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Dynamic Headspace Vacuum In-Tube Extraction and GC-MS for Analyzing Volatile Compounds in Various Matrices

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17. September 2024

3rd European Sample Preparation Conference, Chania-Crete, Greece

Introduction

- Classical headspace in-tube extraction (HS-ITEX) is a known technique for extraction of volatiles
  - But extraction efficiency is limited by long extraction times

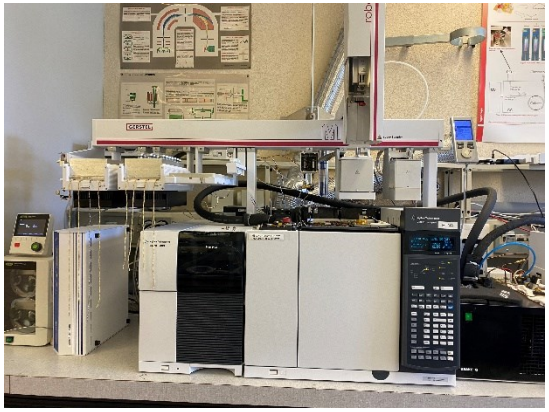
- Vacuum in-tube extraction (V-ITEX) applies reduced pressure during extraction
  - This enhances the gas phase transfer of volatiles
  - Is faster
  - More efficient
  - Applicable to many different samples matrices

Aim

- Develop a microextraction method that is applicable to all the types of samples we get:
  - Foods (cheese, yoghurt, berries, juices, bread, honey, …)
  - Plants, plant oils, dried plants (Hop, basil, coriander, …)
  - Alcoholic beverages (Wine, damassine, grappa, …)
  - Biological samples from human or bacterial cells, human or animal studies (blood, urine, feces, exhalome, raw milk …)

Material

- Artificially Constructed Matrix (ACM) was prepared containing 43 target compounds in polyethylene glycol 200 and Miglyol® 812 at 10 mg/L and pH 1.3
- Parameter optimization: two-level full factorial design of experiment (sample temperature and extraction time)
- Autosampler: MPS2 (Gerstel), extraction parameters (see later)
- GC: Agilent 7890B, TRB-FFAP column (60 m x 0.32 mm 1.0 µm), carrier gas helium at 2.5 mL/min
- MS: Agilent 5977A, Transfer line 230 °C, Ion source 230 °C, scan from 29-250 amu



Material - Extraction setup modification

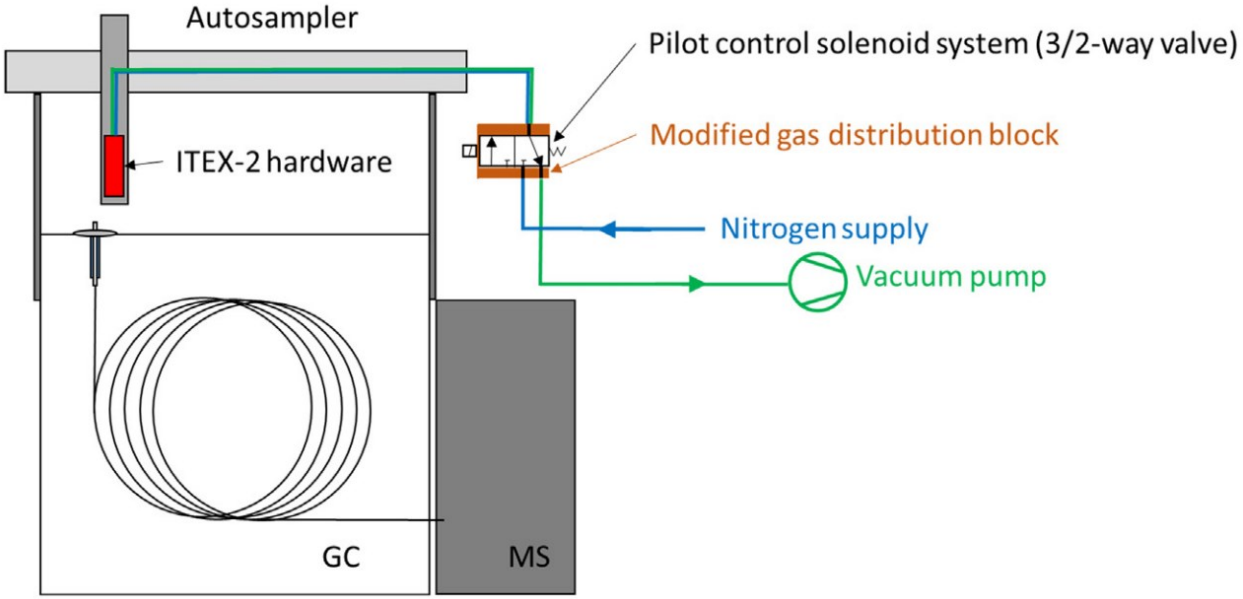


Fig. 1 *Setup of the modified gas flow paths for the V-ITEX System. Taken from doi: 10.1016/j.chroma.2019.05.016*

- Gas distribution block was modified
- N_2 supply for trap and pipe cleaning and trap desorption
- Vacuum pump for reduced pressure during extraction
- 2nd generation used N_2 for desorption, current 3rd generation uses carrier gas for desorption

Material - Flow paths of modified gas distribution block

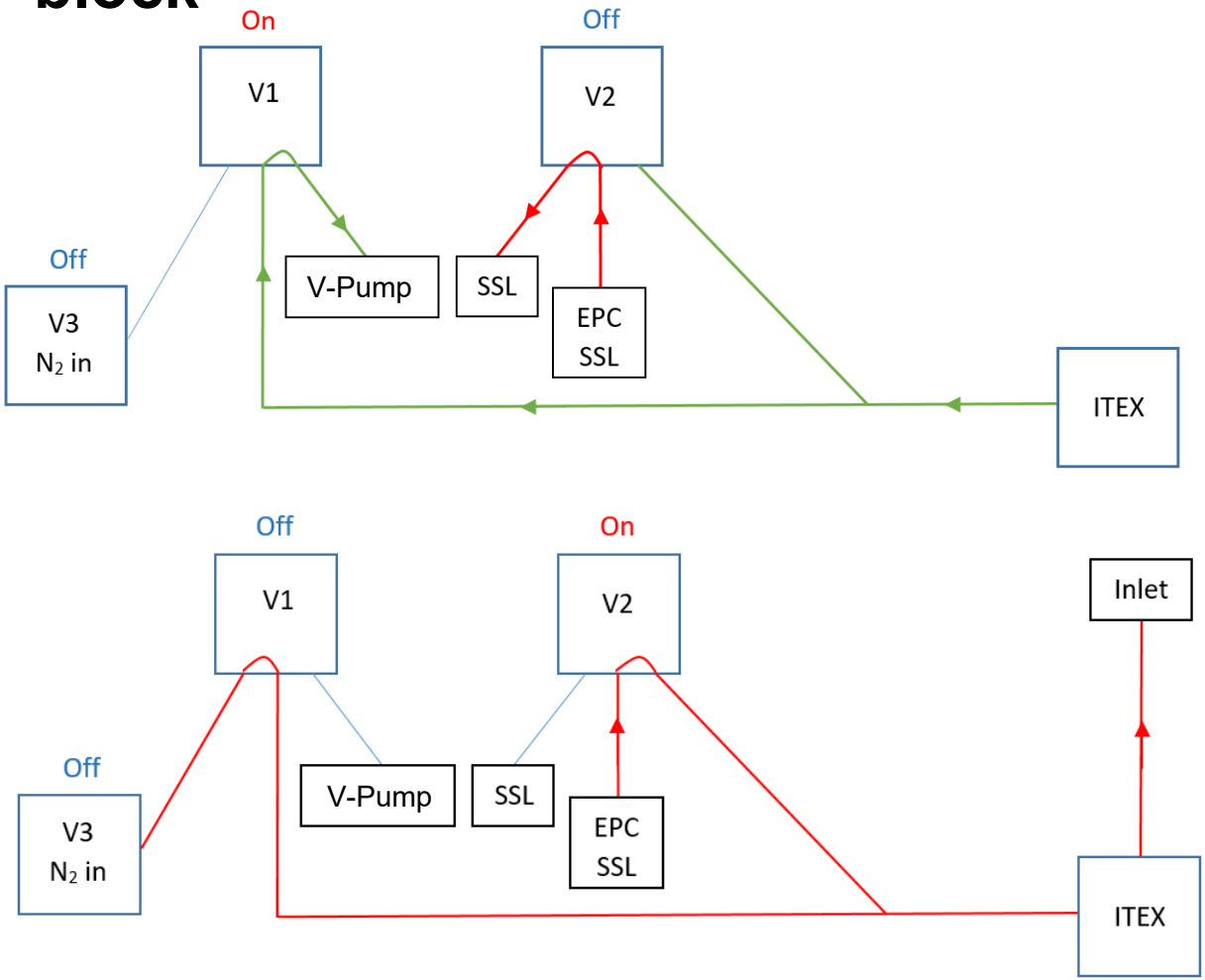


Fig. 2 *Gas flow paths for extraction and desorption for the V-ITEX System.*

Results – Technical improvements

- Pressure in vials with blue silikon/Teflon caps was stable for 10 min
- Water accumulation in the system → Trap drying and tube cleaning were optimized
- Liquid sample amount: 10 µL-2 mL
- Temperature of PTV injector (tested from 20 °C to -50 °C): No significant effect (10 °C for general method)
- Reproducible over 850 injections

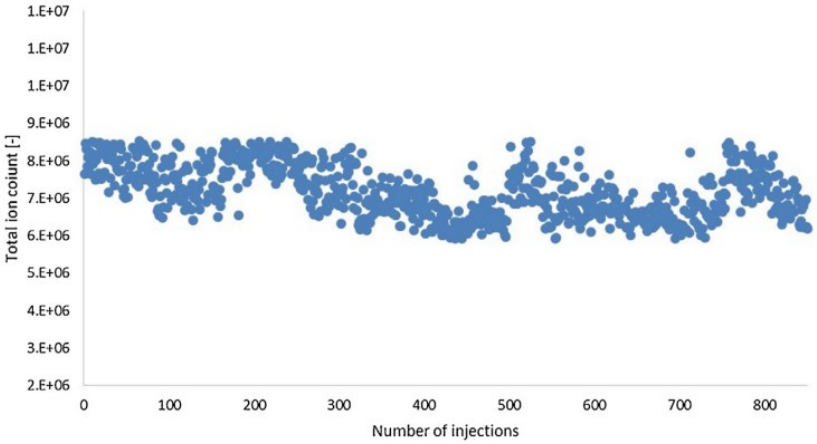


Fig. 3 *Reproducibility of peak area in the compound mix over 850 injections. Taken from: 10.1016/j.chroma.2019.05.016*

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Results – Technical improvements

- Pressure optimization during extraction
  - ➢ Tested from 0-200 mbar (setpoint pressure)
  - ➢ 0 mbar rapidly enhances extraction efficiency (real pressure 5mbar)

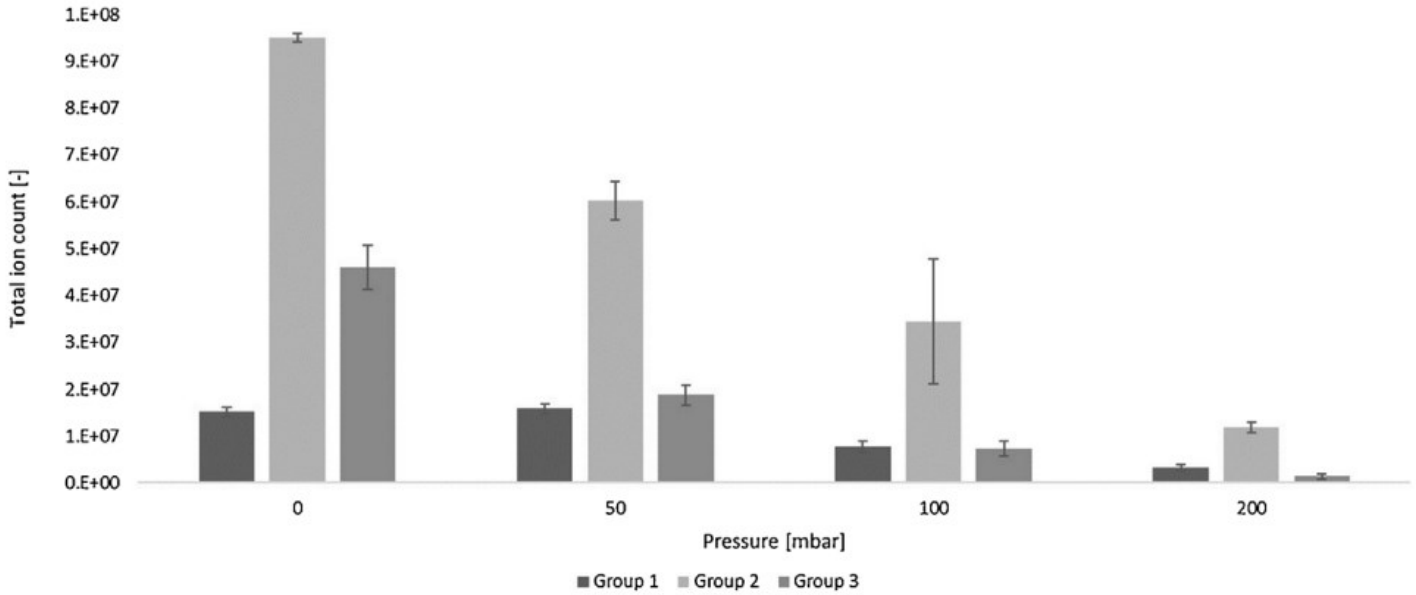
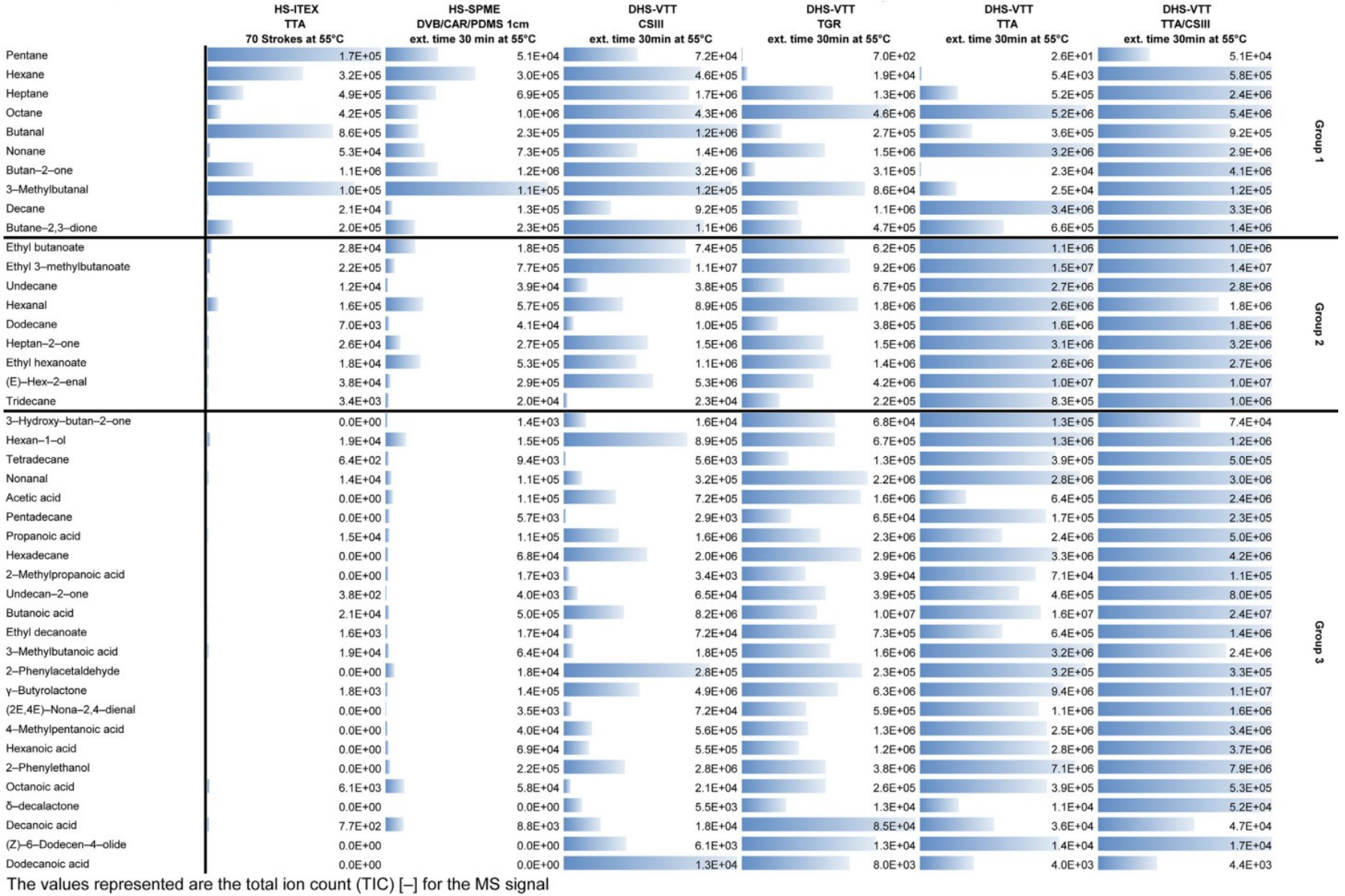


***Fig. 4** Influence of the pressure during V-ITEX extraction. Taken from: 10.1016/j.chroma.2019.05.016*

Results – Comparison with HS-SPME and HS-ITEX



	HS-ITEX TTA 70 Strokes at 55°C	HS-SPME DVB/CAR/PDMS 1cm ext. time 30 min at 55°C	DHS-VTT CSIII ext. time 30min at 55°C	DHS-VTT TGR ext. time 30min at 55°C	DHS-VTT TTA ext. time 30min at 55°C	DHS-VTT TTA/CSIII ext. time 30min at 55°C	
Pentane	1.7E+05	5.1E+04	7.2E+04	7.0E+02	2.6E+01	5.1E+04	Group 1
Hexane	3.2E+05	3.0E+05	4.6E+05	1.9E+04	5.4E+03	5.8E+05	
Heptane	4.9E+05	6.9E+05	1.7E+06	1.3E+06	5.2E+05	2.4E+06	
Octane	4.2E+05	1.0E+06	4.3E+06	4.6E+06	5.2E+06	5.4E+06	
Butanal	8.6E+05	2.3E+05	1.2E+06	2.7E+05	3.6E+05	9.2E+05	
Nonane	5.3E+04	7.3E+05	1.4E+06	1.5E+06	3.2E+06	2.9E+06	
Butan–2–one	1.1E+06	1.2E+06	3.2E+06	3.1E+05	2.3E+04	4.1E+06	
3–Methylbutanal	1.0E+05	1.1E+05	1.2E+05	8.6E+04	2.5E+04	1.2E+05	
Decane	2.1E+04	1.3E+05	9.2E+05	1.1E+06	3.4E+06	3.3E+06	
Butane–2,3–dione	2.0E+05	2.3E+05	1.1E+06	4.7E+05	6.6E+05	1.4E+06	
Ethyl butanoate	2.8E+04	1.8E+05	7.4E+05	6.2E+05	1.1E+06	1.0E+06	Group 2
Ethyl 3–methylbutanoate	2.2E+05	7.7E+05	1.1E+07	9.2E+06	1.5E+07	1.4E+07	
Undecane	1.2E+04	3.9E+04	3.8E+05	6.7E+05	2.7E+06	2.8E+06	
Hexanal	1.6E+05	5.7E+05	8.9E+05	1.8E+06	2.6E+06	1.8E+06	
Dodecane	7.0E+03	4.1E+04	1.0E+05	3.8E+05	1.6E+06	1.8E+06	
Heptan–2–one	2.6E+04	2.7E+05	1.5E+06	1.5E+06	3.1E+06	3.2E+06	
Ethyl hexanoate	1.8E+04	5.3E+05	1.1E+06	1.4E+06	2.6E+06	2.7E+06	
(E)–Hex–2–enal	3.8E+04	2.9E+05	5.3E+06	4.2E+06	1.0E+07	1.0E+07	
Tridecane	3.4E+03	2.0E+04	2.3E+04	2.2E+05	8.3E+05	1.0E+06	
3–Hydroxy–butan–2–one	0.0E+00	1.4E+03	1.6E+04	6.8E+04	1.3E+05	7.4E+04	Group 3
Hexan–1–ol	1.9E+04	1.5E+05	8.9E+05	6.7E+05	1.3E+06	1.2E+06	
Tetradecane	6.4E+02	9.4E+03	5.6E+03	1.3E+05	3.9E+05	5.0E+05	
Nonanal	1.4E+04	1.1E+05	3.2E+05	2.2E+06	2.8E+06	3.0E+06	
Acetic acid	0.0E+00	1.1E+05	7.2E+05	1.6E+06	6.4E+05	2.4E+06	
Pentadecane	0.0E+00	5.7E+03	2.9E+03	6.5E+04	1.7E+05	2.3E+05	
Propanoic acid	1.5E+04	1.1E+05	1.6E+06	2.3E+06	2.4E+06	5.0E+06	
Hexadecane	0.0E+00	6.8E+04	2.0E+06	2.9E+06	3.3E+06	4.2E+06	
2–Methylpropanoic acid	0.0E+00	1.7E+03	3.4E+03	3.9E+04	7.1E+04	1.1E+05	
Undecan–2–one	3.8E+02	4.0E+03	6.5E+04	3.9E+05	4.6E+05	8.0E+05	
Butanoic acid	2.1E+04	5.0E+05	8.2E+06	1.0E+07	1.6E+07	2.4E+07	
Ethyl decanoate	1.6E+03	1.7E+04	7.2E+04	7.3E+05	6.4E+05	1.4E+06	
3–Methylbutanoic acid	1.9E+04	6.4E+04	1.8E+05	1.6E+06	3.2E+06	2.4E+06	
2–Phenylacetaldehyde	0.0E+00	1.8E+04	2.8E+05	2.3E+05	3.2E+05	3.3E+05	
γ–Butyrolactone	1.8E+03	1.4E+05	4.9E+06	6.3E+06	9.4E+06	1.1E+07	
(2E,4E)–Nona–2,4–dienal	0.0E+00	3.5E+03	7.2E+04	5.9E+05	1.1E+06	1.6E+06	
4–Methylpentanoic acid	0.0E+00	4.0E+04	5.6E+05	1.3E+06	2.5E+06	3.4E+06	
Hexanoic acid	0.0E+00	6.9E+04	5.5E+05	1.2E+06	2.8E+06	3.7E+06	
2–Phenylethanol	0.0E+00	2.2E+05	2.8E+06	3.8E+06	7.1E+06	7.9E+06	
Octanoic acid	6.1E+03	5.8E+04	2.1E+04	2.6E+05	3.9E+05	5.3E+05	
δ–decalactone	0.0E+00	0.0E+00	5.5E+03	1.3E+04	1.1E+04	5.2E+04	
Decanoic acid	7.7E+02	8.8E+03	1.8E+04	8.5E+04	3.6E+04	4.7E+04	
(Z)–6–Dodecen–4–olide	0.0E+00	0.0E+00	6.1E+03	1.3E+04	1.4E+04	1.7E+04	
Dodecanoic acid	0.0E+00	0.0E+00	1.3E+04	8.0E+03	4.0E+03	4.4E+03	

The values represented are the total ion count (TIC) [–] for the MS signal

Fig. 5 *Comparison of HS-ITEX, HS-SPME and V-ITEX with different sorbent materials. Taken from: 10.1016/j.chroma.2019.05.016*

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Results – Comparison with HS-SPME and HS-ITEX

	HS-ITEX TTA 70 Strokes at 55°C	HS-SPME DVB/CAR/PDMS 1cm ext. time 30 min at 55°C	DHS-VTT CSIII ext. time 30min at 55°C	DHS-VTT TGR ext. time 30min at 55°C	DHS-VTT TTA ext. time 30min at 55°C	DHS-VTT TTA/CSIII ext. time 30min at 55°C	
Pentane	1.7E+05	5.1E+04	7.2E+04	7.0E+02	2.6E+01	5.1E+04	Group 1
Hexane	3.2E+05	3.0E+05	4.6E+05	1.9E+04	5.4E+03	5.8E+05	
Heptane	4.9E+05	6.9E+05	1.7E+06	1.3E+06	5.2E+05	2.4E+06	
Octane	4.2E+05	1.0E+06	4.3E+06	4.6E+06	5.2E+06	5.4E+06	
Butanal	8.6E+05	2.3E+05	1.2E+06	2.7E+05	3.6E+05	9.2E+05	
Nonane	5.3E+04	7.3E+05	1.4E+06	1.5E+06	3.2E+06	2.9E+06	
Butan–2–one	1.1E+06	1.2E+06	3.2E+06	3.1E+05	2.3E+04	4.1E+06	
3–Methylbutanal	1.0E+05	1.1E+05	1.2E+05	8.6E+04	2.5E+04	1.2E+05	
Decane	2.1E+04	1.3E+05	9.2E+05	1.1E+06	3.4E+06	3.3E+06	
Butane–2,3–dione	2.0E+05	2.3E+05	1.1E+06	4.7E+05	6.6E+05	1.4E+06	
Ethyl butanoate	2.8E+04	1.8E+05	7.4E+05	6.2E+05	1.1E+06	1.0E+06	Group 2
Ethyl 3–methylbutanoate	2.2E+05	7.7E+05	1.1E+07	9.2E+06	1.5E+07	1.4E+07	
Undecane	1.2E+04	3.9E+04	3.8E+05	6.7E+05	2.7E+06	2.8E+06	
Hexanal	1.6E+05	5.7E+05	8.9E+05	1.8E+06	2.6E+06	1.8E+06	
Dodecane	7.0E+03	4.1E+04	1.0E+05	3.8E+05	1.6E+06	1.8E+06	
Heptan–2–one	2.6E+04	2.7E+05	1.5E+06	1.5E+06	3.1E+06	3.2E+06	
Ethyl hexanoate	1.8E+04	5.3E+05	1.1E+06	1.4E+06	2.6E+06	2.7E+06	
(E)–Hex–2–enal	3.8E+04	2.9E+05	5.3E+06	4.2E+06	1.0E+07	1.0E+07	
Tridecane	3.4E+03	2.0E+04	2.3E+04	2.2E+05	8.3E+05	1.0E+06	
3–Hydroxy–butan–2–one	0.0E+00	1.4E+03	1.6E+04	6.8E+04	1.3E+05	7.4E+04	Group 3
Hexan–1–ol	1.9E+04	1.5E+05	8.9E+05	6.7E+05	1.3E+06	1.2E+06	
Tetradecane	6.4E+02	9.4E+03	5.6E+03	1.3E+05	3.9E+05	5.0E+05	
Nonanal	1.4E+04	1.1E+05	3.2E+05	2.2E+06	2.8E+06	3.0E+06	
Acetic acid	0.0E+00	1.1E+05	7.2E+05	1.6E+06	6.4E+05	2.4E+06	
Pentadecane	0.0E+00	5.7E+03	2.9E+03	6.5E+04	1.7E+05	2.3E+05	
Propanoic acid	1.5E+04	1.1E+05	1.6E+06	2.3E+06	2.4E+06	5.0E+06	
Hexadecane	0.0E+00	6.8E+04	2.0E+06	2.9E+06	3.3E+06	4.2E+06	
2–Methylpropanoic acid	0.0E+00	1.7E+03	3.4E+03	3.9E+04	7.1E+04	1.1E+05	
Undecan–2–one	3.8E+02	4.0E+03	6.5E+04	3.9E+05	4.6E+05	8.0E+05	
Butanoic acid	2.1E+04	5.0E+05	8.2E+06	1.0E+07	1.6E+07	2.4E+07	
Ethyl decanoate	1.6E+03	1.7E+04	7.2E+04	7.3E+05	6.4E+05	1.4E+06	
3–Methylbutanoic acid	1.9E+04	6.4E+04	1.8E+05	1.6E+06	3.2E+06	2.4E+06	
2–Phenylacetaldehyde	0.0E+00	1.8E+04	2.8E+05	2.3E+05	3.2E+05	3.3E+05	
γ–Butyrolactone	1.8E+03	1.4E+05	4.9E+06	6.3E+06	9.4E+06	1.1E+07	
(2E,4E)–Nona–2,4–dienal	0.0E+00	3.5E+03	7.2E+04	5.9E+05	1.1E+06	1.6E+06	
4–Methylpentanoic acid	0.0E+00	4.0E+04	5.6E+05	1.3E+06	2.5E+06	3.4E+06	
Hexanoic acid	0.0E+00	6.9E+04	5.5E+05	1.2E+06	2.8E+06	3.7E+06	
2–Phenylethanol	0.0E+00	2.2E+05	2.8E+06	3.8E+06	7.1E+06	7.9E+06	
Octanoic acid	6.1E+03	5.8E+04	2.1E+04	2.6E+05	3.9E+05	5.3E+05	
δ–decalactone	0.0E+00	0.0E+00	5.5E+03	1.3E+04	1.1E+04	5.2E+04	
Decanoic acid	7.7E+02	8.8E+03	1.8E+04	8.5E+04	3.6E+04	4.7E+04	
(Z)–6–Dodecen–4–olide	0.0E+00	0.0E+00	6.1E+03	1.3E+04	1.4E+04	1.7E+04	
Dodecanoic acid	0.0E+00	0.0E+00	1.3E+04	8.0E+03	4.0E+03	4.4E+03	

The values represented are the total ion count (TIC) [–] for the MS signal

Fig. 5 *Comparison of HS-ITEX, HS-SPME and V-ITEX with different sorbent materials. Taken from: 10.1016/j.chroma.2019.05.016*

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Results – Comparison with HS-SPME and HS-ITEX

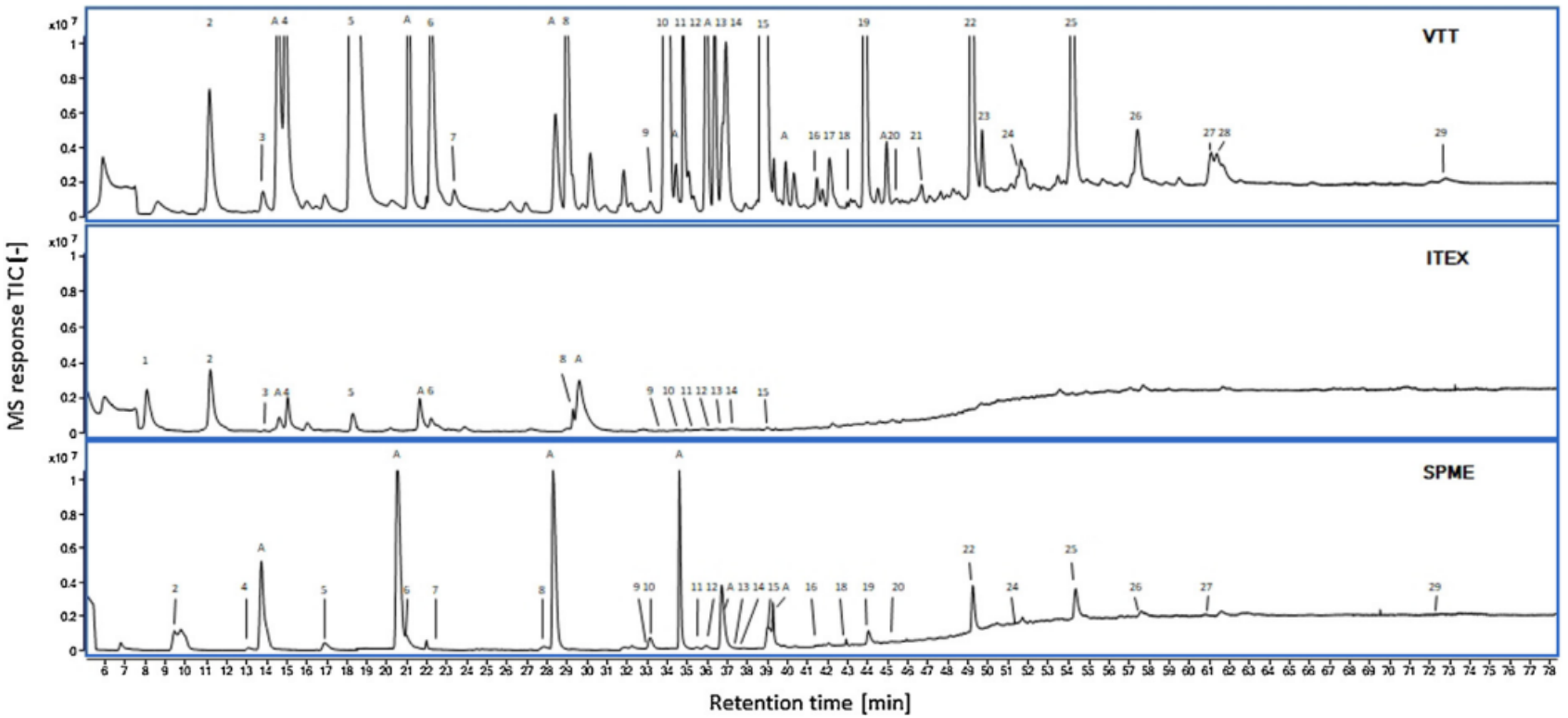
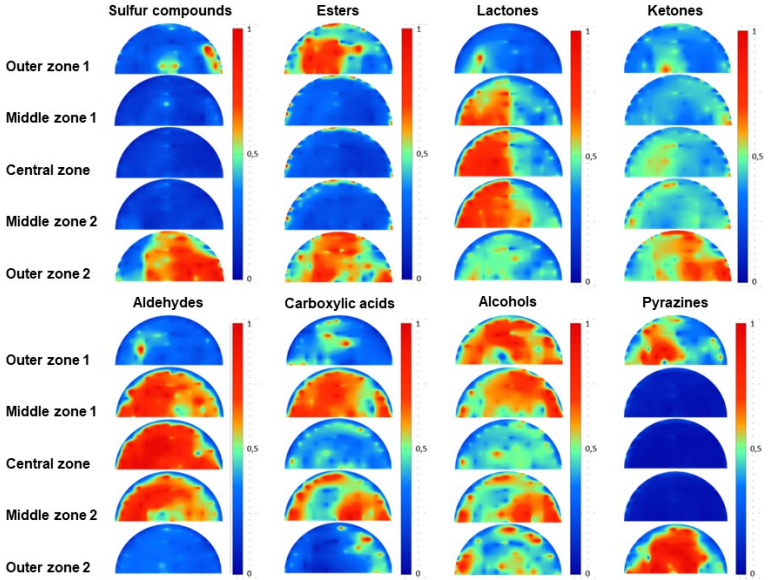


Fig. 6 *Comparison of plain yoghurt chromatograms of HS-ITEX, HS-SPME and V-ITEX. Taken from: 10.1016/j.chroma.2019.05.016*

Results - Required pre-treatment of samples

- For heterogeneous foods (e.g. Cheese) homogenization with liquid N_2 is proposed
- For gaseous samples or pre-concentration SPE cartridges can be used
- Most of the samples can be measured directly (urine, blood, milk, joghurt, dried plants, …)

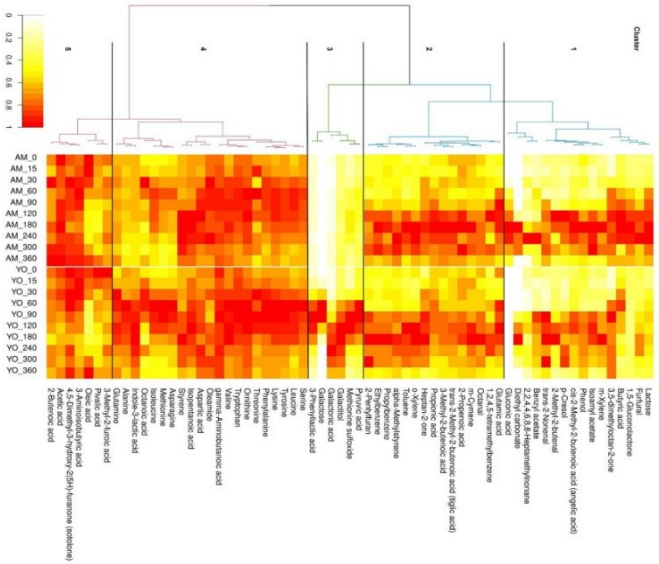
Results – Application examples



Heterogeneity mapping of cheese (>290 samples)

Aroma analysis with olfactometry (large quantity injected, >2 panelists in parallel)

Cow exhalome (>2000 samples)



Biomarkers after food consumption in serum, urine, blood etc. (>800 samples)

Conclusions

- **V-ITEX can extract up to 450 times higher compound amounts compared to HS-SPME and HS-ITEX**
- The most efficient V-ITEX sorbent material was Tenax TA/Carbosieve III
- The extraction time and/or sample volume could be greatly reduced for most applications (in general 10 min are used)
  - ➢ In agreement with Green Analytical Chemistry requirements
- Is applicable to most of the sample types that we get
- Currently in discussions with CTC Analytics and Gerstel for commercialization of the V-ITEX System

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Publication and patent

Journal of Chromatography A, 1601 (2019) 60–70

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Development and performance evaluation of a novel dynamic headspace vacuum transfer “In Trap” extraction method for volatile compounds and comparison with headspace solid-phase microextraction and headspace in-tube extraction

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Patent Registration

Internationale Patentanmeldung PCT /CH2019/000002
Schweizerische Eidgenossenschaft
Novel Dynamic Headspace Vacuum Transfer "in Trap" Extraction Method and Apparatus for its Performance






















Thank you for your attention!

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