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The application of headspace gas chromatography coupled to tandem quadrupole mass spectrometry for the analysis of furan in baby food samples

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ABSTRACT

Selective methodology employing a tandem quadrupole mass spectrometer coupled to a gas chromatograph with headspace autosampler (HS-GC–MS/MS) was elaborated in this study. Application of the elaborated procedure resulted in a limit of detection of 0.021 μg kg^{-1} and a limit of quantification of 0.071 μg kg^{-1}. The mean recoveries during in-house validation ranged from 89% to 109%, and coefficients of variation for repeatability ranged from 4% to 11%. The proposed analytical method was applied for monitoring the furan content of 30 commercial baby food samples available on the Latvian retail market. The level of furan found in these samples varied from 0.45 to 81.9 μg kg^{-1}, indicating that infants whose sole diet comprises baby food sold in jars and cans are exposed constantly to furan. Samples containing vegetables and meat had higher levels of furan than those containing only fruits.

1. Introduction

Furan is a small, heterocyclic organic compound present in the volatile fraction of many thermally processed foods and drinks. It is a lipophilic, highly volatile, colourless liquid with a boiling point of 31 °C (Mesias & Morales, 2015).

Early reports of furan in foods were summarised by Maga (1979) who reported it was present in a number of foods, with the highest concentrations found in coffee.

Although the presence of furan in foods has been known for years, interest in this compound increased after the International Agency for Research on Cancer (IARC) classified furan as a possible human carcinogen (Group 2B) following extensive research in animals (IARC, 1995).

In 2004, the US Food and Drug Administration (US FDA) published a report on the occurrence of furan in a number of foods that undergo heat treatment, such as canned and jarred foods (US FDA, 2009). Subsequently, the European Food Safety Authority (EFSA) initiated collection of data from all Member States for the presence of furan in food in order to carry out a risk analysis. The latest EFSA report included data obtained between 2004 and 2010. The analysis included a total of 5050 analytical results for furan in foods, as submitted by 20 countries. The highest furan levels were found in coffee with the mean values varying around 45 μg kg^{-1} for brewed coffee and 3660 μg kg^{-1} for roasted coffee beans (EFSA, 2011).

Several authors have focussed on the occurrence of furan in baby foods due to the susceptibility of this population group. Reports have been published describing relatively high concentrations of furan with up to 153 μg kg^{-1} in Switzerland (Zoller, Sager, & Reinhard, 2007), 141 μg kg^{-1} in Italy (Bianchi, Careri, Mangia, & Musci, 2006) and 95.5 μg kg^{-1} in Brazil (Pavesi Arisseto, Vivente, & De Figueiredo Toledo, 2010) for vegetable- and meat-based baby foods. At the same time, furan levels in fruit-based baby foods are very low, on average below 5 μg kg^{-1}. Many researchers have reported non-detection of furan because its relatively high limits of detection, e.g. 2.4 μg kg^{-1} (Pavesi Arisseto et al., 2010), 4.0 μg kg^{-1} (Jestoi et al., 2009; Ruiz, Santillana, Nieto, Cirugeda, & Sanchez, 2010), 0.17 μg kg^{-1} (Sijia, Enting, & Yuan, 2014), 0.12 μg kg^{-1} (Kim, Kim, & Lee, 2010), 0.60 μg kg^{-1} (Lachenmeier, Reusch, & Kuballa, 2009). Therefore, development of new methods with higher sensitivity for furan in baby foods is still a very important task.

Possible pathways for the formation of furan in foods have been assessed by several researchers. These mechanisms are mainly related to: (1) thermal degradation of carbohydrates, such as

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glucose, lactose and fructose, or the Maillard reaction of reducing sugars, alone or in the presence of amino acids, such as aspartic acid, alanine, and threonine (Maga, 1979; Perez Locas & Yaylayan, 2004); (2) thermal degradation of certain amino acids, such as serine and cysteine, capable of forming acetaldehyde and glycolaldehyde (Perez Locas & Yaylayan, 2004; Limacher, Kerler, Davidek, Schmalzied, & Blank, 2008); (3) thermal oxidation of ascorbic acid (Becalski & Seaman, 2005; Fan, 2005); (4) oxidation of polyunsaturated fatty acids, and (5) oxidation of carotenoids (Yaylayan, 2006).

Owczarek-Fendor et al. (2012) used a model food system that mimicked baby foods concluded that, apart from vitamin C and polyunsaturated fatty acids, sugars are an important source of furan, especially when heated in combination with proteins. The most important carbohydrate causing generation of furan was lactose at pH 6 (Owczarek-Fendor et al. (2012)). However, previous studies have suggested the main promoter for furan from carbohydrates was fructose (Bule et al., 2010).

Because of its high volatility, headspace sampling is the most common method for analysing furan (Crews & Castle, 2007). Furan is also analysed using a solid-phase microextraction (SPME) method in combination with GC–MS (Crews & Castle, 2007; Mesias & Morales, 2015). SPME allows the concentration of the analyte, and affords high sensitivity and minimum interference from matrix compounds (Altaki, Santos, & Galceran, 2007). However, this technique has some essential drawbacks, not least an appropriate stationary phase, stable SPME fibre, and optimised coating techniques, which are crucial for extraction of trace amounts of furan making it more expensive than other methods.

Direct headspace sampling appears to be a simple, rapid and economic procedure but, as stated above, the limits of quantification are sometimes too high to obtain precise furan concentrations in baby foods. Two different scan modes (selected ion monitoring (SIM) and selected reaction monitoring (SRM)) were compared in our study for sensitivity and selectivity. For the first time in scientific literature, tandem mass spectrometry has been used for the analysis of furan. Taking into account the trace level of furan in foods, application of the SRM mode is important since it provides higher selectivity and sensitivity for the analysis of this compound.

2. Experimental

2.1. Chemicals and materials

All analytical standards used within this study, such as furan and furan-d_4 ($\geqslant$99% purity), fructose, lactose, saccharose, glucose and β-carotene, were purchased from Sigma-Aldrich (St. Louis, MO, USA). Isopropanol was of LC–MS grade, hexane, methanol, and acetone were of HPLC-grade, and were also purchased from Sigma-Aldrich. Sodium chloride and sodium sulphate were of analytical purity grade and purchased from Merck Millipore (Darmstadt, Germany). Deionised water was purified with a Millipore Milli-Q system.

2.2. Samples

Thirty samples of baby food in jars were purchased from the most popular local supermarkets in Riga (Latvia). Samples comprised three different brands containing various product groups, such as meat, vegetables, cereals and fruits, and covered the majority of baby foods available on market. The samples were stored unopened and refrigerated until analysis. The main ingredients of the analysed samples are shown in Table 1.

2.3. Sample preparation procedure

Sample preparation was based on previous publications (Altaki et al., 2007; Kim et al., 2010; Nie et al., 2013). Briefly, a 5 g portion of refrigerated homogeneous sample was weighed into a chilled 20 mL headspace vial, and 2 g of NaCl and 10 mL of deionised water were added. After adding the internal standard furan-d_4 (25 μg kg^{-1}), the vials were immediately closed to avoid analyte losses and shaken for 1 min to obtain a homogeneous mixture. Samples were analysed using HS-GC–MS/MS. Quality control samples at a concentration of 10 μg furan per kg were prepared along with the study sample.

2.4. HS-GC–MS/MS analysis

Furan was analysed using a Trace GC Ultra gas chromatograph equipped with a TriPlus RSH headspace autosampler, coupled with a TSQ Quantum XLS tandem mass spectrometer (ThermoScientific, MA, USA). The capillary column used was 60 m × 0.32 mm, 1.8 μm Rtx-624 (Restek, Bellefonte, USA). The analysis was performed in splitless mode.

Operating conditions: the carrier gas was helium at a constant flow rate of 1.7 mL min^{-1}, the injector temperature was 200 °C, MS transfer line temperature was 250 °C, the ion source temperature was 200 °C. The initial oven temperature was 35 °C (held for 2 min), then increased to 230 °C at a rate of 20 °C min^{-1} and held for 20 min. The total analysis time was 13 min. Injection volume was 1.5 mL, incubation for 10 min at 70 °C. The emission current was set at 50 μA, and electron energy at 70 eV and 35 eV, respectively, for selected ion monitoring and reaction monitoring modes. The collision gas (argon) pressure for SRM mode was set at 0.17 Pa (1.3 mTorr). The collision energy for the transition of m/z 68 → 40 was set at 10 eV, and for the transitions of m/z 68 → 39 and m/z 72 → 42 it was set at 15 eV. Two scan types were compared: SIM and SRM for the detection of furan and the internal standard.

2.5. Method performance

The elaborated HS-GC–MS/MS method was validated in terms of linearity, selectivity, limit of detection (LOD), limit of quantification (LOQ), precision, and accuracy (recovery). The linearity was evaluated at five calibration concentrations over the range 0–100 μg kg^{-1}. Selectivity was tested by verifying the absence of an analytical signal at the retention time for the analyte in a blank sample. Inter-day and intra-day precision and recovery were evaluated by spiking blank samples with furan at 1, 10 and 30 μg kg^{-1} for five replicates at each level over three days. The LOD and LOQ values were determined using six independent sample blanks fortified at 0.1 μg kg^{-1} and calculated as three- and 10-fold standard deviation of the concentrations obtained for the fortified sample.

2.6. Quality control and quality criteria

The quality control of the method was performed through routine analysis of procedural blanks as well as quality control standards and samples to confirm the absence of contaminants and possible carryover between samples, and assess the quality of the results.

The identification criteria for furan were based on its retention time and the ion/transition intensity ratios of furan and furan-d_4. A deviation in the ion/transition intensity ratios within 20% of the mean values for calibration standards, and ±0.5% of the retention time compared to the retention time of the labelled standard in each sample, was considered acceptable. Quantification of furan in the samples was performed using a linear calibration curve (1–100 μg kg^{-1}) and furan-d_4 as the internal standard.