Analysis of furan and alkylfurans in food commodities using headspace SPME arrow and GC-MS

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RAFA 2022

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Introduction

- Furan and alkylfurans are produced during heating of foodstuff

- The International Agency for Research of Cancer classified furan as a possible carcinogenic compound

- Methods reported for the analysis of these volatile organic compounds include static headspace (HS) and solid phase microextraction (SPME) in combination with GC-MS.

- The use of SPME for the analysis of these highly volatile analytes has demonstrated improved method sensitivity and higher S/N for some of the alkylfurans.

  - The fragility of traditional SPME fibers can be a concern.
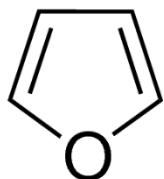
Furan

Crews and Castle *Trends Food Sci. Technol.* 2007, 18, 365–372.
Limacher et al. DOI: 10.1021/jf800268t.
Frank et al. *J. Chromatogr. A* 2020, 1622, 461119.
Märk et al. *J. Agric. Food Chem.* 2006, 54, 2786–2793.
International Agency for Research on Cancer, IARC Monographs on the Evaluation of the Carcinogenic Risks to Humans. 1995.
Frank et al. *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* 2021, 1179, 122765.

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Goals

To develop a workflow using the SPME arrow coupled to GC-MS for the analysis of furan and alkylfurans in baby formula and coffee

- Target analytes: furan, 2-methylfuran, 3-methylfuran, 2-ethylfuran, 2,5-dimethylfuran and 2-pentylfuran

- Internal standards: furan-d4, 2-methylfuran-d6, 2-ethylfuran-d5 and 2-pentylfuran-d11


Furan
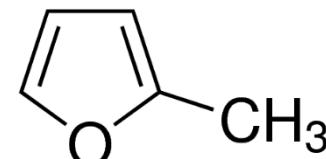
2-Methylfuran
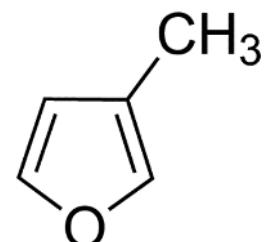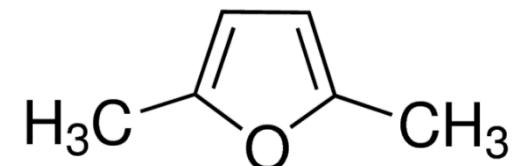
3-Methylfuran

2,5-Dimethylfuran
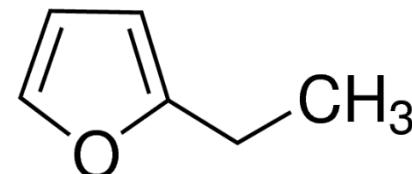
2-Ethylfuran
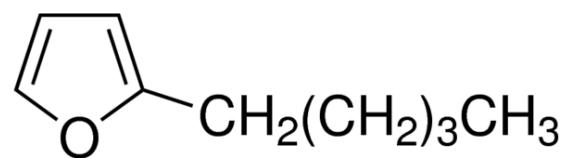
2-Penthylfuran

Instrumental Analysis

Instrument	Agilent 7890B GC & 5977B MSD
Column	Rxi-624Sil MS, 30 m, 0.25 mm ID, 1.40 µm (Restek cat.# 13868)
Injection Mode	Split (1:10 and 1:100)
Liner	Topaz 1.8 mm ID SPME/straight liner (cat# 23280)
Inj. Temp.	280°C
Oven	35°C (hold 3 min) to 75°C by 8°C/min, then to 200°C (hold 1 min) by 25°C/min
Carrier Gas and Flow	He, constant flow at 1.4 mL/min
Acquisition Type	SIM
Transfer Line Temp.	280 °C
Source Temp.	325 °C
Quadrupole Temp.	200 °C
Solvent delay	2.2 min

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How does the resolution look like?
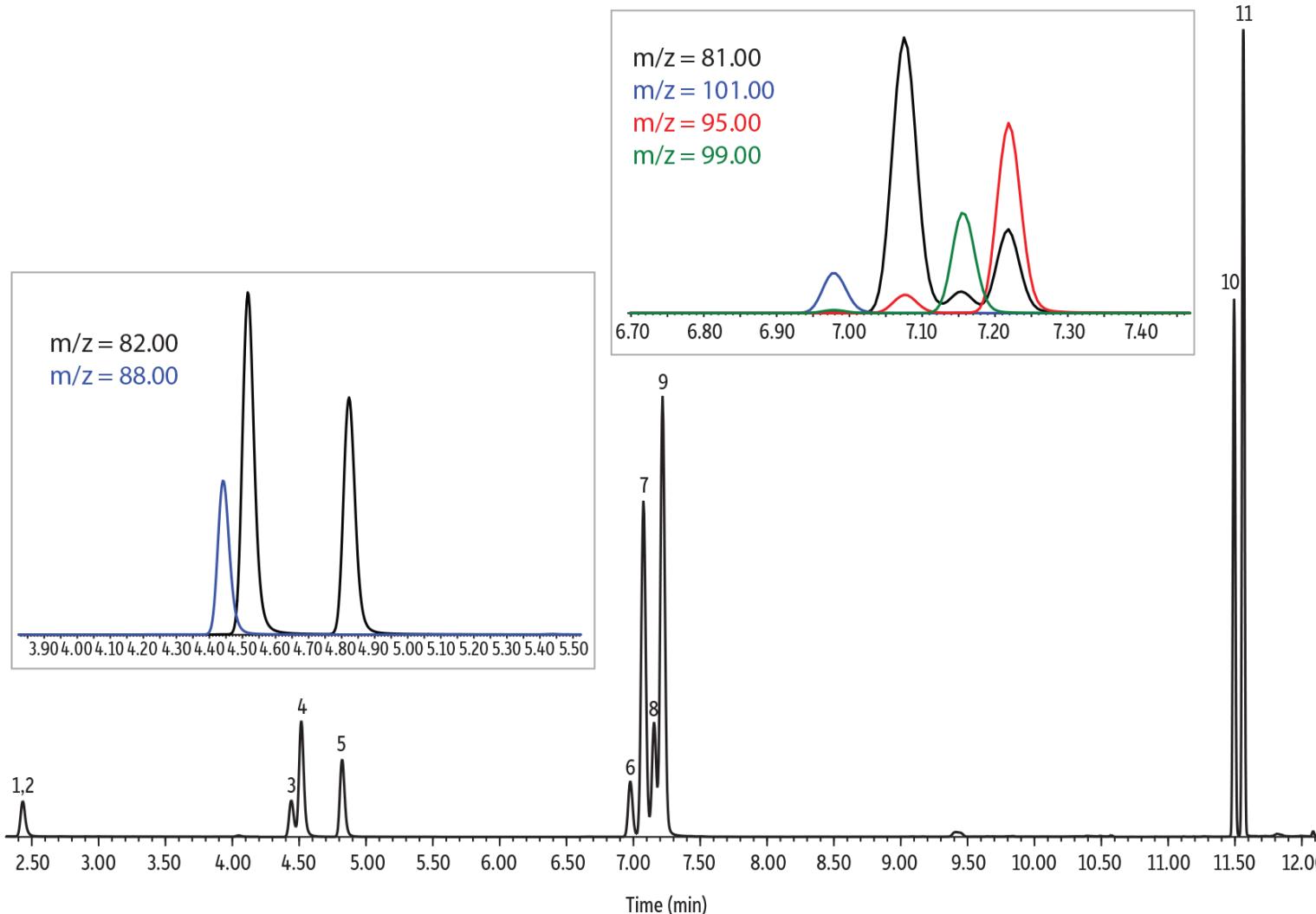
1. Furan-d4
2. Furan
3. 2-Methylfuran-d6
4. 2-Methylfuran
5. 3-Methylfuran
6. 2-Ethylfuran-d5
7. 2-Ethylfuran
8. 2,5-Dimethylfuran-d3
9. 2,5-Dimethylfuran
10. 2-Pentylfuran-d11
11. 2-Pentylfuran

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Comparison of SPME, SPME Arrow and Headspace
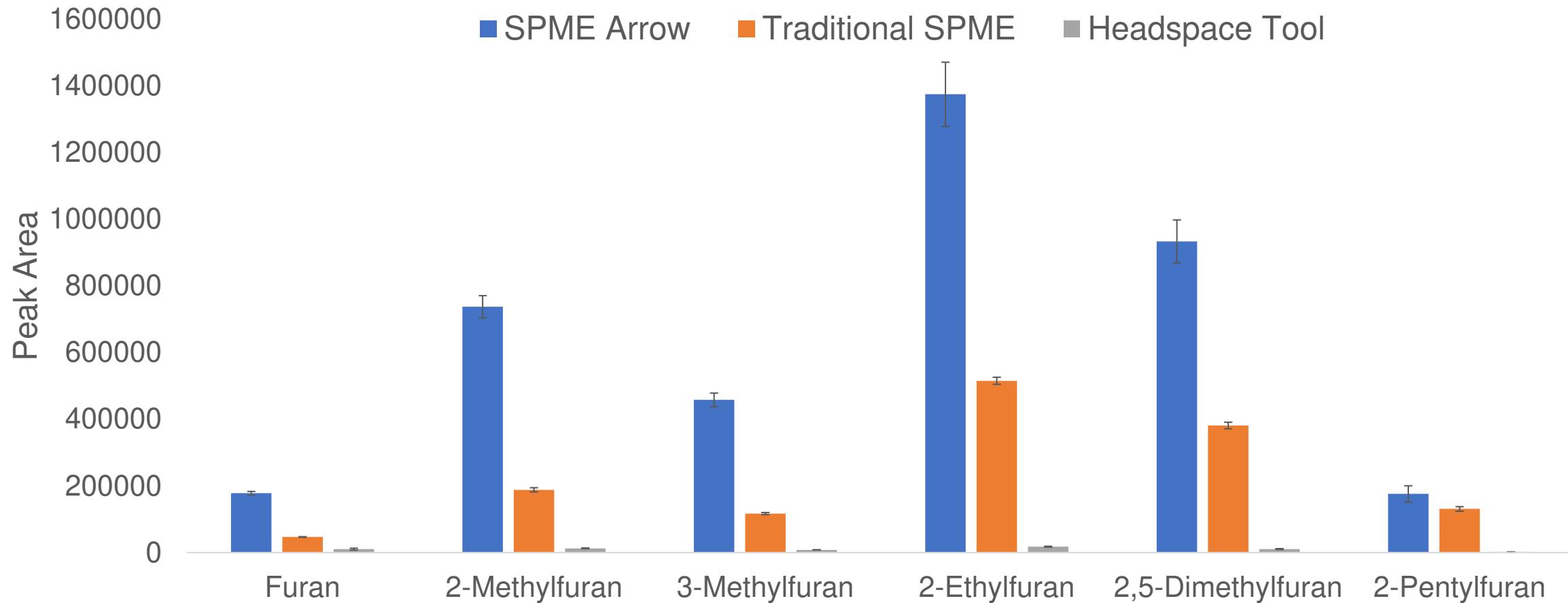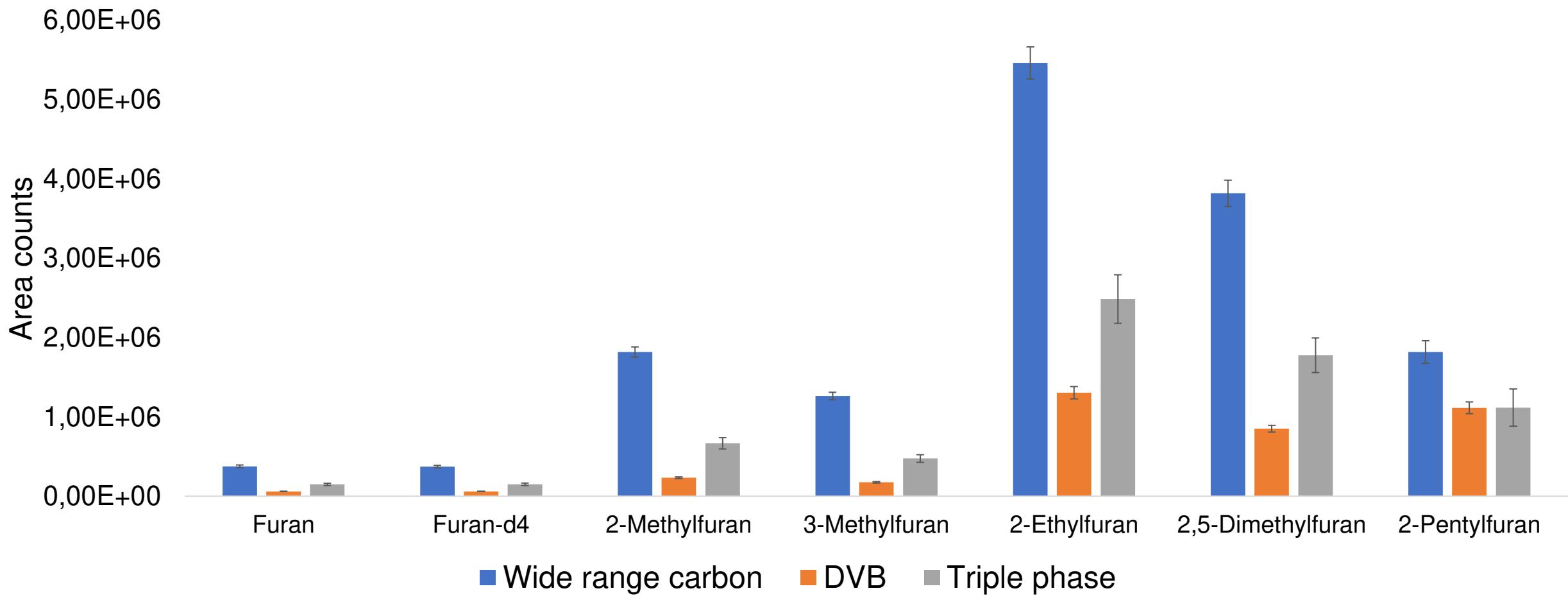
Extraction Temperature Evaluation
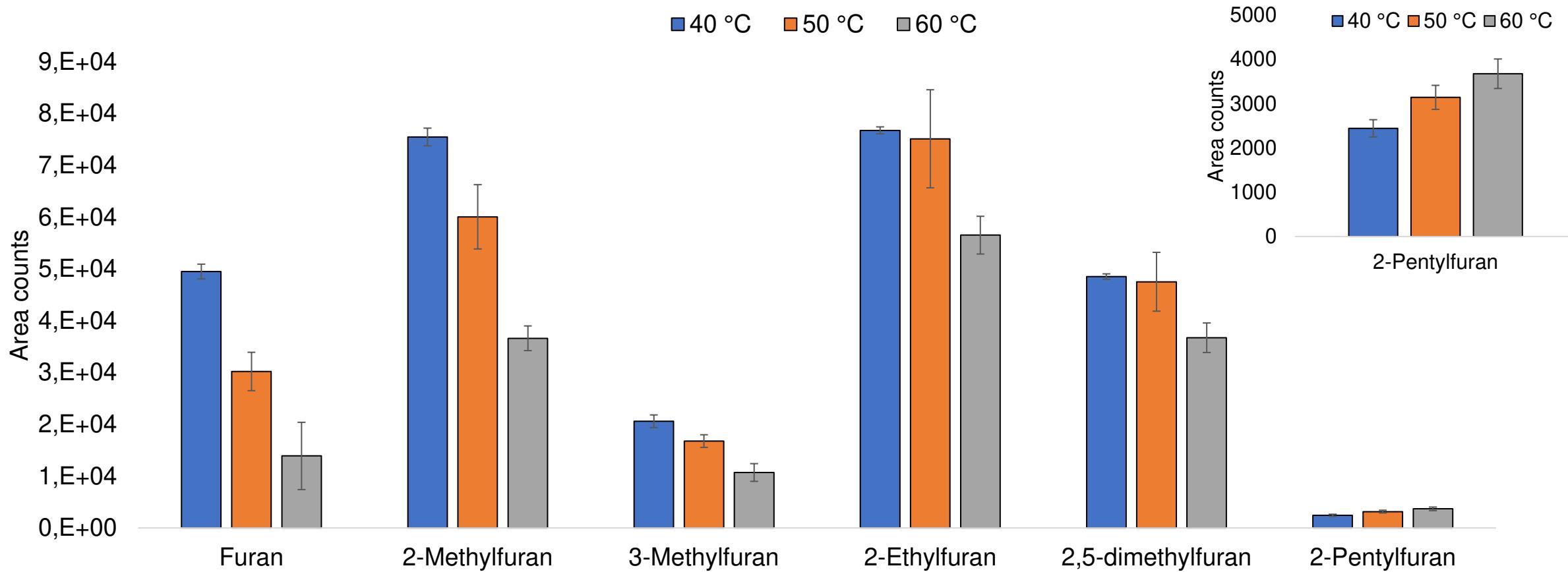
50°C was chosen as compromise

Extraction Time Evaluation

Furan

2-Pentylfuran
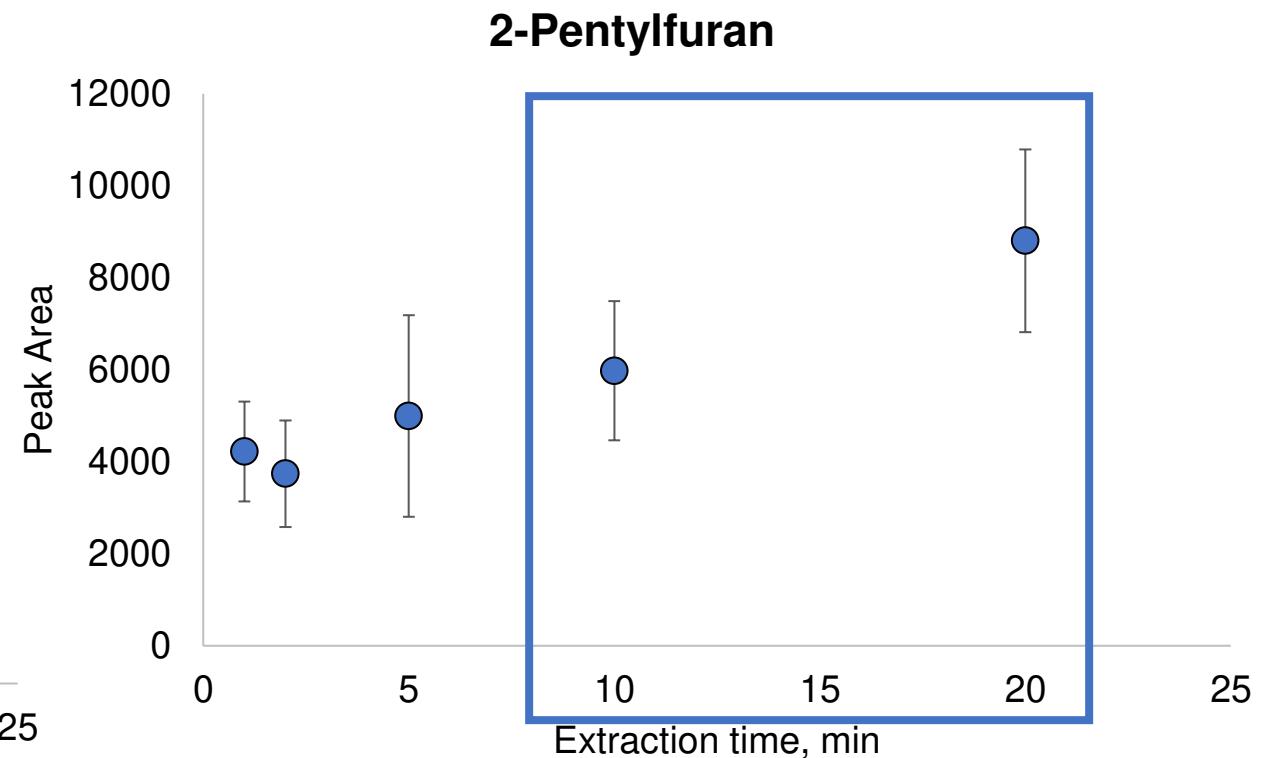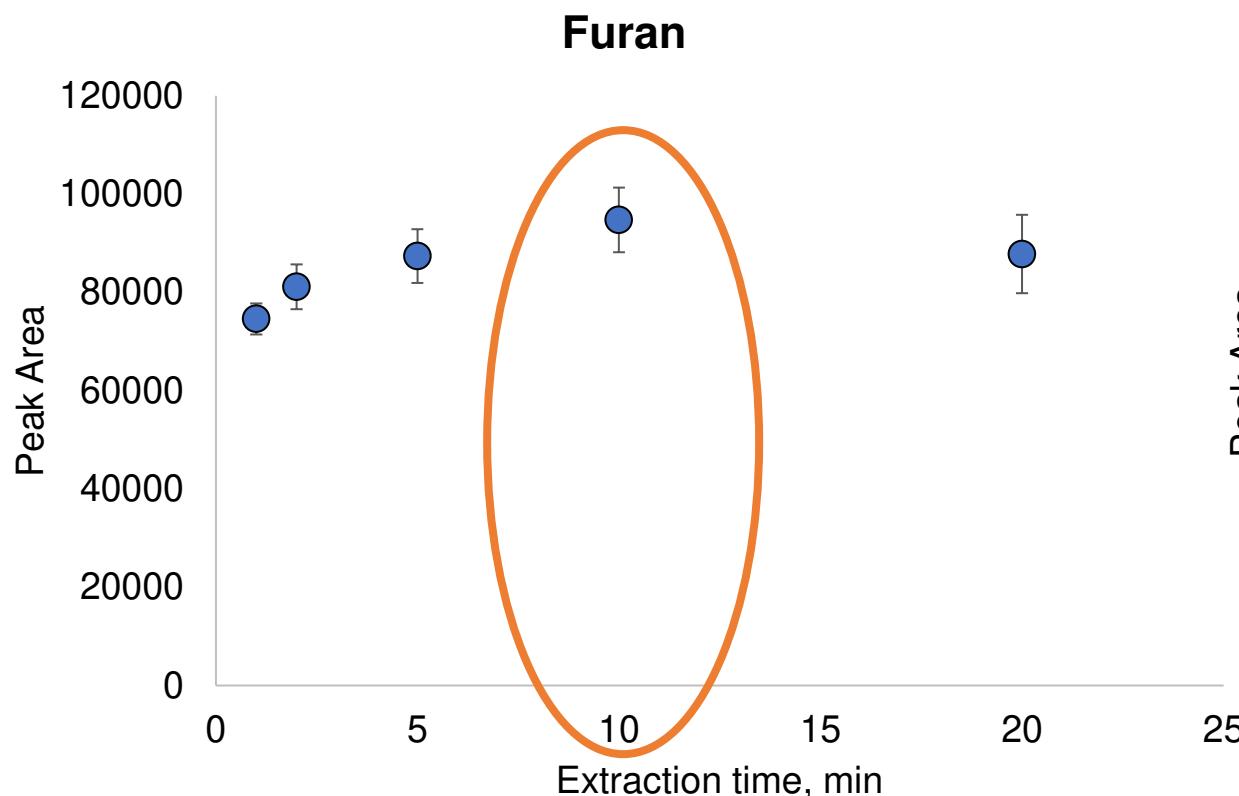
At 10 minutes volatile furans reached equilibrium

At 20 minutes less volatile furans have not plateaued

10 minutes was chosen as compromise between sensitivity and throughput

Sample Preparation – Baby Formula

Baby formula 0.5 g + **10 mL** of 30% NaCl solution

Analytes + IS

50°C, 250 rpm, 10 min

50°C, 250 rpm

10 min extraction

280°C, 1 min
Split 1:10

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10

Sample Preparation - Coffee

Coffee 0.5 g + **5 mL** of 30% NaCl solution

Analytes + IS

50°C, 250 rpm, 10 min

50°C, 250 rpm

1 min extraction

280°C, 1 min
Split 1:100
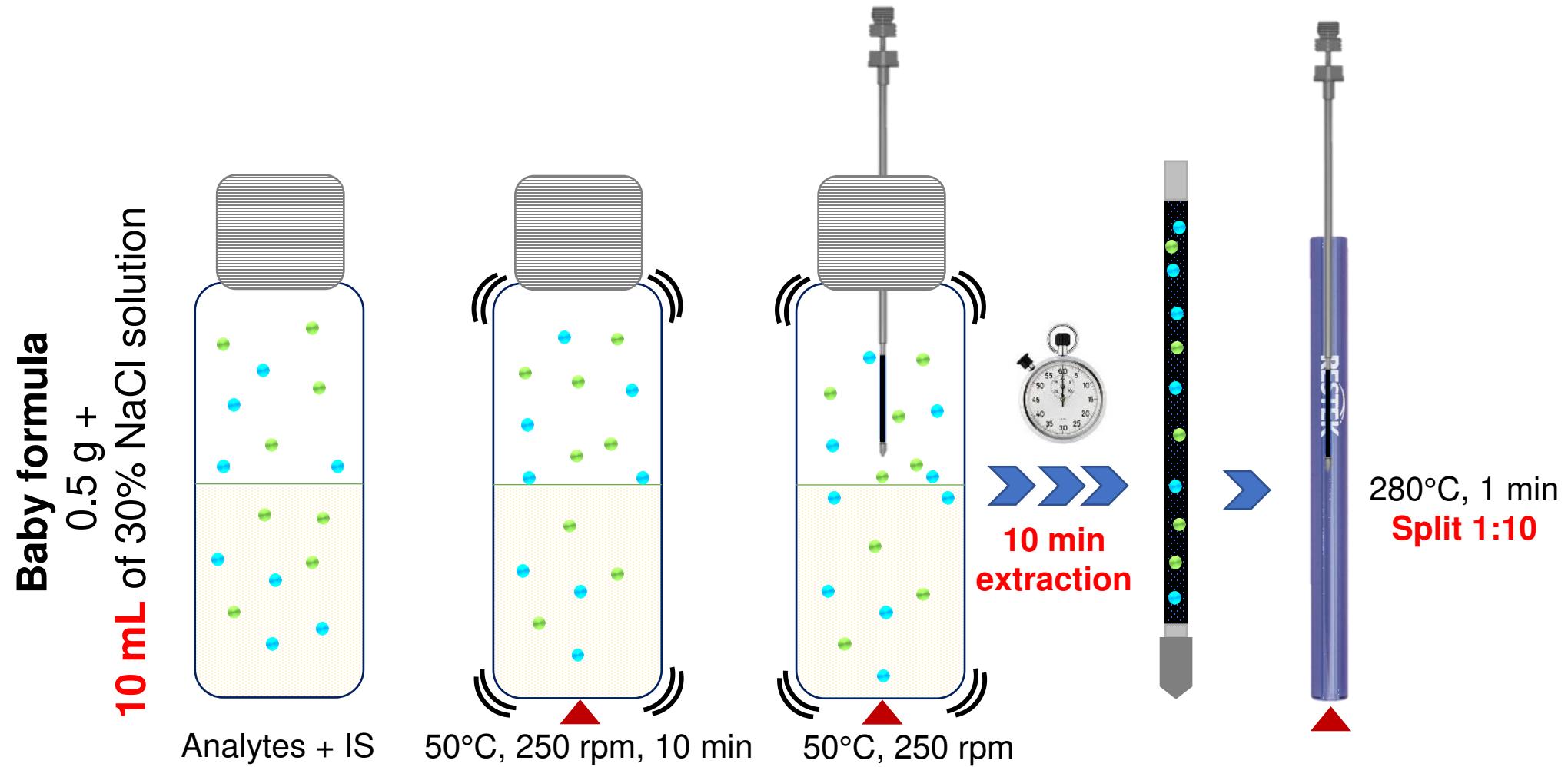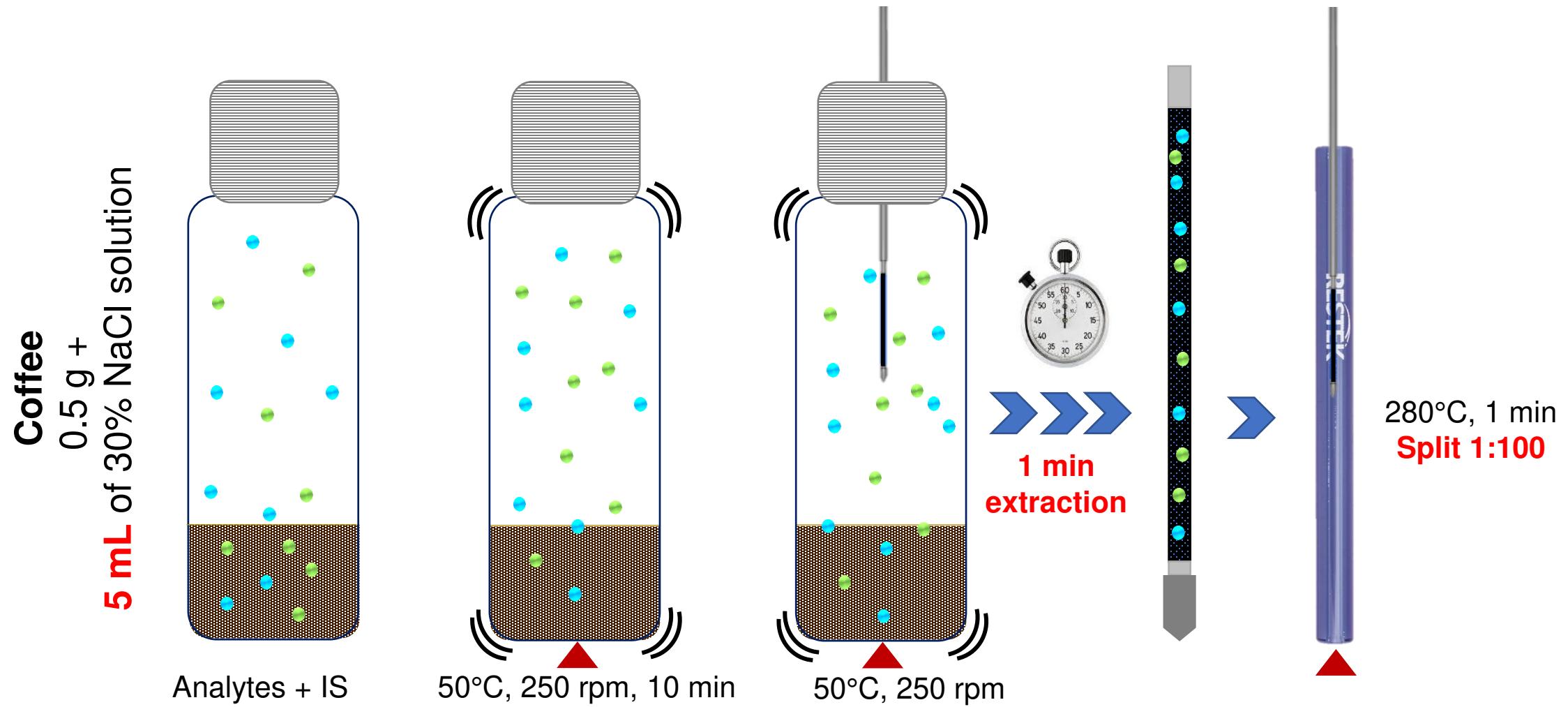
Sample Preparation - Comparison

Sample	Baby formula	Coffee
Amount	0.5 g	
Volume of 30% NaCl solution added	10 mL	5 mL
Volume of internal standard solution added	50 µL (1 µg/mL solution)	40 µL (25 µg/mL solution)
Incubation time	10 min	
Incubation and extraction temperature	50°C	
Agitation	250 rpm	
HS-SPME extraction time	10 min	1 min
Desorption temperature	280°C	
Desorption time	1 min	

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Baby formula spiked at 5 ng/g
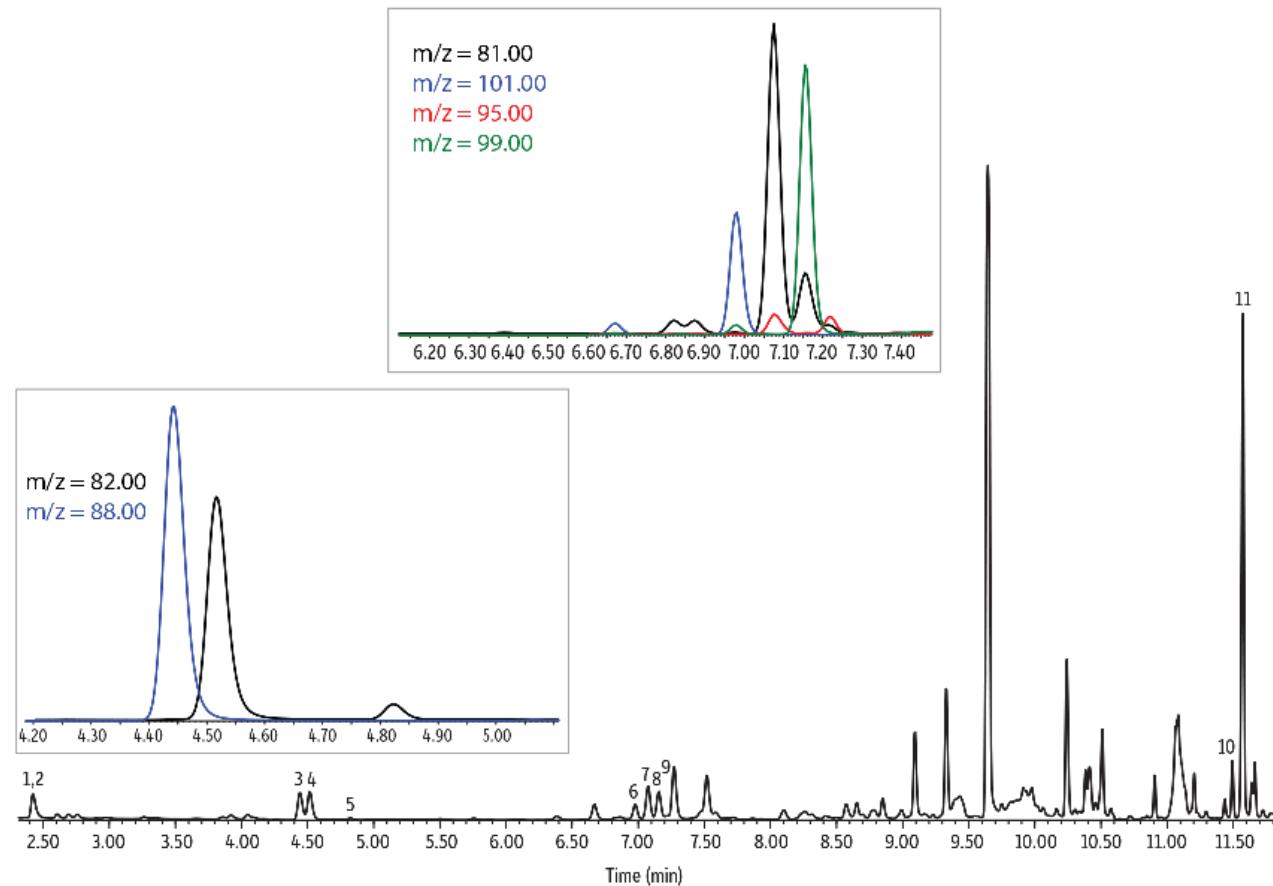
1. Furan-d4
2. Furan
3. 2-Methylfuran-d6
4. 2-Methylfuran
5. 3-Methylfuran
6. 2-Ethylfuran-d5
7. 2-Ethylfuran
8. 2,5-Dimethylfuran-d3
9. 2,5-Dimethylfuran
10. 2-Pentylfuran-d11
11. 2-Pentylfuran

Instant Coffee spiked at 1000 ng/g

1. Furan-d4
2. Furan
3. 2-Methylfuran-d6
4. 2-Methylfuran
5. 3-Methylfuran
6. 2-Ethylfuran-d5
7. 2-Ethylfuran
8. 2,5-Dimethylfuran-d3
9. 2,5-Dimethylfuran
10. 2-Pentylfuran-d11
11. 2-Pentylfuran
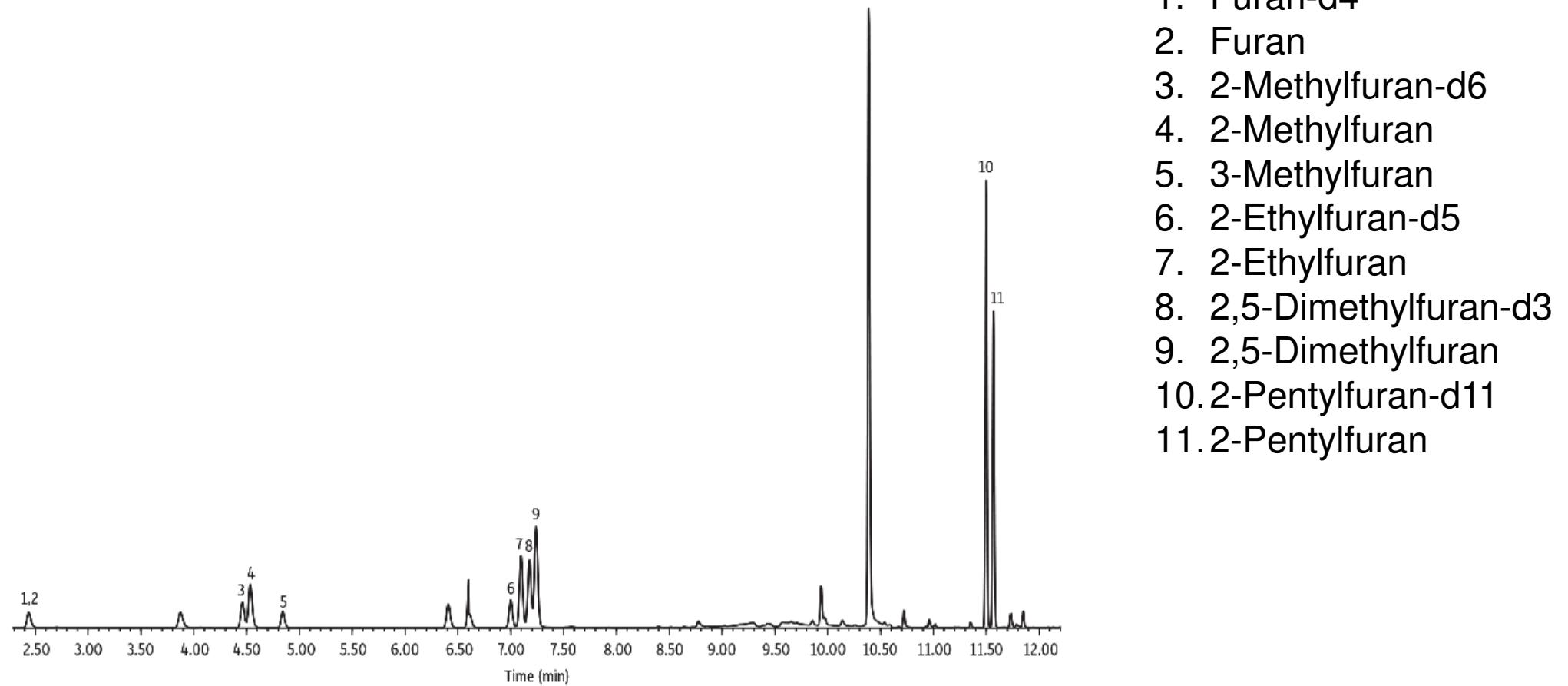
Calibration Curves – Low Concentrations
1.25–150 ng in vial

2-Methylfuran

Response Ratio

$R^2 = 0.9997$

Concentration Ratio: 0, 50, 100, 150

2-Pentylfuran

Response Ratio

$R^2 = 0.9955$

Concentration Ratio: 0, 50, 100
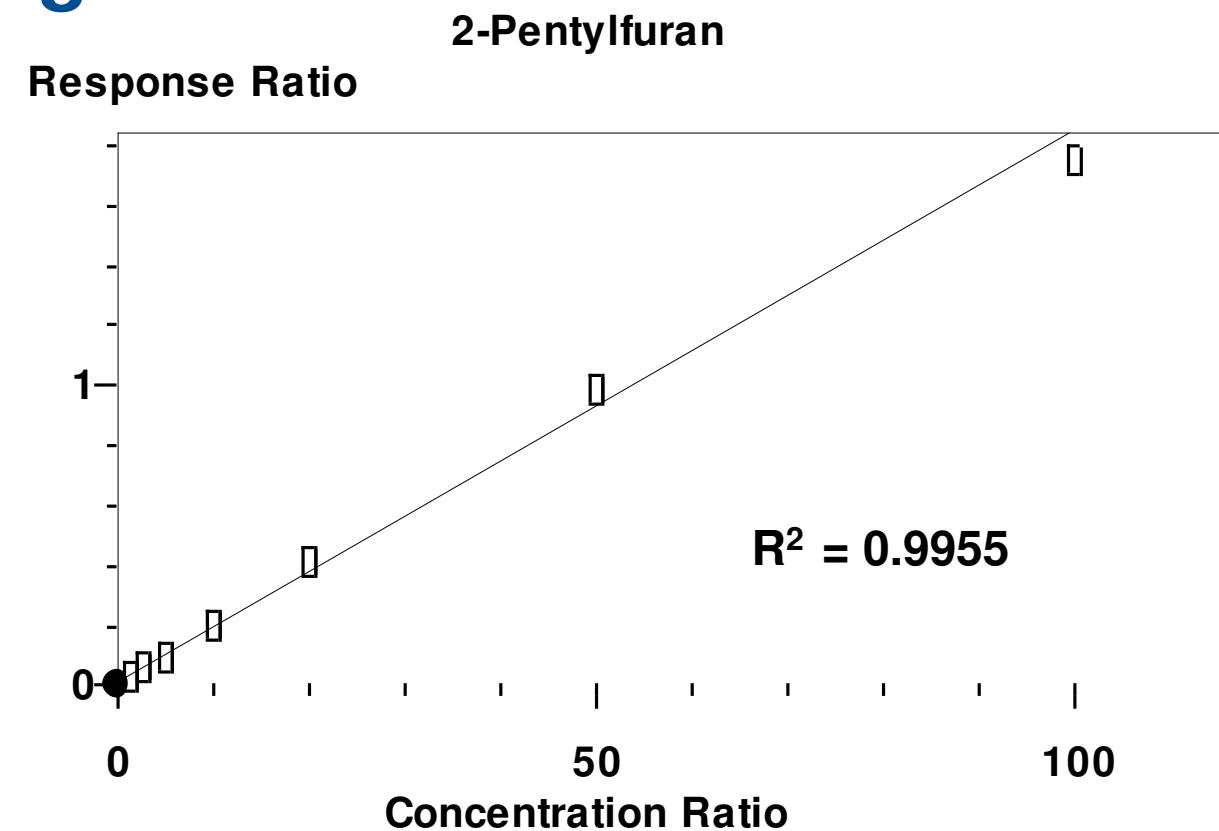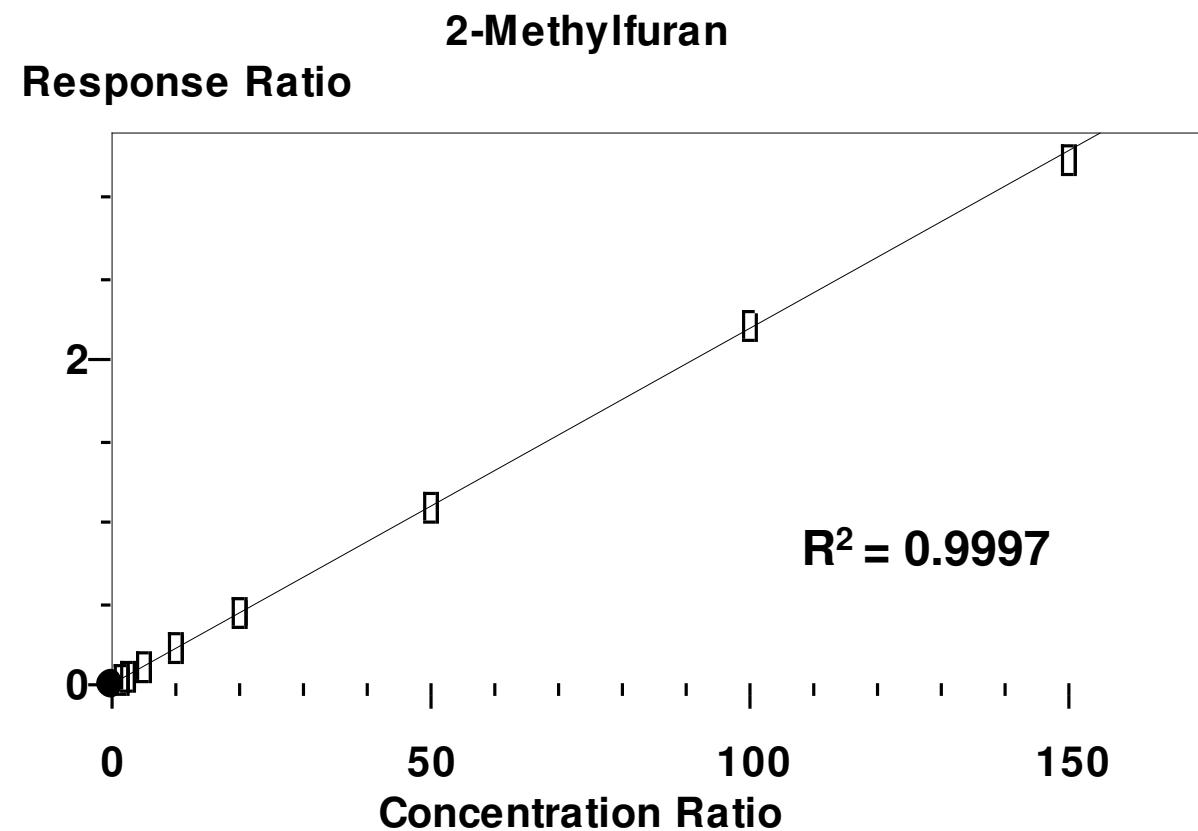
Calibration Curves – High Concentrations
25–8000 ng in vial

2-Methylfuran

Response Ratio

$R^2 = 0.9993$

Concentration Ratio

2-Pentylfuran

Response Ratio

$R^2 = 0.9954$

Concentration Ratio
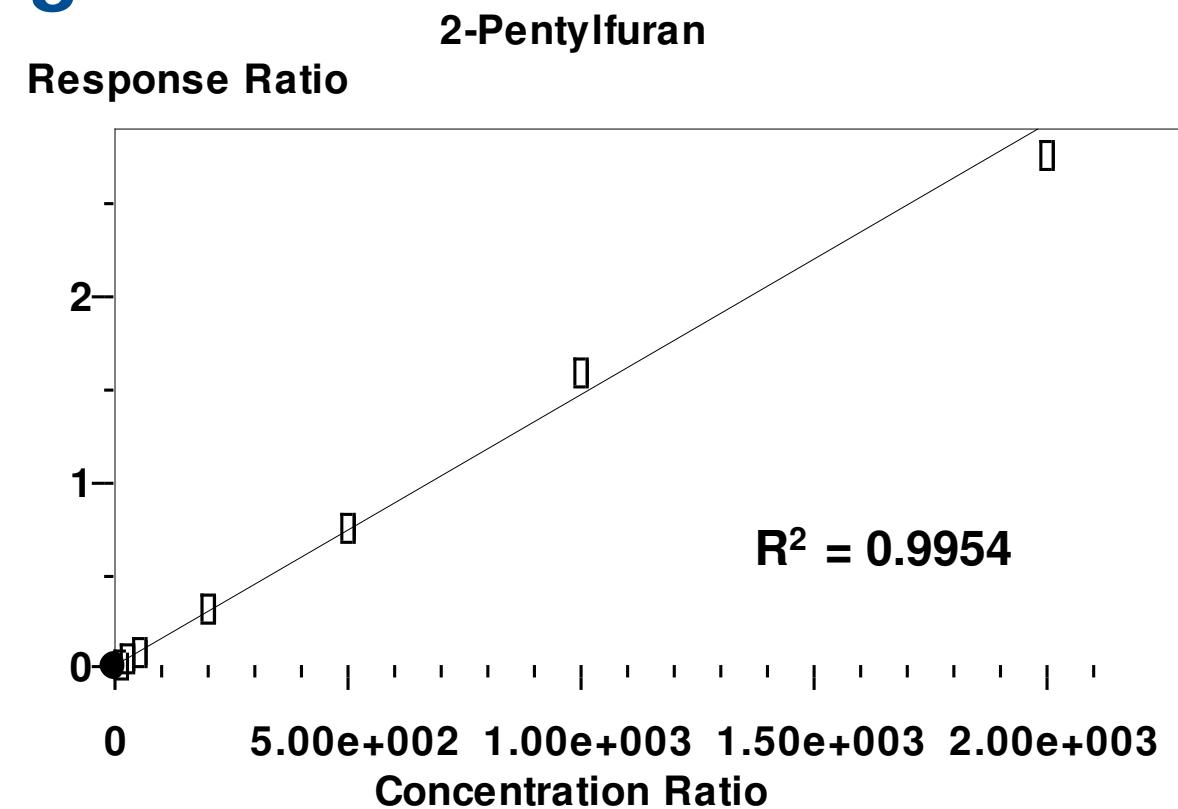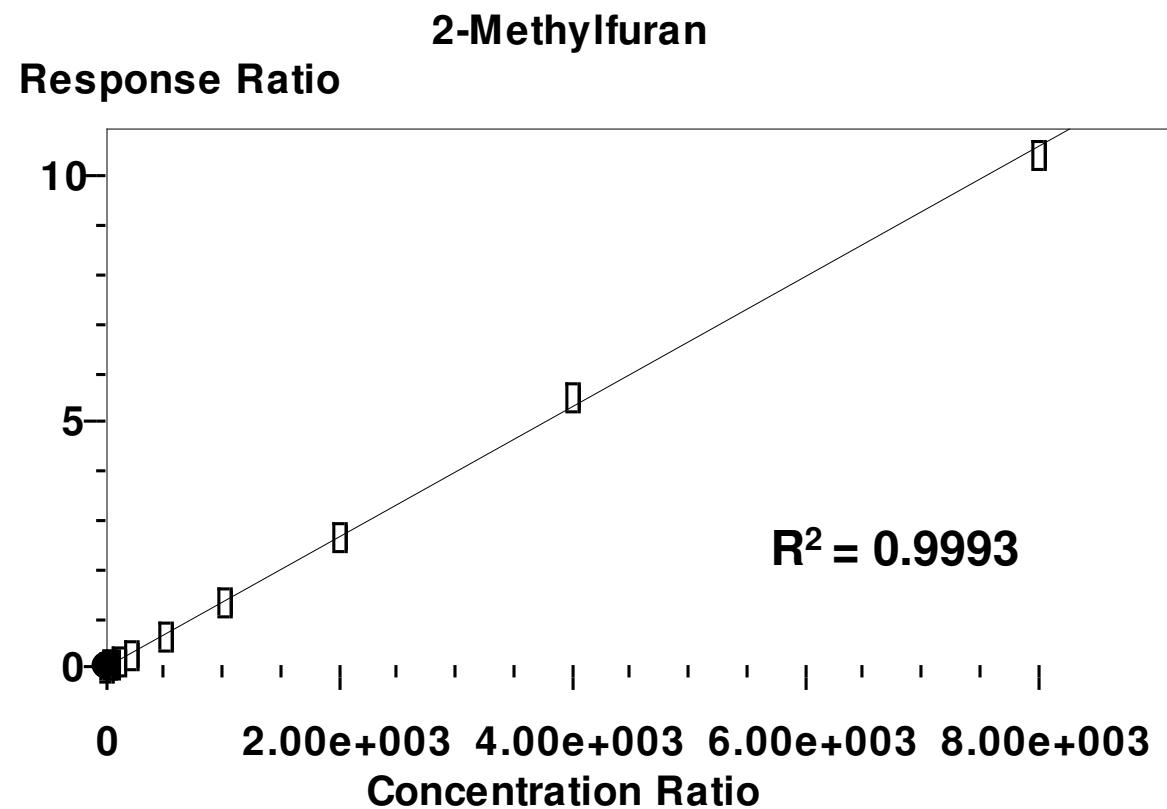
Analysis in Baby Formula

Analyte	Blank (n=3)		Low conc.(n=3), 5 µg/kg*		High conc. (n=3), 50 µg/kg*	
	µg/kg	RSD, %	Rec., %	RSD, %	Rec., %	RSD, %
Furan	16	1	110	2	94	4
2-Methylfuran	60	2	97	2	100	3
3-Methylfuran	-	-	113	3	107	6
2-Ethylfuran	67	2	93	3	105	5
2,5-Dimethylfuran	-	-	101	4	97	14
2-Pentylfuran	219	3	87	11	108	12

Recovery was corrected as follows: ((measured concentration – concentration in blank)/spiked concentration)*100

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Analysis in Instant Coffee

Analyte	Blank (n=3)		Low conc.(n=3), 1000 µg/kg*		High conc. (n=3), 4000 µg/kg*	
	µg/kg	RSD, %	Rec., %	RSD, %	Rec., %	RSD, %
Furan	394	10	87	2	125	3
2-Methylfuran	843	10	94	3	116	2
3-Methylfuran	96	10	87	2	119	3
2-Ethylfuran	29	11	93	2	115	5
2,5-Dimethylfuran	46	11	98	2	120	4
2-Pentylfuran	-	-	83	3	83	11

Recovery was corrected as follows: ((measured concentration – concentration in blank)/spiked concentration)*100

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Conclusions

- A HS-SPME-GC-MS method was developed for the analysis of furans and alkyl furans in baby formula and coffee.

- Different experimental conditions were evaluated and optimized.
  - Adjustments were made to address the different levels in the commodities
  - Satisfactory results in terms of linearity, accuracy and precision were obtained in the majority of the cases.

- Accuracy values above 111% in coffee samples spiked at 4000 µg/kg could be due to sample handling, but additional experimental work may be needed to further understand this bias.

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Acknowledgments

Joe Konschnik, Colton Myers and Naomi Lovallo

Thank you for your attention!

SIM data

Segment starting time, min	Compound (Rt, min)	Ions	Dwell time, ms
2.2	Furan (2.447)	39	50
		68*	
	Furan-d4 (2.428)	42	
		72*	
4.2	2-Methylfuran (4.536)	53	30
		81	
		82*	
	3-Methylfuran (4.846)	53	30
		81	
		82*	
	2-Methylfuran-d6 (4.464)	58	30
		88*	
6.6	2-Ethylfuran (7.100)	53	30
		81*	
		96	
	2-Ethylfuran-d5 (7.001)	55	30
		101*	
	2,5-Dimethylfuran (7.243)	67	30
		95*	
	2,5-Dimethylfuran-d3 (7.179)	84	30
		99*	
10.6	2-Pentylfuran (11.570)	81	30
		138*	30
	2-Pentylfuran-d11 (11.501)	83	30
		149*	30

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