GC/MS Determination of Furan in Food and Beverages using a PLOT Column

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Abstract

Purpose: To demonstrate the suitability of the Thermo Scientific TracePLOT TG-Bond Q column fitted with a particle trap to monitor the presence of furan in food and beverages by GC/MS with headspace sampling.

Methods: GC/MS with Porous Layer Open Tubular (PLOT) column and headspace sampling.

Results: The FDA furan method was successfully transposed to a Thermo Scientific analysis system allowing accurate quantification of furan levels in all the food types tested.

Introduction

The toxic heterocyclic organic compound, furan, is a contaminant of prepared foods thought to be formed principally by the oxidation of polyunsaturated fatty acids at high temperatures, the decomposition of ascorbic acid or its derivatives or the thermal degradation of carbohydrates. There is evidence that furan is carcinogenic and cytotoxic to rodents [1-3], and it has been classified as a possible carcinogen to humans by the International Agency for Research on Cancer [4]. Therefore, it is important to have available robust, selective and sensitive analytical methods to monitor the presence of this compound in food and beverages and to access the risk to human health. The FDA has issued a prescribed method for furan determination by GC/MS with headspace sampling [5]. In this method furan is quantified by the method of standard additions using furan-d_4 as the internal standard.

The work presented in this paper illustrates a successful adaptation of the FDA method employing a PLOT column and particle trap, and the preparation of standard addition curves for retail samples of coffee, red wine, beer and peanut butter. The FDA method recommends a 15 meter column and 1.7 mL/min carrier gas flow rate but these conditions would have compromised the vacuum required by the MS detection system. A 30 meter PLOT column was used and the column flow rate was reduced to 1.2 mL/min. Traditional PLOT columns suffer from poor particle stability and very often these are released from the column causing blockages and flow irreproducibility. TracePLOT columns use a proprietary particle adsorption process which minimises particle release and therefore improves chromatography. However, to ensure no particles entered the detector a particle trap was used between the analytical column and the MS detector. Under these conditions, linear standard addition calibration curves were achieved for all the food and beverage samples examined giving R^2 values above 0.99 in all cases.

The FDA furan method was successfully transposed to a Thermo Scientific analysis system allowing accurate quantitation of furan levels in all the food types tested.

Materials & Methods

Sample preparation

Branded peanut butter, coffee, red wine and beer/lager were obtained from a local supermarket.

Liquid samples – 10g

Solid samples – 5g + 5 mL of water

Peanut butter – 5g + 5 mL of saturated NaCl in water

The sample weights / volumes above were placed in headspace vials and fortified with furan and furan-d_4 as indicated in table 1. Vials were sealed and placed in the headspace tray.

Quantification is based on a standard additions curve for each sample type, where x equals the ng amount of furan added to the test portion and y equals the response ration of furan to furan-d_4.The amounts of furan added to the test portions are based on an estimate (x_0) of the furan concentration present in the food. Estimation of the concentration of furan in the food sample is performed by using the integrated response ration of furan / furan-d_4 (m/z 68/72) and the amount of internal standard.

TABLE 1. Preparation of test portions.

Sample 5 g (10g) test portion	µL of 5 µg/mL furan standard	µL of 5 µg/mL furan-d_4 standard	ppb of furan added
$0x_0$	0	40	0
$0x_0$	0	40	0
$0x_0$	0	40	0
$0.5x_0$	10	40	10
$0.5x_0$	10	40	10
$1x_0$	20	40	20
$2x_0$	40	40	40

Columns: TracePLOT™ TG-Bond Q, 30 m x 0.32mm x 10 µm
Particle Trap: 2.5 m × 0.32 mm

The analytical column and the particle trap were connected via a glass fitting. This process takes place under high temperature and pressure.

GC/MS Conditions:

TriPlus Headspace Autosampler:
Sample Volume: 1 mL
Sample analysis time: 30min
Agitator temperature: 60 ºC
Incubation time: 30 min
Agitator shake: On 15s, Off 15s
Syringe temperature: 100 ºC
Post injection flush: 30s

TRACE GC Ultra: Oven Program: 40 ºC, 10 ºC/min, 225 ºC (12.5 min)
Equilibration time: 0.5 min.
Injector: 200 ºC, Split
Split Flow: 80 mL/min
Column Flow: 1.2 mL/min
Transfer line temperature: 225 ºC

DSQII MS: Source temperature: 200 ºC
Ion volume: Closed EI
Emission current: 50 µA
Detector gain: 3 × 10e5 (1200V)
Electron energy: -70 V
Filament delay: 5.5 min
Scan parameters: Selected Ion monitoring: m/z 68 for furan and m/z 72 for furan-d_4.
Dwell time: 100 ms.

Consumables: BTO™ 17mm Septa
5mm ID Focus Liner, 105 mm long
Liner Graphite seal
2.5mL Headspace Syringe
Graphite ferrules to fit 0.32 mm ID columns
Graphite/vespel 0.32 mm ID ferrules for GC/MS interface
20 mL clear crimp top vial
Aluminium 20mm cap and Si/PTFE seal

Results

The method of standard additions was used to quantify the furan present in coffee, beer, wine and peanut butter. Linear regression analysis for each sample type was performed according to the FDA method [5]. Quantification was achieved by calculating the integrated response ratio of m/z 68 for furan and m/z 72 for furan-d_4. Linear regression curves were constructed with concentrations of furan added to the test portions and response ratios. Furan concentration in the samples was calculated at y = 0 on the calibration curve.

Good linearity was achieved for the standard addition calibration curves for all samples tested, using the method presented, with r^2 values above 0.99. Figure 1 shows chromatograms of furan and internal standard furan-d_4 fortified in beer at 20 ng/mL. Table 2 shows the linearity and the amount of Furan found in each food/beverages calculated from the standard addition curve.

FIGURE 1. Total Ion Chromatograms for 20 ng/mL of Furan and Furan-d_4 fortified in beer.

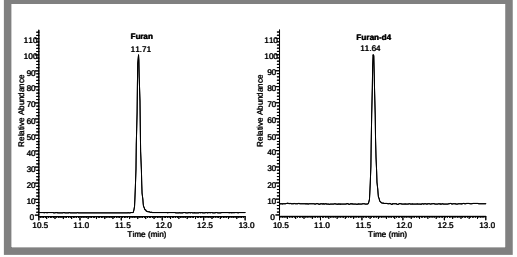

FIGURE 2. Standard additions calibration curve for red wine sample.

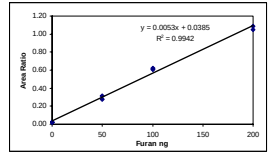

TABLE 2. Furan content of food and beverages analysed.

Sample	Furan in ppb	r^2
Peanut butter	16.7	0.9911
Brewed coffee	0.9	0.9901
Beer	1.3	0.9925
Red wine	0.73	0.9942

Conclusions

- The headspace – GC/MS method with PLOT column was found to be suitable for the analysis of furan at low ppb level in all food and beverage samples tested.
- The constructed calibration curves showed good linearity for all samples tested.
- The PLOT column used provided very symmetrical peak shapes for furan and furan-d_4 and overall excellent performance.

References

(1) H. Glatt, H. Schneider, Y. Liu, Mutat. Res., 580 (2005) 41
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(4) Monographs on the Evaluation of Carcinogenic Risks to Humans, International Agency for Research on Cancer, Lyon, France, 1995, vol. 63, pp 393.
(5) http://www.cfsan.fda.gov/~dms/furan.html

For additional information, please visit our Chromatography Resource Centre which can be found at:
www.thermo.com/columns

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