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Analysis of furan in heat-processed foods in China by automated headspace gas chromatography-mass spectrometry (HS-GC-MS)

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ABSTRACT

In order to assess furan content in thermal processed commercial foods available in China, an optimized automated headspace gas chromatography-mass spectrometry method (HS-GC-MS) was developed and validated. Internal standard d_4-furan was used with addition of salt (NaCl) into the headspace with an oven temperature 70 °C and equilibration time 30 min which was coupled with HP-PLOT/Q GC column. The proposed HS-GC-MS method was applied to furan quantization in 11 categories of foods (totally 133 kinds of food samples). Average level of furan detected in ng g^{-1} for various food products were: infant formula 15.0, bread 4.0, coffee 60.6, fruit juice 5.3, dairy product 1.5, nutritional drink 16.2, canned jam 30.4, spice 9.3, vinegar, 38.3, beer 4.9, and soy sauce 128.8. The results indicated soybean should be one kind of raw materials or precursor that is easier to form furan during food heat processing because soybean contains high fat and protein.

1. Introduction

Furan (C_4H_4O) is a colorless, volatile (boiling point 31 °C) and lipophilic organic compound which has been detected in a variety of solid foods and beverages that have undergo heat treatment (Bolger, Tao, & Dinovi, 2009). Several government agencies including the International Agency for Research on Cancer (IARC, 1995, pp. 393-407), the US Department of Health and Human Service (NTP, 2005), and the National Toxicology Program (NTP, 1993) have classified furan as a potential human carcinogen in Group 2B. Thermal treatment is one of the potential causes of furan presence in a variety of canned and jarred foods, including baby foods and infant formulas (FDA, 2004).

The levels of furan based on a screening in 340 food samples analyzed by the United States Federal Department of Agriculture (US FDA), ranged from non-detectable to approximately 170 ng g^{-1}. Since furan in heat-processed foods has become a potential food safety issue and may be pose a panic to consumers, several international food organizations including the United States Federal Department of Agriculture (US FDA) and the European Food Safety Authority (EFSA) have initiated additional research programs to quantify the furan content in foods as well as to develop a better understanding of furan formation during food processing, its toxicity levels, and its effect on human health.

To date, food researchers have observed that the formation of furan is mainly related to five possible mechanisms: 1) the thermal degradation of carbohydrates such as glucose, lactose and fructose or the Maillard reaction involving the reaction of a specific amino acid with a reducing sugar in the presence of heat (Maga, 1979); 2) the thermal degradation of some amino acids such as serine, alanine and threonine etc.; 3) the oxidation of polyunsaturated fatty acids; 4) the decomposition of ascorbic acid or its derivatives; and 5) the thermal oxidation of carotenoids (Becalski & Seaman, 2005; Fan, 2005; Perez-Locas & Yaylayan, 2004; Yaylayan, 2006).

Researches about the origin of furan and its safety evaluation had been run very well, but the EFSA issued a call for more information on the occurrence of furan in foods that will be helpful for completing a sound dietary exposure assessment (EFSA, 2006 and 2007). Therefore, developing rapid, selective, and sensitive analytical method to obtain actual levels of furan in foods becomes one of major dominant themes in the current furan research (Altaki, Santos, & Galceran, 2009). The analysis of furan in food, however, is challenging because of its high volatility and relatively low amounts in foods (i.e.

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ng g^{-1}). Two common methodologies are presently used for quantitative furan analysis including, headspace gas chromatography-mass spectrometry (HS-GC-MS) and solid phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS). These methodologies are continuously being modified and updated to improve their sensitivity, robustness, and also to reduce or eliminate the influence from an interferencing ions/molecules originating from the matrix compounds (Bicchi et al., 2011; Goldmann, Perisset, Scanlan, & Stadler, 2005; Nyman, Morehouse, Mcneal, Perfetti, & Diachenko, 2006; Sarafraz-Yazdi, Abbasian, & Amiri, 2012).

The automated headspace sampling (HS) GC/MS method recommended for furan analysis by the US FDA has been proved to be accurate (FDA, 2004). Typically, this method involves using 10 g samples that are fortified with d_4-furan and sealed in headspace vials. Automated headspace sampling is followed by GC-MS analysis to detect furan and d_4-furan in full-scan mode. The furan content is quantified by using a standard curve (requiring seven extractions per sample) where the concentration of furan in the fortified test portions is plotted against the furan/d_4-furan response factors using ions at *m*/*z* 68 and *m*/*z* 72 (for d_4-furan). SPME equipped with GC-MS has been proved to be another good technique for the analysis of volatile compounds at low levels in food samples because of its minimum interferences by matrix compounds. Intensive research has been done for the optimization of HS-SPME-GC for furan analysis by some researchers (Bicchi et al., 2011; Goldmann et al., 2005; Sarafraz-Yazdi et al., 2012). For SPME, an appropriate stationary phase, stable SPME fiber, and optimized coating technique are crucial for extracting trace amounts of furan but make it more costing.

Direct headspace sampling appears to be a simple and economical procedure thus making it competitive for producing reliable furan analysis results. In our present study, we aimed to develop a simple, sensitive, and feasible HS-GC-MS method for the determination of furan in a variety of heat-processed commercial food products in China by optimizing headspace sampling parameters and GC separating capacity, with the method being applicable to foods around the world. The results obtained from this work provide the updated data on the furan levels in a number of food products available in the Chinese market.

2. Materials and methods

2.1. Food samples collection and preparation

Eleven categories of commercially available foods including infant formula, bread, coffee, fruit juice, dairy product, nutritional drink, canned jam, flavors, vinegar, beer and soy sauce (133 kinds of foods) were purchased from local supermarkets in China. To protect the commercial interests of the produces, information on tested samples including brands, food composition, heating treatment, etc. has been excluded from this publication. All food samples were stored at 4 °C (>4 h) before analysis to reduce any possible loss of furan.

2.2. Chemicals and reagents

Furan and d_4-furan (≥99% purity) and methanol (HPLC grade) were purchased from Aldrich Chemical Company (St. Louis, MO, USA) except for Sodium sulfate, sodium chloride, sodium carbonate, sodium acetate and potassium chloride were from Sinopharm Chemical Reagent Co., Ltd.

2.3. Gas chromatograph/mass spectrometer (GC-MS) analysis

Agilent Model 7890A/7000 gas chromatography/mass spectrometer equipped with an Agilent Model G1888 Headspace Sampler (Agilent Technologies, Santa Clara, California, USA); capillary column 19091P-Q04 HP-PLOT/Q, 30 m × 0.32 mm × 20 μm (film) with particle trap 5181-3351 (Agilent Technologies); headspace crimp vials, 20 mL with silicon septa, aluminum crimp seals, hand crimper, and decapper (Agilent Technologies) were used for the analysis.

2.3.1. Headspace operating conditions

The oven temperature was set at 70 °C, the loop temperature was set at 110 °C, the transfer line was set at 130 °C, the thermal equilibration time was 30 min with low shake on. The injection time was 1 min and vial was pressurized to 10 psi in 0.5 min.

2.3.2. GC-MS operating conditions

The injection mode: split was set to a 3:1 ratio. The following GC oven temperature was applied: initial oven temperature was set at 50 °C and held for 1 min. The oven temperature was then increased to 200 °C at a rate of 10 °C min^{-1} which was held for 10 min. The injector temperature was at 200 °C and a constant flow rate of 1.0 mL min^{-1} (UHP helium).

2.3.3. Mass selective detection parameters

The high sensitivity EI ion source and transfer line temperatures were at 230 °C and 225 °C, respectively with the quadrupole temperature set at 150 °C. The MS operating conditions were as follows: positive electron ionization mode (EI+) using automatic gain control with 70 eV of electron energy. The mass spectrometer was operated in selected-ion monitoring mode (SIM) by recording the abundance of the following ions: *m*/*z* 68 $[M]^+$ and *m*/*z* 72 $[M]^+$ for furan and d_4-furan determination, respectively. For confirmation of furan and d_4-furan, the ions, *m*/*z* 39 $[M\text{-}CHO]^+$ and *m*/*z* 42 $[M\text{-}C_2HO]^+$ were monitored; dwell time: 100 ms each ion. Solvent delay was set for 10 min. Furan was quantified by comparing the peak area ratios of the response at *m*/*z* 68 and *m*/*z* 72 for the sample with that of the calibration.

2.4. Standard solutions

Furan and d_4-furan stock standards at concentration of 2.5 mg mL^{-1} methanol were prepared following previous publication (Nyman et al., 2006). Furan stock standards were stored at 4 °C for less than 2 weeks.

2.4.1. Intermediate stock standards

Intermediate stock standards (2.5 μg mL^{-1}) of furan and d_4-furan were prepared by transferring 200 μL of 2.5 mg mL^{-1} furan stock standards with a 200 μL syringe to a sealed HS vial containing 20.0 mL water, and mixed by shaking the vial. A corresponding solution of d_4-furan was prepared using the same procedure. The furan and d_4-furan stock standards were stable for at least two weeks at 4 °C.

2.4.2. Working standards at ca 2.5 μg mL^{-1} of furan and d4-furan

1000 μL of 25 μg mL^{-1} of the furan intermediate standard was transferred using a 1000 μL syringe to a sealed HS vial containing 9.0 mL water, and mixed by shaking. A corresponding solution of d_4-furan was prepared using the same procedure. Fresh working standards were prepared daily.

2.4.3. Working standard at ca 0.25 μg mL^{-1} of furan

1000 μL of 2.5 μg mL^{-1} furan stock standard was transferred using a 1000 μL syringe to a sealed HS vial containing 9 mL water, and mix by shaking the vial.

2.4.4. Calibration curve

Calibration standards for furan at different concentrations (5, 25, 50, 125, 250, 800, 1000 and 1200 ng mL^{-1}) were prepared by