Solid phase microextraction in food analysis: method development considerations and artifact formation

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Introduction & Theory

In food analysis, sample preparation represents one of the most important steps of the analytical process and it is crucial that selected sample preparation technique is *i)* fast to allow high-throughput analysis and *ii)* non-invasive so that production of artifacts is minimized. When implemented under appropriate conditions, solid phase microextraction, SPME meets these criteria and also allows for solventless sample preparation, use of small sample amounts, extraction of analytes from solid, liquid and gaseous sample matrices, easy automation, generation of clean chromatograms, and integration of sampling, extraction, concentration and sample introduction into one step.

Based on the thermodynamic theory of SPME, the main parameter affecting SPME extraction sensitivity & selectivity is fibre coating/sample matrix distribution constant, K_{fs}.

liquid extraction phase → $K_{fs} = C_f^\infty / C_s^\infty$

solid extraction phase → $K_{fs} = S_f^\infty / C_s^\infty$; $S_f^\infty = m / S_a$

C_f^∞; C_s^∞ equilibrium concentrations in fibre coating & sample;

S_f^∞ surface concentration at equilibrium;

S_a active surface of fibre;

m mass extracted at equilibrium;

V_s sample volume

fibre constant $\beta_c = K_{fs} \cdot V_f$

describes chemical composition of extraction phase & enrichment factors

negligible depletion: $\beta_c = m / C_s^\infty$

non-negligible depletion: $\beta_c = m V_s / (V_s C_s^\infty - m)$

Project Objectives

- use of GCXGC structurally ordered chromatograms to study extraction & desorption efficiency of commercial SPME coatings;
- calculation of absolute recoveries and fibre constants for analytes frequently encountered in food matrix and possessing wide range of physicochemical properties;
- standardizing 'which type of SPME coating to use for a particular analyte';
- exploitation of artifact generation in SPME preparation of honey samples;
- limitations of *ex vivo* SPME sample preparation ???

Experimental

TARGET ANALYTES & HOMOLOGIUS SERIES

HS-SPME CONDITIONS

water & apple: 15 min incubation, 60 min extraction, 30 °C sample temperature, 15 min desorption at 5 °C < max recommended coating temperature

honey: 1 g honey + 1 mL saturated aqueous solution of NaCl, 5 min incubation, 30 min extraction (PDMS/DVB fibre), 5 min desorption at 250 °C

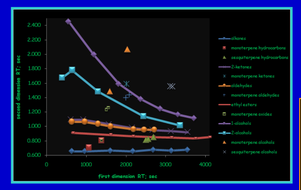
INSTRUMENT & ANALYSIS CONDITIONS

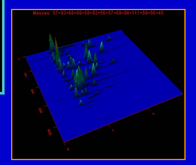
MPS 2 AUTOSAMPLER
Gerstel GmbH, Mulheim an der Ruhr, Germany;

Pegasus 4D GCxGC- ToFMS system
LECO, St. Joseph, MI, USA;
RXI-5 SIL MS x SUPELCOWAX 10 columns, 35 °C (5 min), 3 °C/min to 245 °C (3 min), 15 °C secondary oven offset, 3 sec modulation, 35 °C modulator temperature offset, *m/z* 33-450 acquisition range at 200 spectra/sec

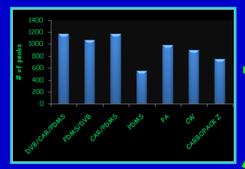
Results & Discussion

GCxGC structurally ordered chromatograms & peak apex plot for target analytes

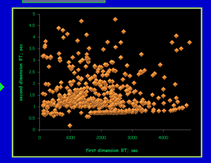




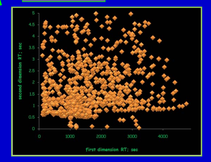
extraction coverage



PDMS

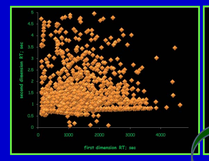


PA

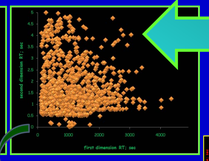


desorption efficiency – targeted analysis

DVB/CAR/PDMS

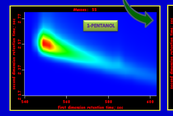


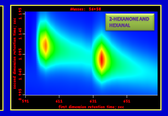
CAR/PDMS

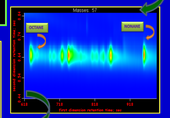


slow & incomplete desorption from thicker CAR/PDMS layer

↓ resolution in first dimension;
↑ higher molecular weight discrimination

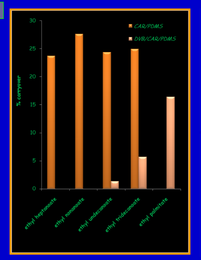


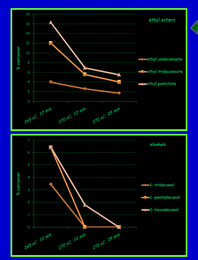




optimizing desorption efficiency – DVB/CAR/PDMS

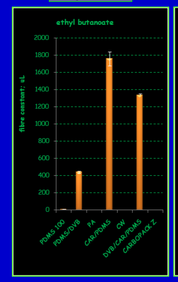
265 °C, 10 min

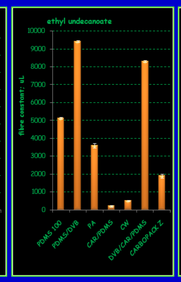


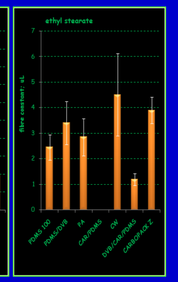


extraction efficiency – targeted analysis

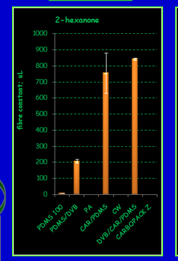
ethyl esters

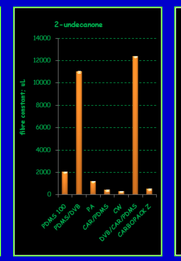


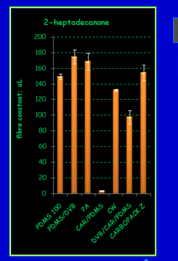




2-ketones

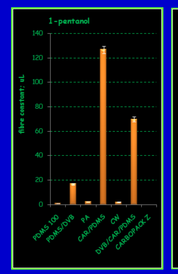


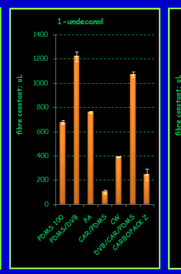


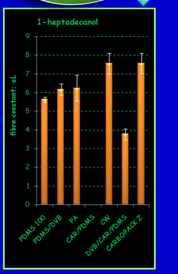


mass transport from sample to headspace is limiting step of HS-SPME process

1-alcohols







fibre constants of food components

Kfs/f; uL

functional group	analyte name	PDMS	PDMS/DVB	PA	CAR/PDMS	CW	DVB/CAR/PDMS	CARBOPACK Z
alkanes	octane	605.8 ± 21.9	48896.9 ± 82.3	na	5140.2 ± 12.1	na	661155.3 ± 112.2	na
	nonane	810.0 ± 29.6	16389.8 ± 82.1	na	8936.3 ± 355.1	na	207795.5 ± 110.6	na
	undecane	8616.1 ± 56.1	17786.1 ± 134.8	444.9 ± 4.2	17976.8 ± 144.5	na	20936.3 ± 64.3	1068.2 ± 169.3
	tridecane	2197.0 ± 37.9	9246.3 ± 44.6	536.0 ± 8.0	196.8 ± 35.2	39.6 ± 1.0	15436.5 ± 38.8	1769.8 ± 158.8
monoterpene hydrocarbons	alpha-pinene	557.8 ± 17.9	2905.9 ± 54.9	55.4 ± 2.9	3438.5 ± 20.7	na	13044.5 ± 59.3	29.4 ± 0.7
	limonene	957.6 ± 24.6	5808.8 ± 42.2	462.2 ± 12.2	1077.0 ± 46.4	54.3 ± 7.9	8521.3 ± 57.7	145.7 ± 17.0
sesquiterpene hydrocarbons	(Z)-beta-farnesene	1000.7 ± 26.8	1436.5 ± 30.3	785.1 ± 13.2	96.8 ± 10.9	161.9 ± 7.5	919.3 ± 7.3	472.6 ± 80.5
	(E)-beta-farnesene	1287.9 ± 28.7	1787.6 ± 35.5	984.2 ± 20.0	77.3 ± 6.4	173.9 ± 7.1	904.2 ± 12.2	639.8 ± 81.6
	(E,E)-a-farnesene	1540.2 ± 37.3	2265.4 ± 54.0	1129.4 ± 25.0	59.8 ± 4.2	189.8 ± 7.4	713.4 ± 14.8	1045.4 ± 141.1
2-ketones	2-hexanone	7.8 ± 0.5	207.7 ± 12.8	na	756.0 ± 123.6	na	843.4 ± 6.9	na
	2-heptanone	29.7 ± 1.4	740.9 ± 15.4	32.7 ± 0.5	806.3 ± 22.6	11.2 ± 1.0	1912.7 ± 7.9	na
	2-nonanone	252.1 ± 7.9	3909.7 ± 62.5	172.2 ± 3.8	603.5 ± 62.2	36.4 ± 1.0	5706.8 ± 21.9	77.4 ± 5.9
	2-undecanone	2017.4 ± 28.9	10975.1 ± 93.4	1188.6 ± 20.0	400.8 ± 66.3	297.4 ± 6.9	12341.7 ± 41.4	497.2 ± 70.4
	2-tridecanone	4724.4 ± 46.8	14094.8 ± 132.4	2950.5 ± 132.5	161.6 ± 40.2	868.2 ± 17.1	8863.1 ± 47.0	2386.0 ± 149.3
	2-pentadecanone	1066.2 ± 34.0	1343.7 ± 62.1	1054.2 ± 31.5	28.3 ± 4.4	265.6 ± 2.5	895.7 ± 62.3	970.1 ± 58.7
	2-heptadecanone	149.5 ± 3.6	174.6 ± 8.8	168.7 ± 10.6	3.6 ± 0.4	132.2 ± 1.3	97.8 ± 8.8	154.3 ± 10.1
ethyl esters	ethyl butanoate	8.9 ± 0.4	442.7 ± 11.9	na	1762.2 ± 80.2	na	1336.9 ± 16.7	na
	ethyl heptanoate	80.4 ± 16.3	5395.1 ± 70.2	237.4 ± 7.7	996.4 ± 142.8	44.0 ± 0.2	7354.5 ± 39.4	42.3 ± 1.3
	ethyl nonanoate	2137.9 ± 35.8	7204.3 ± 76.5	1138.6 ± 14.9	453.3 ± 85.1	243.5 ± 4.6	7037.2 ± 29.5	492.8 ± 49.7
	ethyl undecanoate	5131.5 ± 45.1	9419.4 ± 52.1	3614.1 ± 124.8	226.5 ± 38.0	525.0 ± 21.1	8310.8 ± 51.0	1909.7 ± 117.4
	ethyl tridecanoate	1537.2 ± 31.3	2003.8 ± 57.2	1315.2 ± 24.5	90.0 ± 9.4	236.0 ± 6.1	1406.6 ± 65.7	1423.4 ± 94.6
	ethyl palmitate	60.3 ± 2.8	73.2 ± 7.0	66.2 ± 7.6	1.5 ± 0.2	67.4 ± 5.8	46.7 ± 1.3	62.4 ± 11.3
	ethyl stearate	2.5 ± 0.5	3.4 ± 0.9	2.9 ± 0.7	na	4.5 ± 1.6	1.2 ± 0.2	3.9 ± 0.5
1-alcohols	1-pentanol	1.0 ± 0.04	16.9 ± 0.8	2.5 ± 0.1	126.8 ± 2.9	2.1 ± 0.1	69.9 ± 1.9	na
	1-heptanol	20.1 ± 0.4	284.8 ± 13.6	34.8 ± 1.1	175.9 ± 12.7	21.5 ± 1.2	479.4 ± 11.4	na
	1-nonanol	173.8 ± 4.2	787.1 ± 28.6	232.1 ± 4.8	151.2 ± 15.0	113.1 ± 2.5	826.6 ± 17.2	42.5 ± 1.5
	1-undecanol	677.8 ± 17.9	1221.5 ± 40.3	761.3 ± 10.5	103.4 ± 18.1	394.2 ± 2.6	1073.5 ± 23.5	248.2 ± 46.9
	1-tridecanol	421.8 ± 12.6	503.9 ± 25.6	474.8 ± 12.3	17.0 ± 2.2	369.7 ± 6.5	399.3 ± 14.9	396.1 ± 37.0
	1-pentadecanol	81.5 ± 7.2	94.4 ± 10.3	97.2 ± 6.5	2.7 ± 0.2	118.4 ± 7.1	54.7 ± 5.7	89.4 ± 3.6
	1-heptadecanol	5.6 ± 0.1	6.2 ± 0.3	6.2 ± 0.7	na	7.6 ± 0.6	3.8 ± 0.3	7.6 ± 0.5

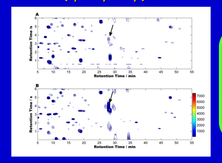
limitations of *ex vivo* SPME

honey

formation of artifact: 5-(hydroxymethyl) furan-2-carbaldehyde

45 °C, 1 hr

45 °C, 48 hrs



aqueous samples: hydrolysis, oxidation & thermolysis

↓

artifact generation

Conclusions

- absolute recoveries & fibre constants for common food components have been determined to standardize SPME coating selection;
- under mild extraction conditions (low sample temperature) & minimized aqueous sample storage; *ex vivo* SPME extract provides true representation of sample

Acknowledgements

- LECO Corporation;
- GERSTEL;
- SUPELCO;
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