Quantification of Furan Derivatives in Coffee Products by SIDA-HS-SPME-GC/MS

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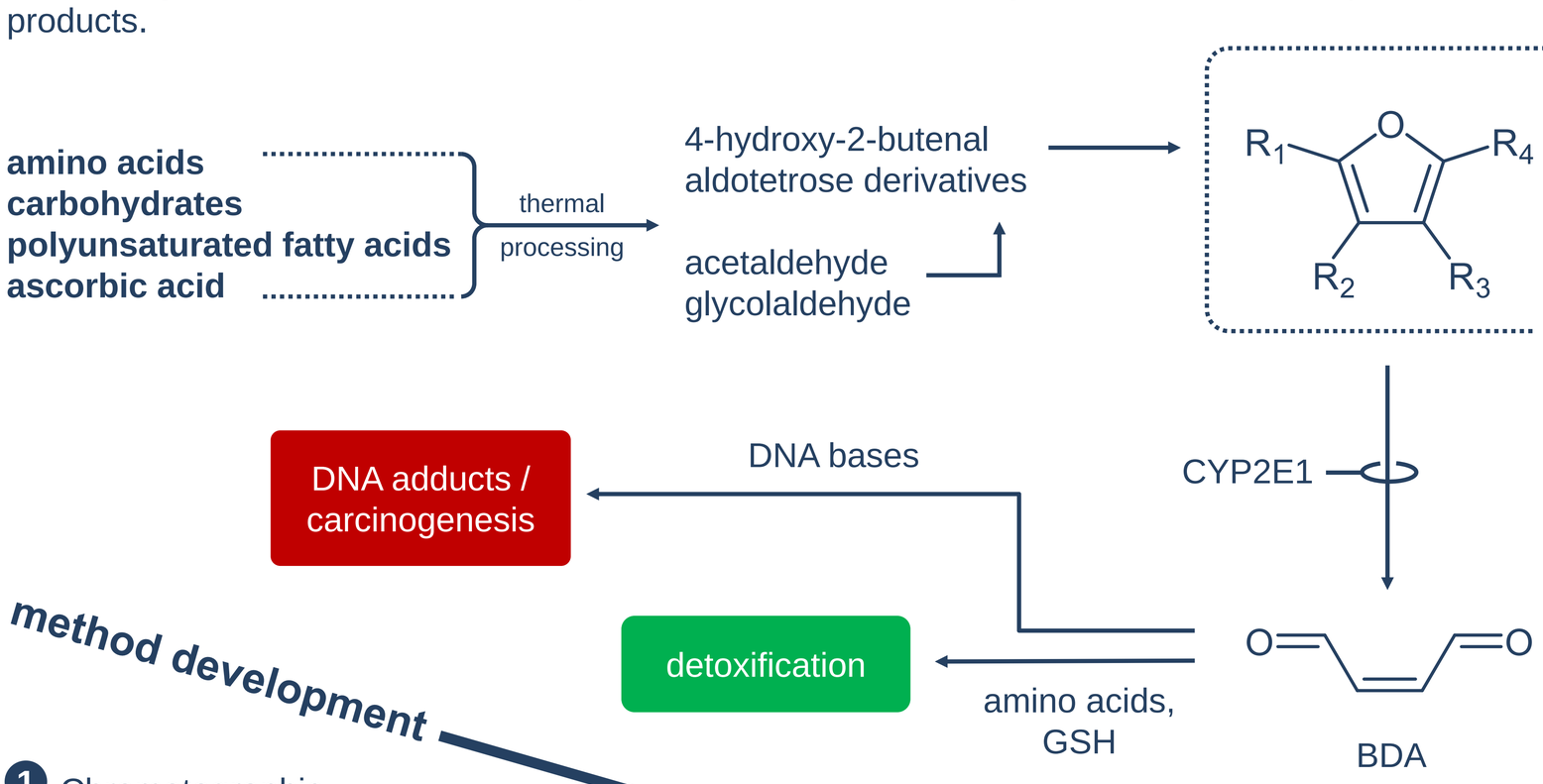
introduction

As food is heated to obtain roasting aromas also undesirable contaminants may be formed. As such furan and a variety of substituted furans may arise from Maillard reactions involving proteins, carbohydrates, polyunsaturated fatty acids and/or ascorbic acid. When ingested these furans will be metabolized by cytochrome-P450-monooxygenases like CYP2E1 to reactive α,β-unsaturated carbonyl compounds like *cis*-but-2-ene-1,4-dialdehyde (BDA), which forms covalent adducts with amino acids, glutathione (GSH) or DNA bases. While the reaction with amino acids or GSH provides a mechanism of detoxification, DNA adduct formation may lead to gene expression alterations, epigenetic changes, inflammation and increased cell proliferation as indirect mechanisms involved in carcinogenesis. A method for the quantification of furan and eight furan derivatives by HS-SPME-GC/MS was developed and applied to a series of coffee products.



analyte	R_1	R_2	R_3	R_4
furan	H	H	H	H
2-methylfuran	CH_3	H	H	H
3-methylfuran	H	CH_3	H	H
2-ethylfuran	C_2H_5	H	H	H
2,5-dimethylfuran	CH_3	H	H	CH_3
2,3-dimethylfuran	CH_3	CH_3	H	H
furfural	COH	H	H	H
furfuryl alcohol	CH_2OH	H	H	H
2-acetylfuran	$COCH_3$	H	H	H

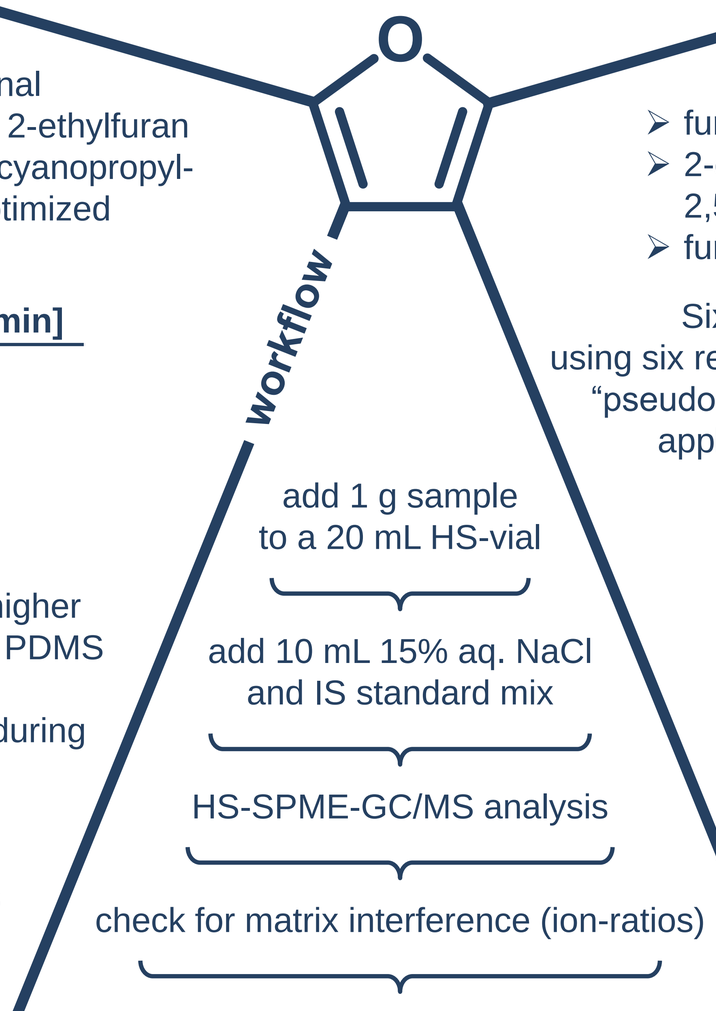
method development

1 Chromatographic separation of furan derivatives is a challenging task due to their high volatility and structural similarity. Baseline separation of constitutional isomers like 2,5-dimethylfuran, 2,3-dimethylfuran and 2-ethylfuran was successfully achieved on a DB-624 column (6% cyanopropyl-phenyl, 94% polydimethylsiloxane) with a carefully optimized temperature program.

rate [°C/min]	temperature [°C]	holdtime [min]
/	30	3
4	120	0
20	250	0

2 HS-SPME extraction provided optimum recovery

- when using a DVB/CAR/PDMS fiber, which binds higher quantities of all furan derivatives than PDMS/DVB, PDMS or CAR/PDMS fibers
- by an increased fiber-penetration-depth of 38 mm during extraction
- when using a 15% NaCl solution as a dispersant (a total of 16 different dispersants was compared, including NaCl solutions of different concentrations and 10 ionic liquids)

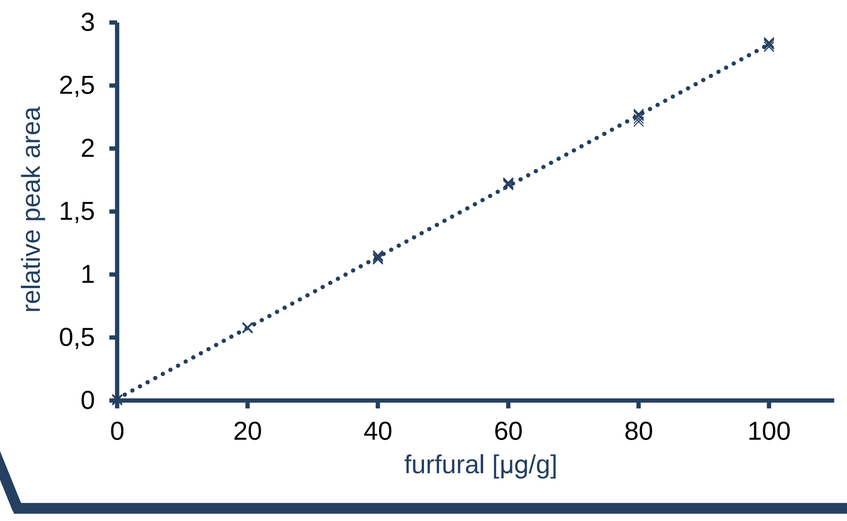


quantification

Three deuterium-labeled **3** internal standards were applied for stable-isotope-dilution analysis (SIDA) calibrating

- furan, 2-methylfuran and 3-methylfuran using 3-methylfuran-d_3
- 2-ethylfuran, 2,5-dimethylfuran and 2,3-dimethylfuran using 2,5-dimethylfuran-d_3
- furfural, furfuryl alcohol and 2-acetylfuran using furfural-d_4.

Six-point calibration curves were prepared for each analyte **4** using six replicates of each level (n = 36) with ground green coffee as a "pseudo-blank matrix". Tests for normal distribution and outliers were applied to each calibration series and linearity assessed through back calculation of calibrators (residual < ±15%).



application to coffee samples

5 The developed SIDA-HS-SPME-GC/MS method was subsequently applied to a series of coffee samples. High levels of furfuryl alcohol and furfural were observed besides lower levels of furan, 2-acetylfuran and 2-methylfuran. Only 2,3-dimethylfuran appeared consistently below LOQ. Espresso coffee showed notably higher furan levels than all other products, which is in accordance with the more intensive heat treatment during roasting. In contrast, a ready-to-drink cappuccino showed no furans above LOQ most probably because of its significant dilution with milk and water.

	furan [µg/g]	2-methylfuran [µg/g]	3-methylfuran [ng/g]	2-ethylfuran [ng/g]	2,5-dimethylfuran [ng/g]	2,3-dimethylfuran [ng/g]	furfural [µg/g]	furfuryl alcohol [µg/g]	2-acetylfuran [µg/g]
LOQ[a]	2,86	1,97	393	70,7	171	424	6,40	167	4,73
ground coffee	3,06	6,07	< LOQ	82,8	476	< LOQ	102	1050	9,98
espresso coffee	3,98	9,27	437	113	729	< LOQ	67,3	1460	10,6
soluble coffee	< LOQ	2,90	< LOQ	< LOQ	< LOQ	< LOQ	66,5	579	< LOQ
coffee pads	< LOQ	3,92	< LOQ	< LOQ	237	< LOQ	88,9	1240	8,77
coffee capsule	3,68	6,85	< LOQ	83,7	535	< LOQ	112	1560	15,3
decaff. coffee	3,88	7,92	< LOQ	115	569	< LOQ	96,7	1200	9,07
cappuccino drink	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

[a] according to ISO 11843-2:2000

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