion monitoring (SIM) mode. Quantification was based on MS signals at m/z 68 for furan and m/z 72 for D_4-furan. The following qualifiers were used: m/z 39 for furan and m/z 42 for D_4-furan.

2.6. Statistical analysis

Differences in furan formation were statistically evaluated by means of standard deviations and Student's t test ($\alpha = 0.05$) (one-tailed).

3. Results

3.1. Furan formation upon heating of 2-butenal

To investigate the efficiency of 2-butenal as a furan precursor, model systems containing 2-butenal were heated at various temperatures. Analysis by means of SPME-GC–MS showed, however, unexpected results (Fig. 1). The amounts of furan detected did not seem to increase with temperature, and especially in the lower temperature range, very high standard deviations were found. From these results, the idea of artefactual furan formation during fiber desorption arose.

Repeating similar measurements applying static headspace analysis instead of SPME showed different results with more acceptable standard deviations (Fig. 1). Furan formation from 2-butenal remained very low until heating at 100 °C, and increased with heating between 130 and 280 °C. At temperatures of 130 °C and higher, data obtained with SPME and static headspace sampling did not differ significantly from each other.

3.2. Influence of desorption conditions and SPME fiber on artefactual furan formation

For SPME-extraction of furan, a CAR/PDMS fiber was used. To investigate the formation of furan from 2-butenal during fiber desorption, different desorption temperatures (250 °C and 300 °C) and

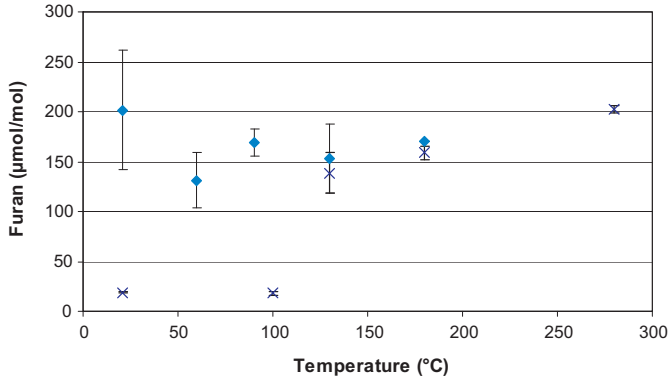

Fig. 1. Amounts of furan (µmol/mol) formed upon heating of 2-butenal at various temperatures, as measured by SPME-GC–MS (♦) and static headspace-GC–MS analysis (×).

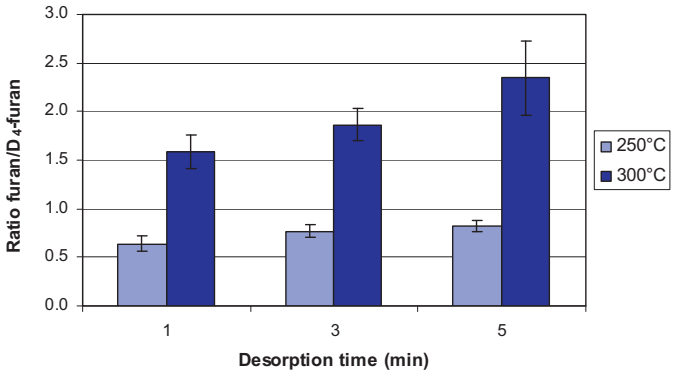

Fig. 2. Ratio of furan/D_4-furan (ion 68/ion 72) after SPME-GC–MS analysis of 0.25 mmol of 2-butenal in 1 ml water, spiked with D_4-furan (0.87 µg), in function of desorption time and temperature.

different desorption times (1, 3 and 5 min) were compared. The 2-butenal samples were spiked with a D_4-furan standard to correct for incomplete desorption of furan at lower desorption conditions. As the peak area of the standard D_4-furan results from adsorption and subsequent desorption from the fiber, while furan is formed on the fiber from adsorbed 2-butenal, reliable quantification of the amounts of furan on the fiber is not possible. In Fig. 2, the ratio of furan towards D_4-furan is reported. This graph clearly shows an increase in furan formation with increasing desorption time, but especially with increasing desorption temperature, as much higher amounts of furan were recovered when applying a desorption temperature of 300 °C. Results obtained after thermal desorption at 230 °C for 1 min were not significantly different from the results obtained at 250 °C for 1 min.

Fig. 3 shows the results obtained when using three different SPME-fibers for the analysis of 2-butenal, spiked with D_4-furan. As significant amounts of furan were detected and as the ratio of furan towards D_4-furan increased with desorption temperature for all three fibers, it can be concluded that formation of furan during fiber desorption occurs on all three fibers. Direct quantitative comparison of artefactual furan formation on these three fibers is difficult, as they each have a specific affinity for furan (and D_4-furan) and for 2-butenal. But, as the detected amounts of furan relative to the detected amounts of D_4-furan (Fig. 3) as well as relative to 2-butenal (data not shown), were highest for the Car/PDMS fiber, it can be stated that the highest conversion of 2-butenal to furan occurs on this fiber.

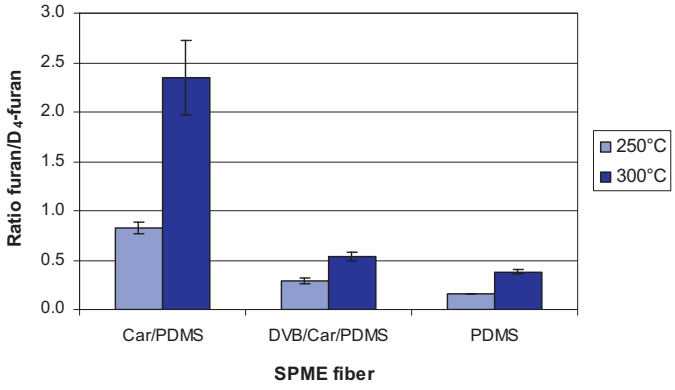

Fig. 3. Ratio of furan/D_4-furan (ion 68/ion 72) after SPME-GC–MS analysis of 0.25 mmol of 2-butenal in 1 ml water, spiked with D_4-furan (0.87 µg), in function of SPME-fiber and desorption temperature.

3.3. On-fiber formation of furan from other precursors

It can be expected that on-fiber formation of furan is not limited to 2-butenal. Furfural was examined as another common food volatile, identified as a relevant furan precursor [24]. Table 1 shows an important increase in furan detection after SPME-GC–MS analysis of furfural with increasing desorption temperature. The ratios of furan/D_4-furan are even higher than those obtained from similar experiments with 2-butenal. In addition, as was the case for heated 2-butenal (Fig. 1), the calculated amounts of furan obtained with unheated and heated furfural (180 °C, 20 min) were not significantly different, indicating that the formation of furan from furfural during heating prior to SPME-extraction, was negligible towards the formation of furan during SPME-desorption of furfural.

A similar comparison of different desorption temperatures on the amounts of furan recovered was made for model Maillard reactions of alanine and glucose, previously shown as a relevant furan precursor system [28]. The results (Table 2) showed no significant difference in furan values obtained at both desorption temperatures.

4. Discussion

When performing trace analysis, extreme care has to be taken to avoid artefact analyte formation during the analytical procedure. For an important food contaminant as furan, regarded as "possibly carcinogenic to humans", very low limits of detection have to be reached in diverse foodstuffs. For furan analysis, SPME has been selected as the method of choice by many researchers. Static headspace sampling has also been described, giving equally good results, but at higher detection limits. One of the problems resulting from SPME-extraction of furan, and to a minor extent also from static headspace sampling, is carry-over of furan between different samples. Many publications related with furan report such difficulties in obtaining blank chromatograms [16,17]. This problem has pushed us to increase our fiber desorption conditions to 300 °C for 5 min and to run a blank analysis before each sample, to monitor and correct for furan carry-over. This increase in severity of desorption conditions has, however, revealed another issue in furan analysis by means of SPME: artefactual furan formation during fiber desorption.

Our results showed a clear increase in furan formation from adsorbed 2-butenal with increasing fiber desorption time and especially with increasing desorption temperature. The SPME fiber of choice for furan extraction, the Car/PDMS fiber, requires quite high desorption temperatures (250–310 °C, according to the manufacturer's recommendations), and literature reports apply a

Table 1
Influence of fiber desorption conditions and heating on furan formation after SPME-GC–MS analysis of 0.25 mmol furfural, spiked with D_4-furan (0.89 μg).

Sample heating conditions	Fiber desorption conditions	Furan (μmol/mol)	Ratio furan/D_4-furan
Not heated	250 °C, 5 min	68.5 ± 15 a	1.3 ± 0.3 a
Not heated	300 °C, 5 min	244.3 ± 44 b	4.3 ± 0.8 b
180 °C, 20 min	300 °C, 5 min	150.5 ± 30 b	2.7 ± 0.5 b

Different letters designate significantly different values within one column.

Table 2
Influence of fiber desorption conditions and heating on furan formation after SPME-GC–MS analysis of an alanine/glucose model mixture, spiked with D_4-furan (0.90 μg).

Sample heating conditions	Fiber desorption conditions	Furan (μmol/mol)	Ratio furan/D_4-furan
Pressure cooking (121 °C, 25 min)	250 °C, 5 min	0.73 ± 0.04 a	0.27 ± 0.01 a
Pressure cooking (121 °C, 25 min)	300 °C, 5 min	0.78 ± 0.07 a	0.30 ± 0.02 a
Dry roasting (180 °C, 20 min)	250 °C, 5 min	47.8 ± 8.0 b	1.7 ± 0.3 b
Dry roasting (180 °C, 20 min)	300 °C, 5 min	55.5 ± 4.4 b	2.0 ± 0.2 b

Different letters designate significantly different values within one column.

desorption temperature ranging from of 230 °C for 1 min [26] up to 300 °C for 2 min [24]. At less severe SPME desorption conditions, artefactual furan formation from volatile precursors will be less important, but it remains present.

A comparison of different SPME fibers showed that this phenomenon also occurs on the other two fibers tested: DVB/Car/PDMS and PDMS, albeit to a lesser extent. The high susceptibility of the Car/PDMS fiber is not unexpected, as it is specifically the high microporosity of the carboxen polymer which give this fiber its unique properties for the efficient adsorption of low molecular weight volatiles, such as furan. Artefact formation during desorption of Car/PDMS SPME fibers has been reported before, in particular the dehydrogenation of amines [22] and the oxidative dimerisation of thiols to the corresponding disulfides [23]. Formation of these artefacts was explained by a long residence time of analytes on the Car/PDMS fiber, due to the high amounts of micropores in carboxen [22], and by the presence of metallic particles on SPME fibers [29], which act as oxidation catalysts. The long residence time within the micropores of the Car/PDMS fiber of volatile precursors, such as 2-butenal and furfural, may well account for the conversion to furan at such high desorption temperatures. In view of the necessary oxidation of 2-butenal to 4-hydroxy-2-butenal to form furan [20], it is obvious that the presence of metallic catalysts and the high specific surface combined with the long residence time and the high desorption temperature create ideal circumstances for the artefactual formation of furan from 2-butenal present on the fiber. Similarly, furfural probably requires oxidation to 2-furoic acid before decarboxylation to furan occurs in dry reaction conditions [9].

It is not straightforward to estimate the importance of this artefactual furan formation on the SPME fiber for the numerous results reported in literature. Obviously, studies examining furan formation from volatile precursors, such as 2-butenal, furfural, 2-furoic acid, acetaldehyde and glycolaldehyde, will suffer a considerable influence of this phenomenon. Based on the fact that no significant differences in amounts of furan were observed after heating 2-butenal and furfural at different temperatures, our results show that the in situ furan formation on the fiber during desorption is the main contributor to the detected amounts of furan, in contrast to the negligible amounts formed by heating the volatile prior to SPME-extraction. Such precursor studies obviously use considerable amounts of precursors, thus creating a high adsorption of these precursors on the SPME-fiber. Based on the fact that D_4-furan, added as an internal standard, could be detected, it can be excluded that the high adsorption of precursor would result in fiber saturation and thus prevent adsorption of furan formed prior to SPME-extraction. Calculated approximate yields (which are not completely correct because of the considerations mentioned in Section 3.2) are about 200 μmol furan/mol precursor. These are, in fact, yields generally reported for furan formation in precursor studies. For instance, Limacher et al. report furan formation from furfural (0.1 mmol, SPME desorption 300 °C, 2 min) ranging from 70 to 265 μmol/mol, depending on the heating conditions [24]. Furfural is actually a very common food volatile, for example in coffee [30], and results from the Maillard reaction and sugar caramelisation [31]. Therefore, the potential bias on previously reported results originating from Maillard reaction systems [28] was estimated by evaluating the influence of the desorption temperature on the furan determination in a glucose/alanine model system. Since no significant impact of the desorption temperature on the furan formation was observed, it seems that, at least in these reaction systems, the impact of the potential additional furan formation on the SPME fiber during desorption was negligible. However, the general impact of the artefactual furan formation on furan data from food samples still needs to be investigated. Especially coffee and baby foods, which have been shown to be prone to form furan during thermal processing [2], should be evaluated for artefact furan formation. For instance, it is known that coffee contains high amounts of volatile Maillard reaction products [30], such as furfural, which can lead to additional formation of furan. Also baby food vegetable purees are susceptible to form Maillard reaction and lipid oxidation products, since they generally contain carbohydrates, amino compounds and vegetable oils. The impact of artefactual furan formation on furan data from food samples can be studied by comparing furan data obtained from headspace sampling on the one hand and SPME sampling on the other hand. To the best of our knowledge, only one study compared both techniques for only five food samples. As the authors did not detect any difference between both techniques, it seems that the general impact of artefactual furan formation on furan data from food systems will probably remain limited.

These results demonstrate that considerable amounts of furan can be formed from volatile precursors during SPME fiber desorption at high temperatures. Therefore, caution is recommended especially when furan is quantified in precursor systems. Hence, static headspace sampling represents a better alternative for furan analysis, but has more limited applications due to a lower sensitivity. The impact of the artefactual furan formation on furan data from food samples still needs to be investigated.

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