SepSolve Analytical

16TH Multidimensional Chromatography Workshop

Investigating the impact of packaging on oat volatiles using GC×GC–TOF MS

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An introduction to SepSolve Analytical

Experts in analytical chemistry

SCHAUENBURG Analytics

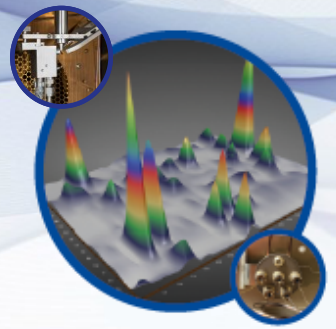
MARKES international

SepSolve Analytical

Sampling technologies

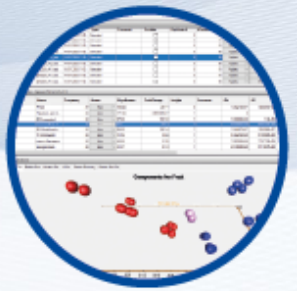
Thermal desorption

Sample enrichment



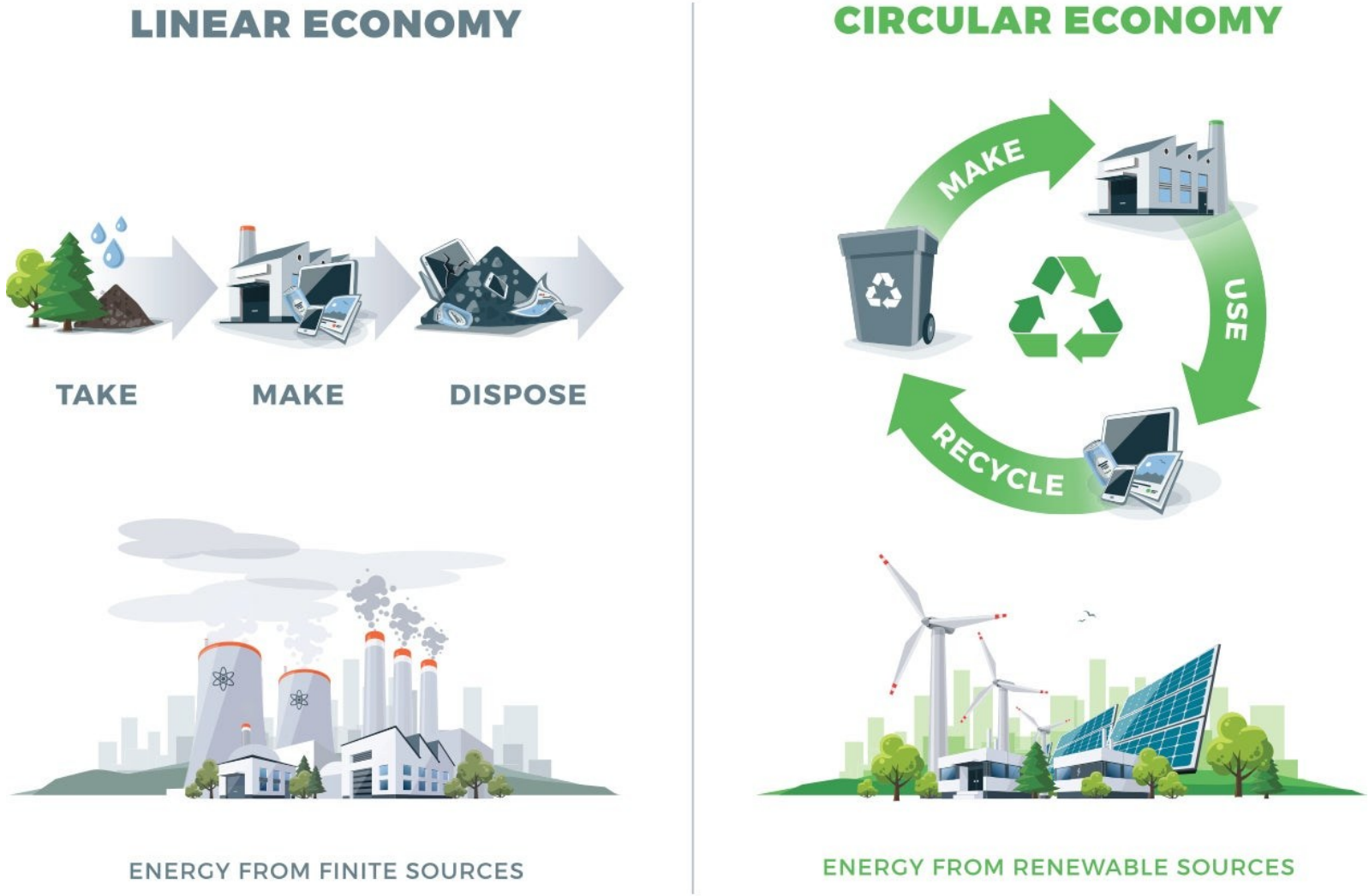
Separation technologies

Unique identification



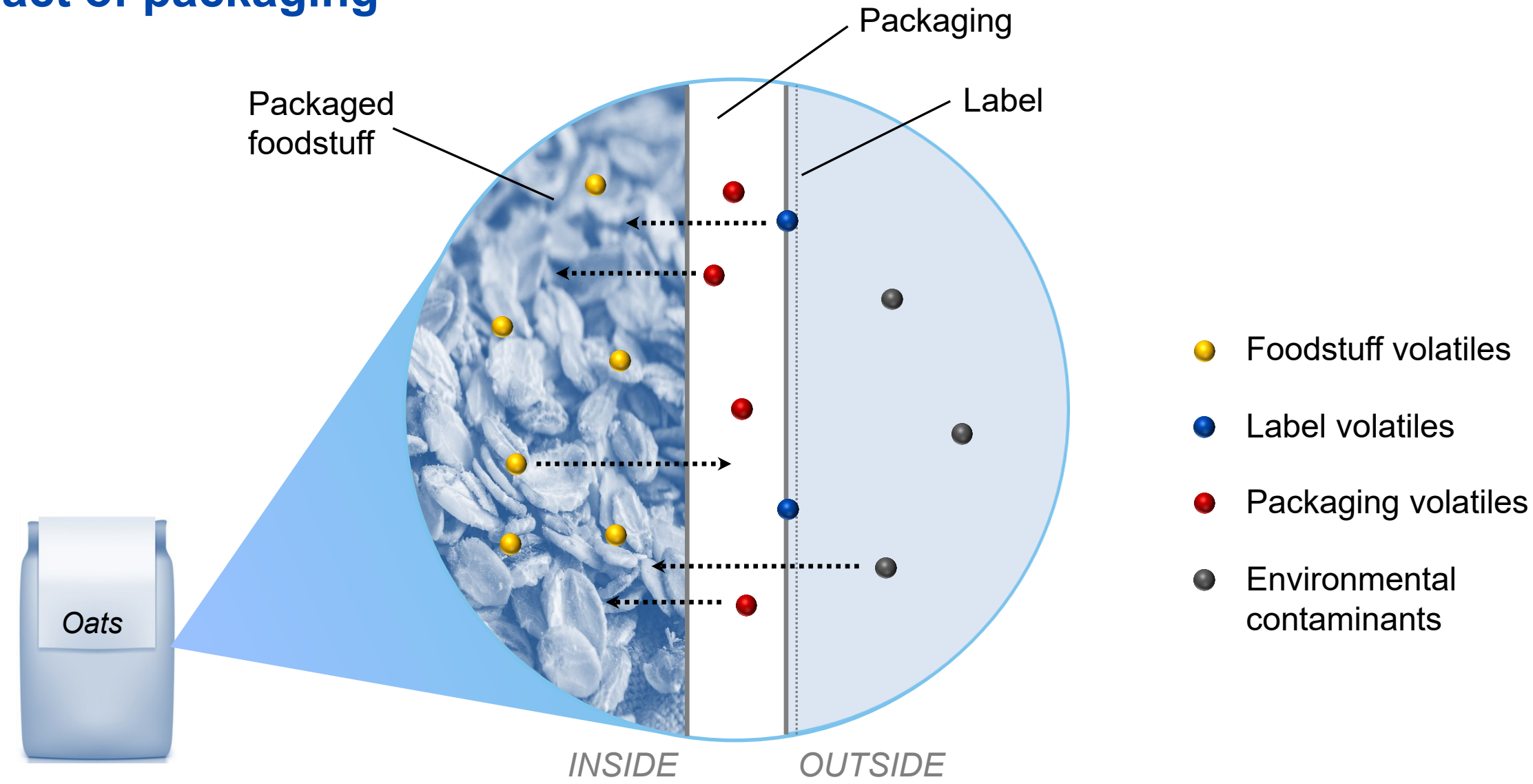
Data analysis

The importance of recycling



Source: Circular Economy: Now or Never [Blog] - https://blogs.iadb.org/sostenibilidad/en/circular-economy-now-or-never/

Impact of packaging



Adapted from: J.Muncke, Tackling the toxics in plastics packaging, 2021, PLoS Biol 19(3).

Why rolled oats?

- Readily absorb volatiles, potentially affecting their quality

- Already sold in many types of packaging:
  - Paper
  - Plastic
  - Cardboard

Sampling approaches

	Headspace	SPME	Sorptive extraction
	✓ Simple and easily automated ✓ Low cost & 'green' ✘ No preconcentration ✘ Limited volumes	✓ Simple and easily automated ✓ 'Greener' than solvent extraction ✘ Fragile fibers ✘ Limited sensitivity (low phase volume) ✘ Immersive sampling is challenging – Fibers may get contaminated or have reduced lifetime	✓ Simple and easily automated ✓ 'Greener' than solvent extraction ✓ Robust probes compatible with headspace or immersive sampling ✓ Larger volume of sorptive phase – 30-65 µL compared to ~0.5 µL for SPME

Sampling approaches

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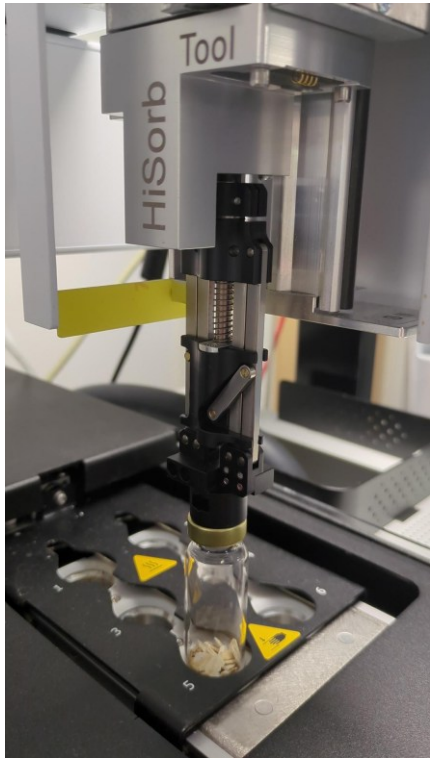
	✓ Simple and easily automated ✓ Low cost & 'green' ✘ ~~No preconcentration~~ ✘ ~~Limited volumes~~ ✓ **Multi-step enrichment & high-volume sampling**	✓ Simple and easily automated ✓ 'Greener' than solvent extraction ✘ Fragile fibers ✘ ~~Limited sensitivity (low phase volume~~) ✘ Immersive sampling is challenging – Fibers may get contaminated or have reduced lifetime ✓ **Multi-step enrichment**	✓ Simple and easily automated ✓ 'Greener' than solvent extraction ✓ Robust probes (for headspace or immersive sampling ✓ Larger volume of sorptive phase – 30-65 µL compared to ~0.5 µL for SPME ✓ **Multi-step enrichment**

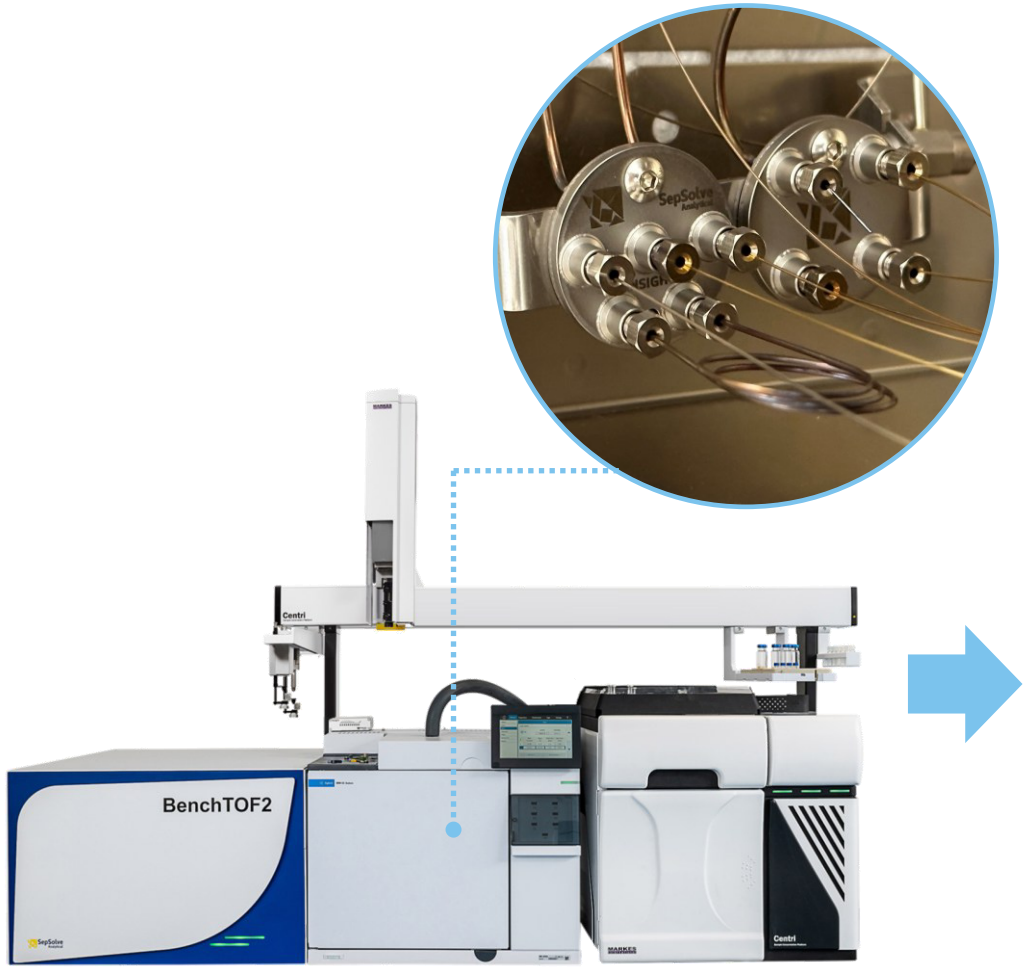
Sample overview

- **Samples:** Six store-bought packs of rolled oats (~1 g)
- **Headspace sampling:**
  - HiSorb high-capacity sorptive extraction probes (Markes International)
  - Phase: PDMS/CWR/DVB (~30 µL)
  - Incubation time: 45 min
  - Incubation temperature: 70 °C

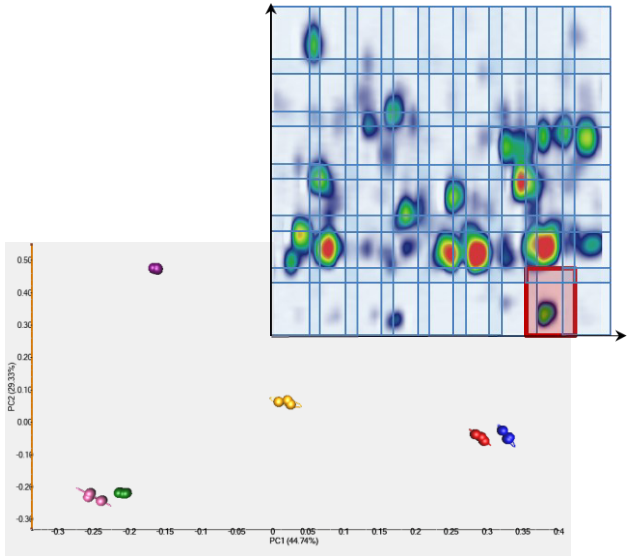
Experimental



Automated headspace sorptive extraction



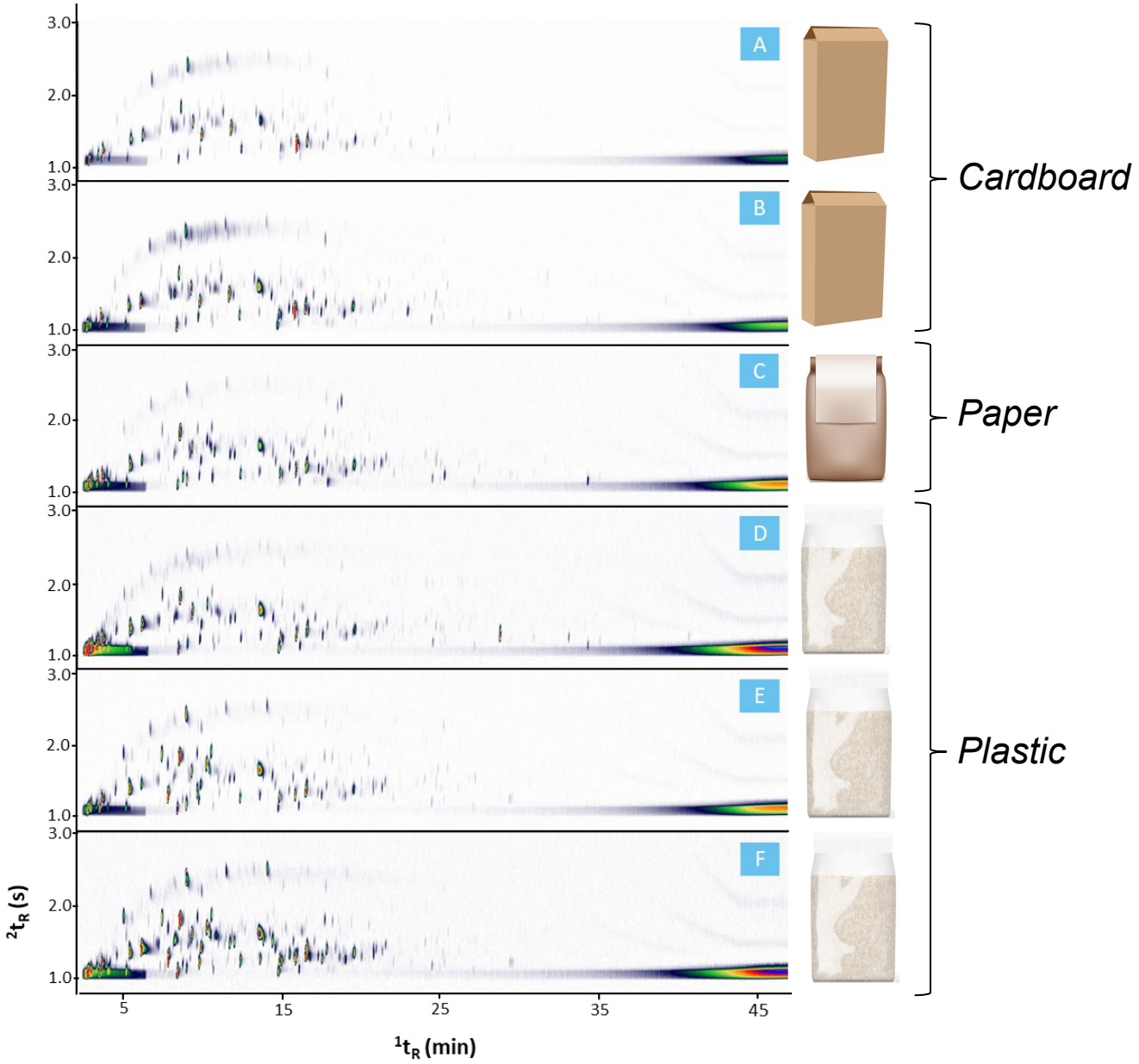
GC×GC–TOF MS with INSIGHT-Flow modulation



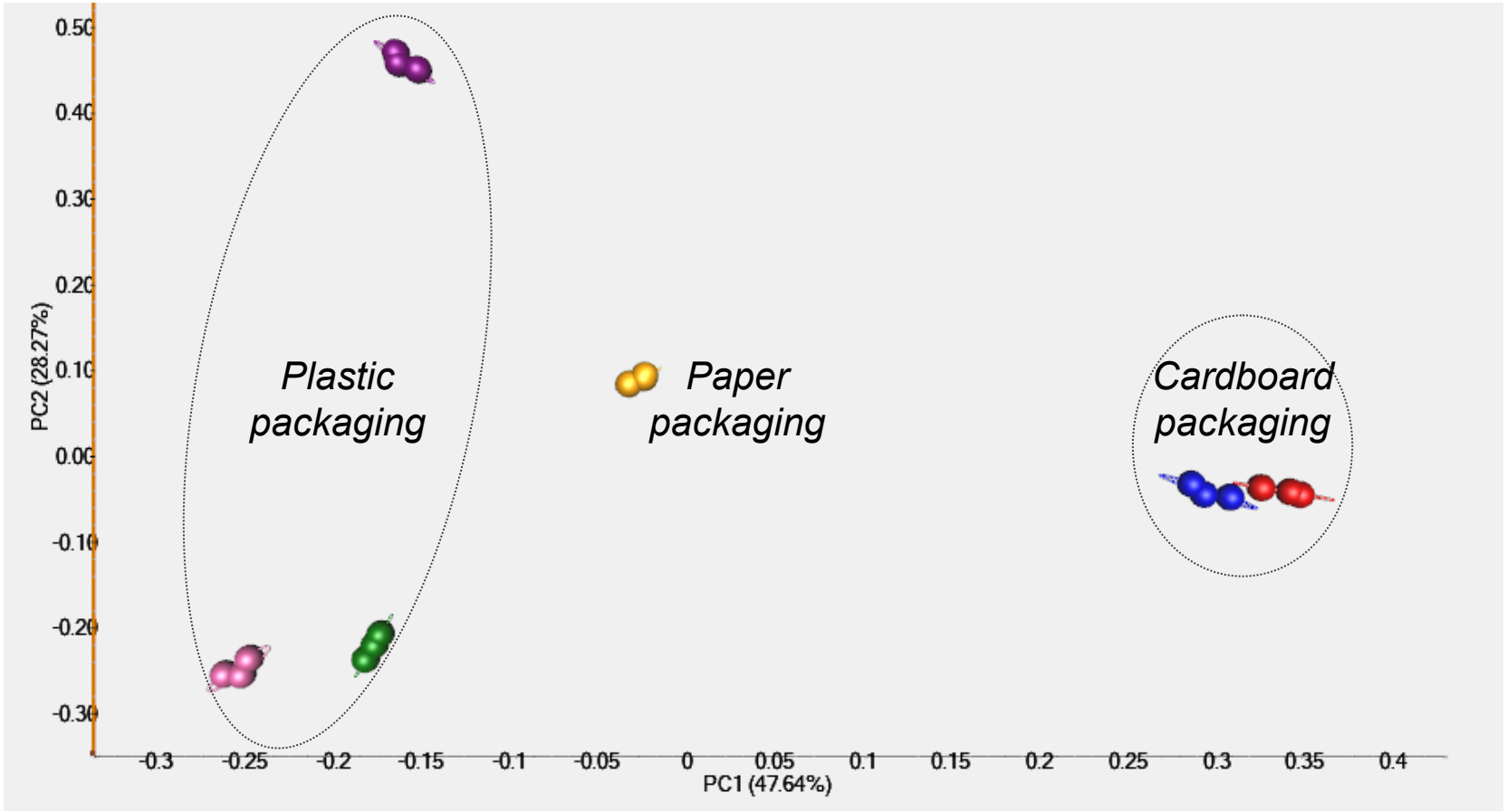
Tile-based chemometrics in ChromCompare+

Oat volatiles by GC×GC–TOF MS

- ~250–300 components per sample
- Triplicate analysis = 18 datafiles
- Processed using tile widths of:
  - ^1t_R = 12 s
  - ^2t_R = 0.75 s
  - Overlap = 20%
- >100,000 unique features



Comparison of oat volatiles

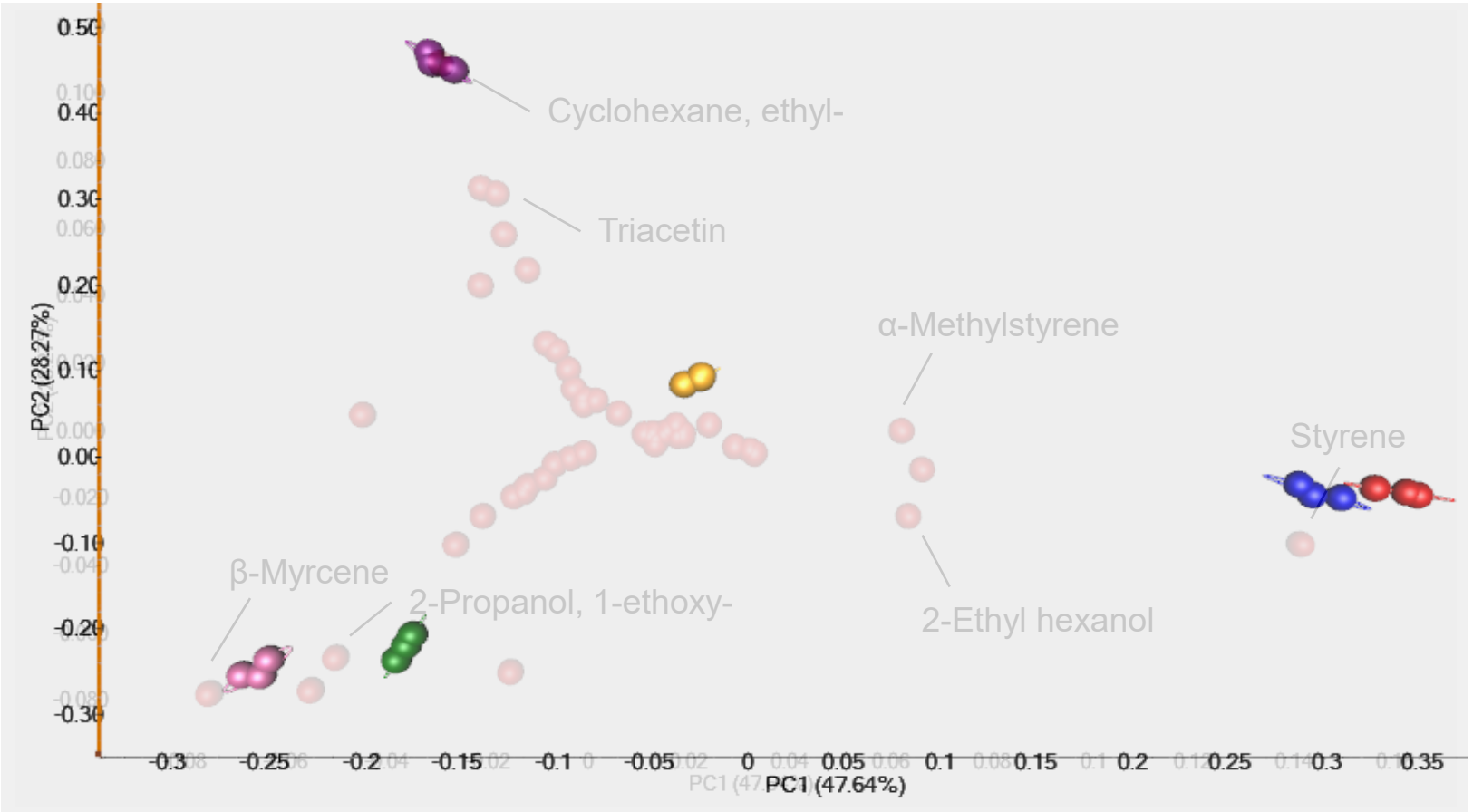


Oat brands

- Brand A
- Brand B
- Brand C
- Brand D
- Brand E
- Brand F

- Principal component analysis (PCA) indicates that packaging is likely to be influencing the volatile profiles of the oats

Comparison of oat volatiles



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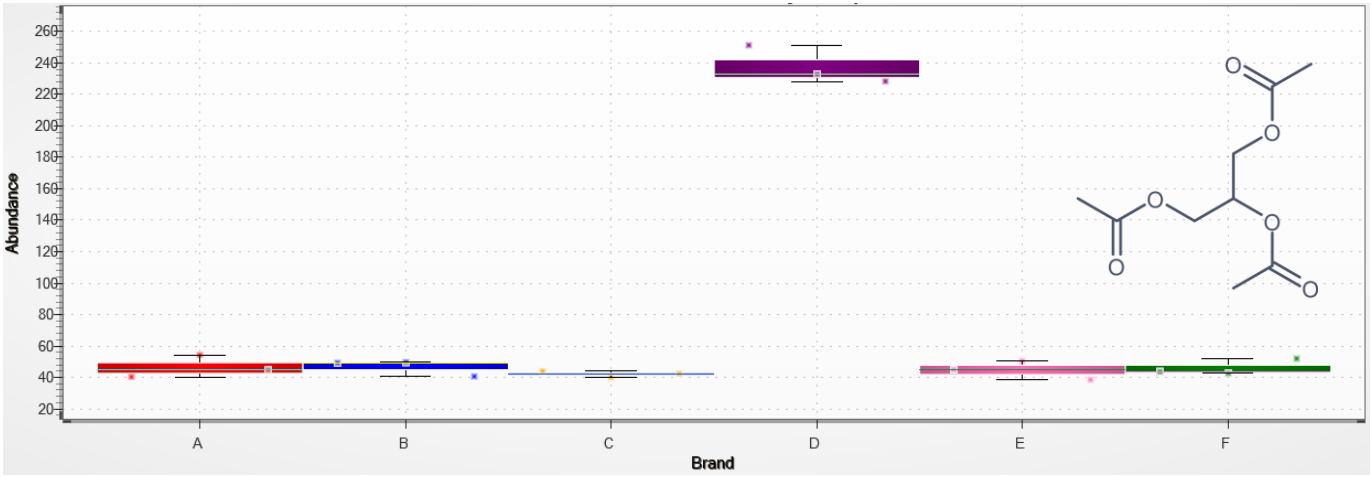
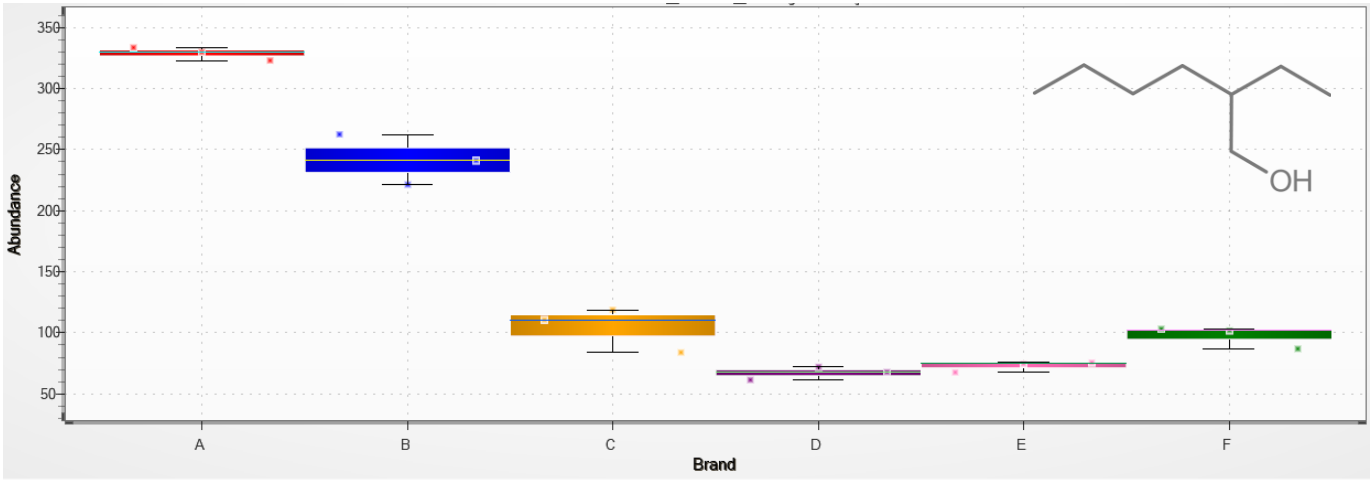
Influence of packaging on oat volatiles



Triacetin was only elevated in the plastic-packaged brand D



2-Ethyl hexanol was increased in both oat brands packaged in cardboard

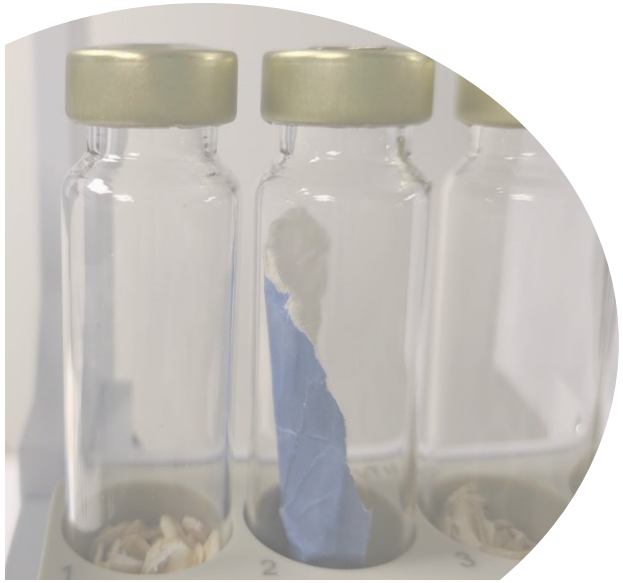
Influence of packaging on oat volatiles

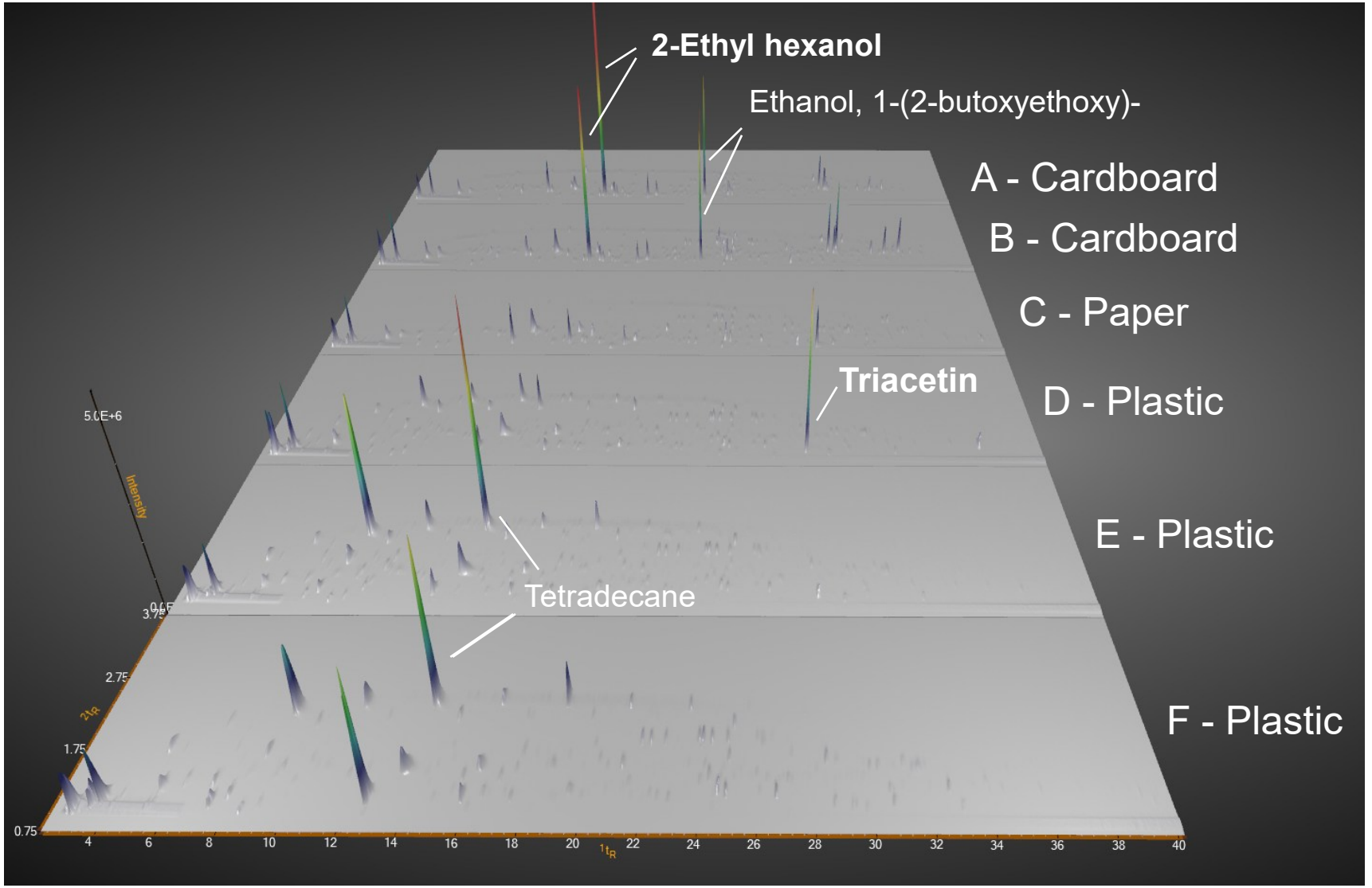
- 33 key oat differentiators identified after removing duplicate features

Feature identity	$^{1}t_R$ (min)	$^{2}t_R$ (s)	Match factor	Relative intensity
Cyclohexane, ethyl-	3.846	1.370	800	↑ Brand D
o-Xylene	7.311	1.479	880	↑ Plastic packaging
β-Myrcene	7.898	1.716	890	↑ Brands E & F
2-Propanol, 1-ethoxy-	7.943	1.214	802	↑ Brands E & F
Benzene, tert-butyl-	9.539	1.669	801	↑ Brand A
2-Propanol, 1-propoxy-	9.759	1.289	906	↑ Brand E
Benzene, (1-methylpropyl)-	9.811	1.692	849	↑ Cardboard packaging
1-Pentanol	9.853	1.152	919	↑ Brand F
2,6-Dimethyldecalin	9.856	2.217	803	↑ Cardboard packaging
Styrene	9.947	1.407	937	↑ Cardboard packaging
Benzene, 2-propenyl-	10.154	1.524	833	↑ Brand E
Cyclohexanone	10.804	1.495	879	↑ Paper packaging
o-Chlorotoluene	11.068	1.503	844	↑ Plastic packaging
Diisopropyl ether	11.154	1.288	875	↑ Brand E
Octanal	11.164	1.576	785	↑ Cardboard packaging
p-Chlorotoluene	11.544	1.459	864	↑ Plastic packaging
Pyrazine, 2,5-dimethyl-	11.702	1.475	900	↑ Brand B
α-Methylstyrene	11.800	1.452	947	↑ Cardboard packaging
Pyrazine, 2-ethyl-3-methyl-	13.431	1.529	802	↑ Brand B
Trimethylpyrazine	13.814	1.525	781	↑ Paper packaging
Pyrazine, tetramethyl-	15.604	1.547	868	↑ Paper packaging
1-Hexanol, 2-ethyl-	15.917	1.223	902	↑ Cardboard packaging
3,5-Octadien-2-one, (E,E)-	16.653	1.365	901	↑ Brand F
Guaiadiene-6,9	18.815	2.197	863	↑ Paper packaging
p-Vinylanisole	20.249	1.346	834	↑ Paper packaging
Benzofuran, 4,7-dimethyl-	20.895	1.423	784	↑ Brand E
Benzene, 1,2-dimethoxy-	21.296	1.317	880	↑ Paper packaging
Phenylethyl alcohol	25.296	1.125	919	↑ Paper packaging
Diphenyl ether	27.304	1.416	859	↑ Brand E
Benzene, 2,4-pentadiynyl-	27.453	1.241	820	↑ Paper packaging
Triacetin	28.786	1.150	923	↑ Brand D
2,6-Xylenol, 4-tert-butyl-	30.150	1.154	785	↑ Brand B
4-Vinylphenol	34.301	1.022	899	↑ Paper packaging

Influence of packaging on oat volatiles

- Analysis of the packaging itself (~0.5 g) confirms these trends & others





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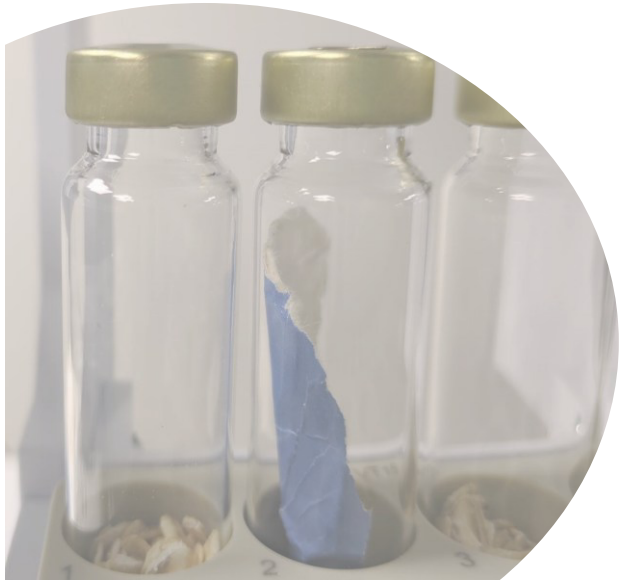

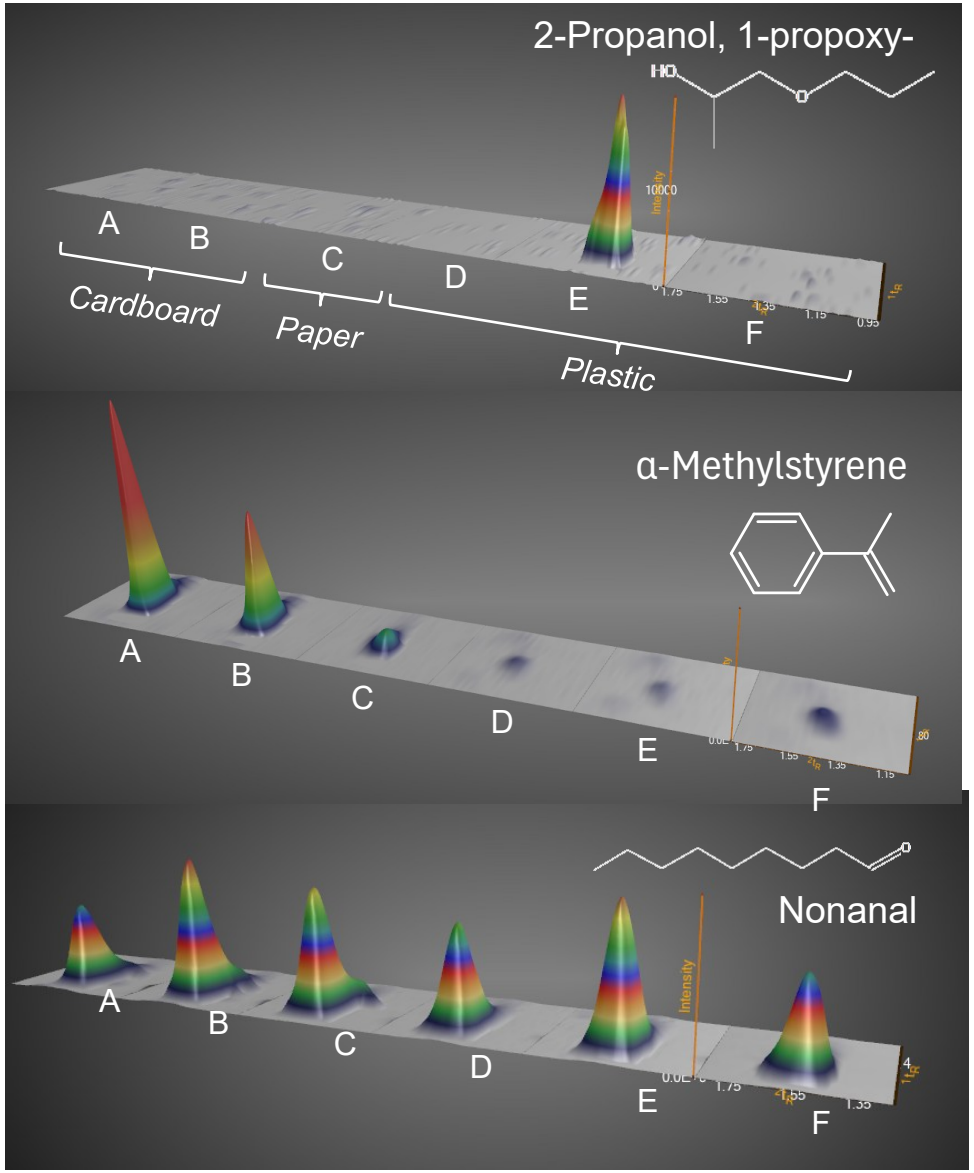

Influence of packaging on oat volatiles

- 25 of the 33 key oat differentiators were also identified in the respective packaging.
- Tile workflows work well for larger datasets investigating packaging
- ***But what if we need fast troubleshooting, e.g. product complaints?***

Feature identity	$^{1}t_R$ (min)	$^{2}t_R$ (s)	Match factor	Relative intensity	Presence also confirmed in packaging
Cyclohexane, ethyl-	3.846	1.370	800	↑ Brand D	×
o-Xylene	7.311	1.479	880	↑ Plastic packaging	✓
β-Myrcene	7.898	1.716	890	↑ Brands E & F	✓
2-Propanol, 1-ethoxy-	7.943	1.214	802	↑ Brands E & F	✓
Benzene, tert-butyl-	9.539	1.669	801	↑ Brand A	✓
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Benzene, (1-methylpropyl)-	9.811	1.692	849	↑ Cardboard packaging	✓
1-Pentanol	9.853	1.152	919	↑ Brand F	×
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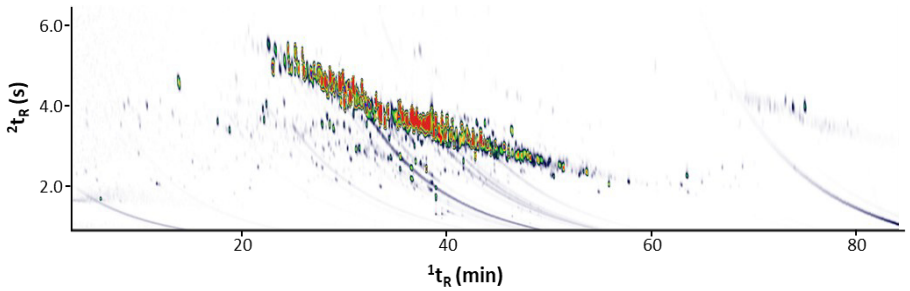
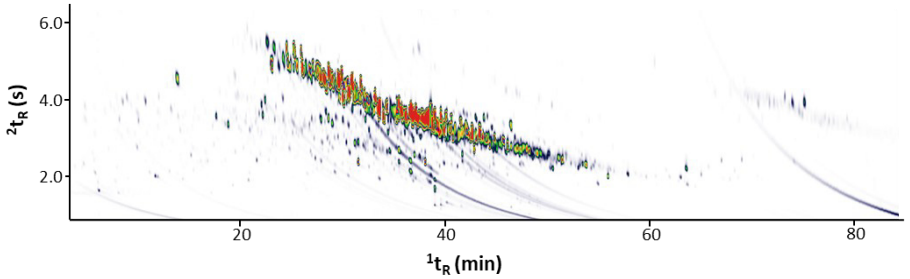
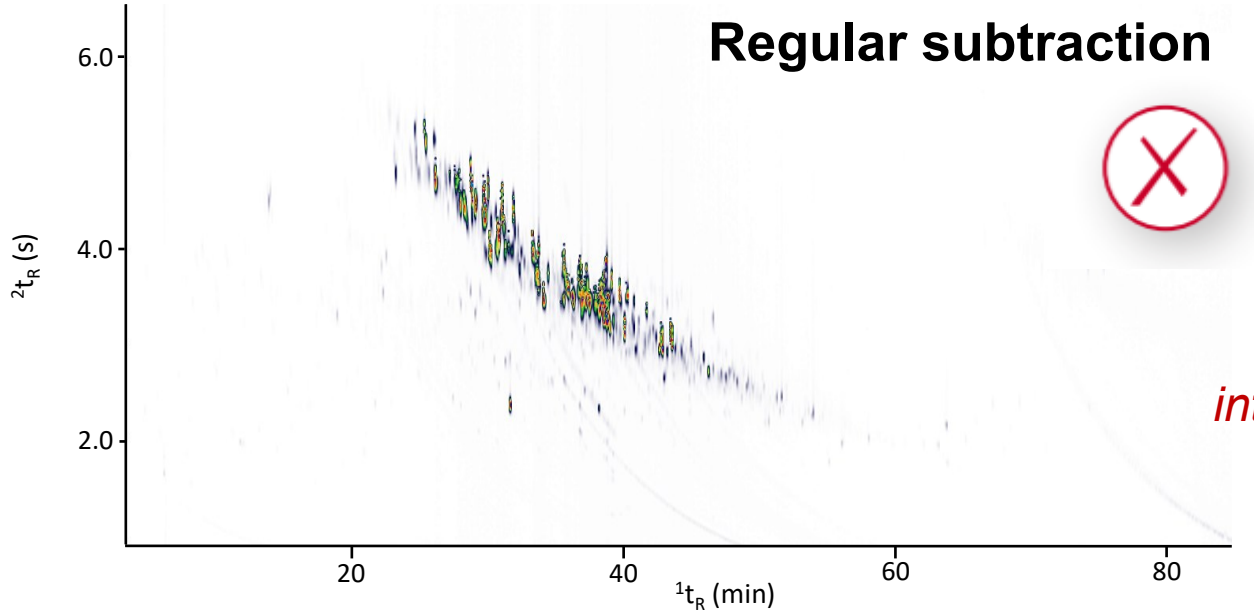
What if we need faster results?



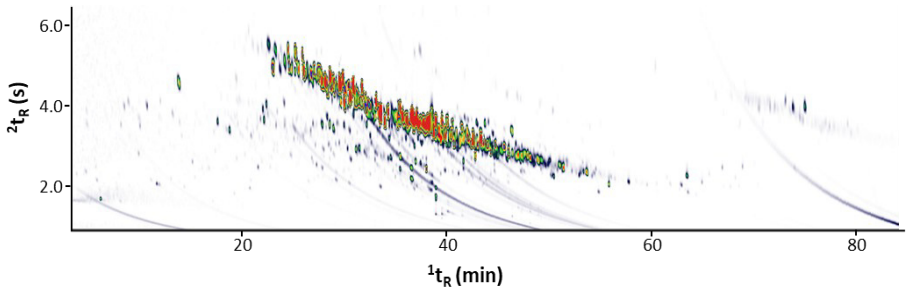


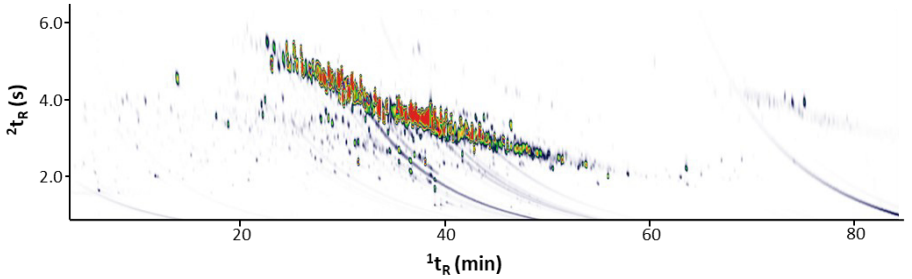
Regular subtraction



Small differences in intense peaks dominate the chromatogram

What if we need faster results?





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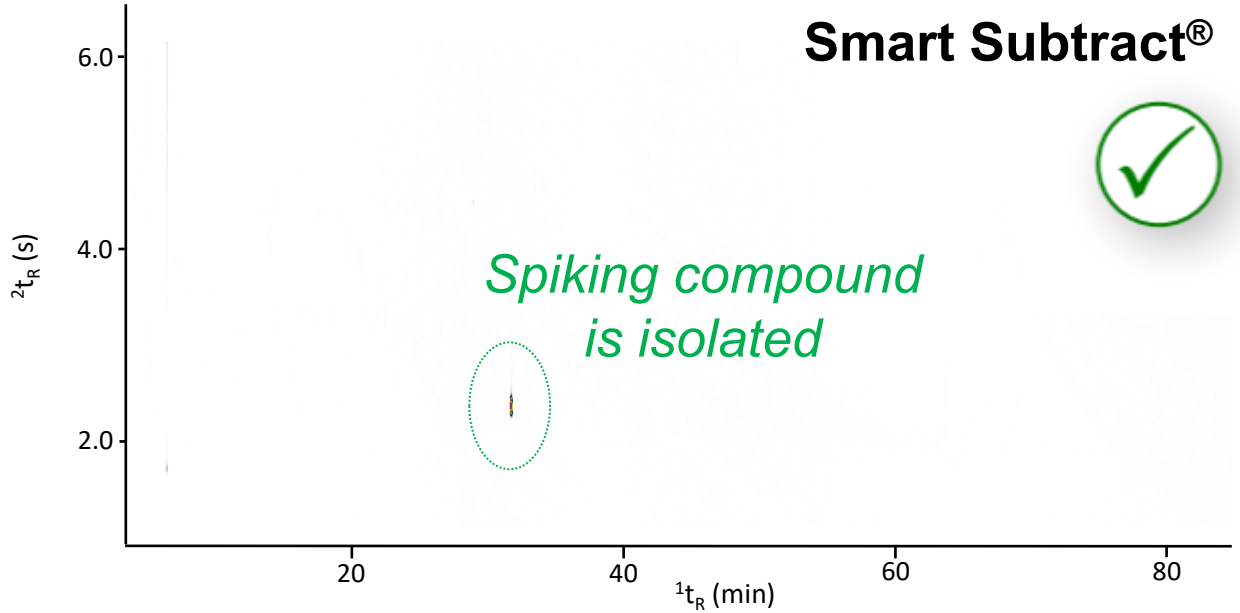
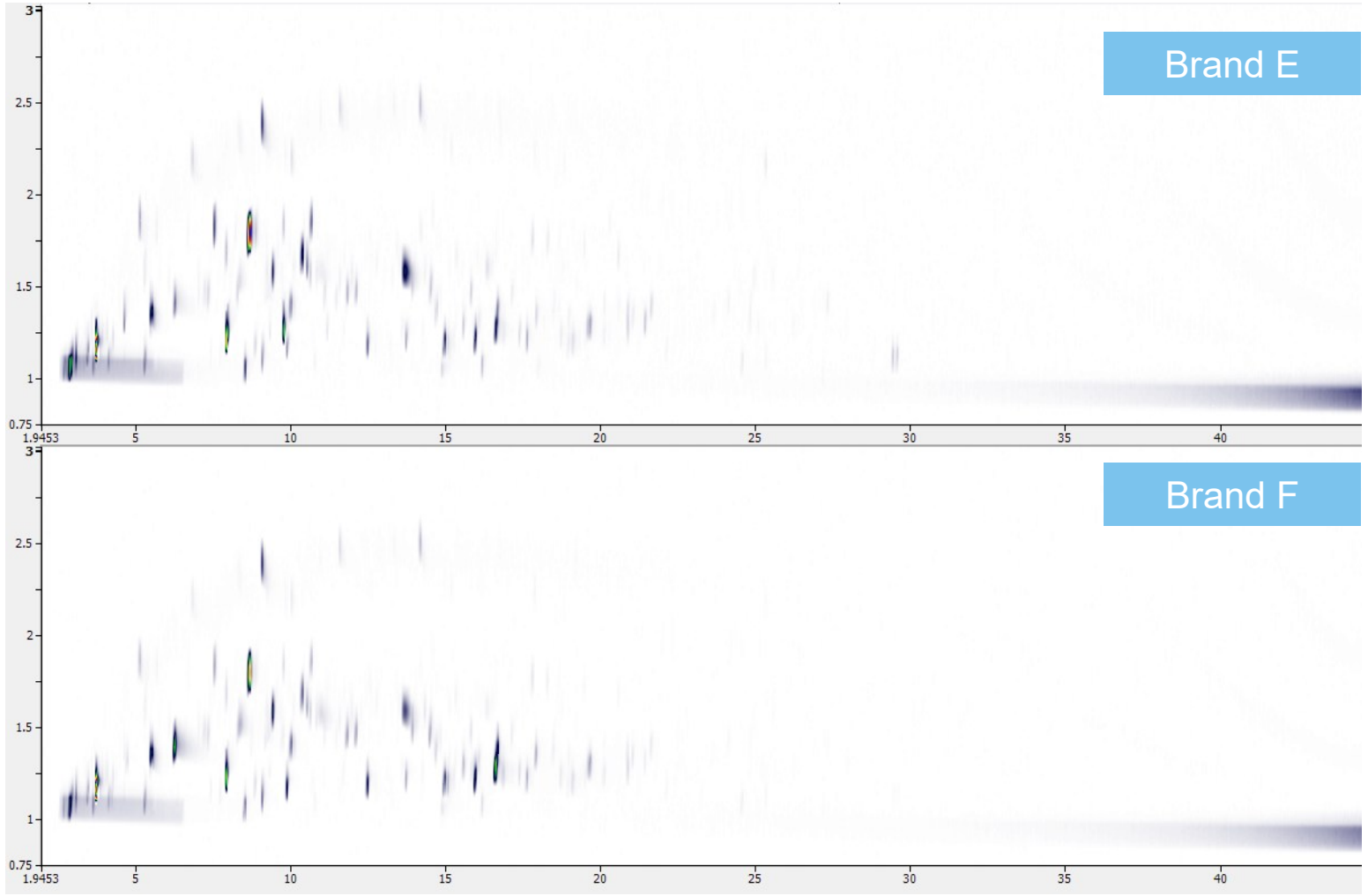


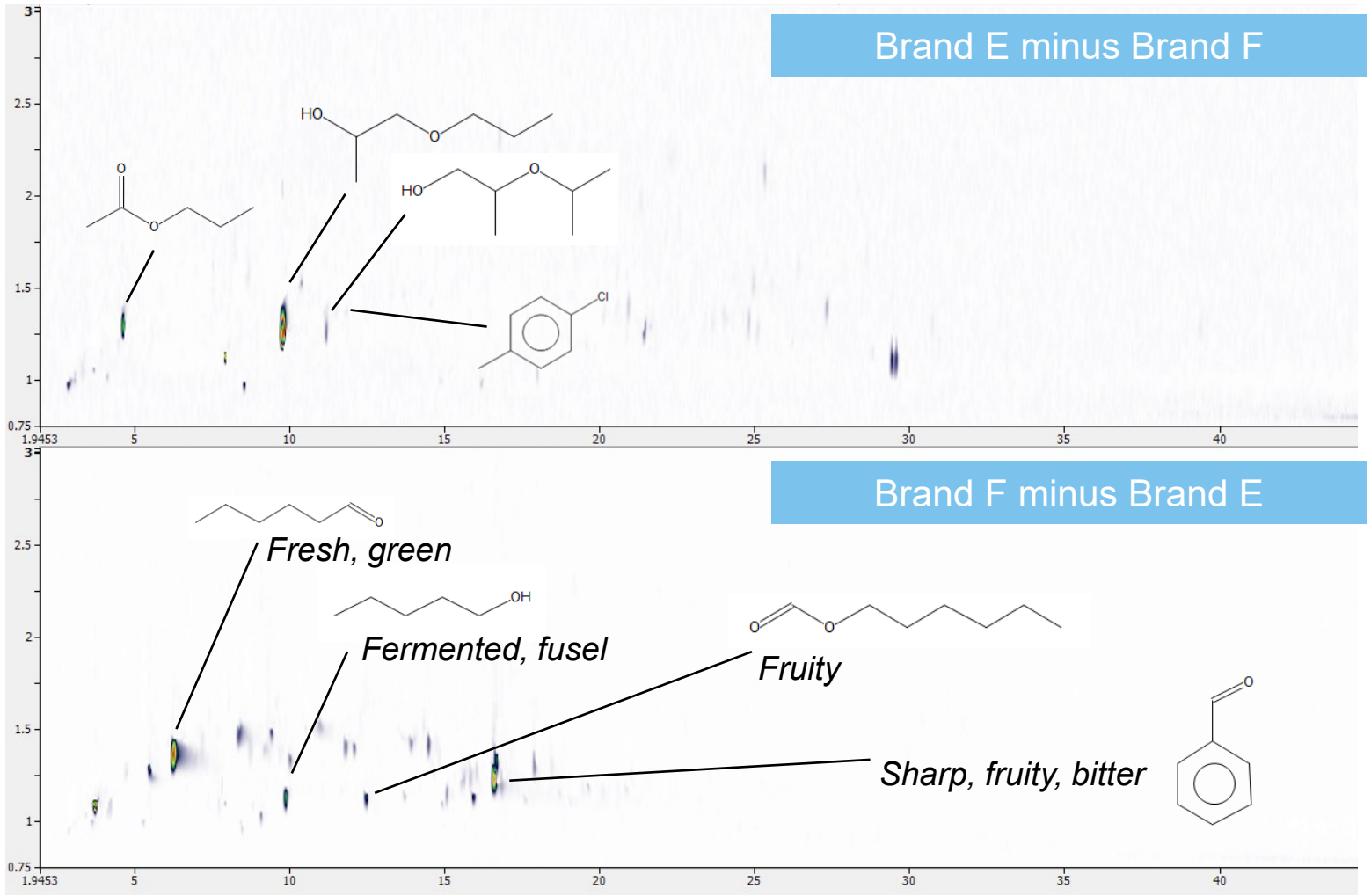
Spiking compound is isolated

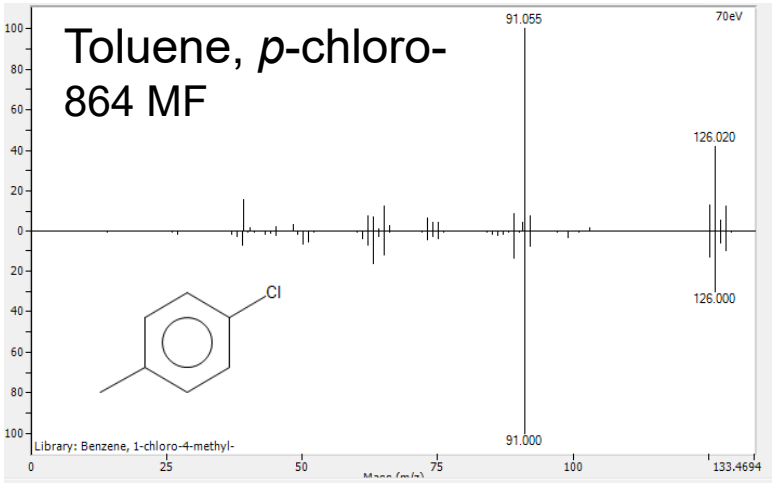
Comparing two plastic-packaged oats



Comparing two plastic-packaged oats

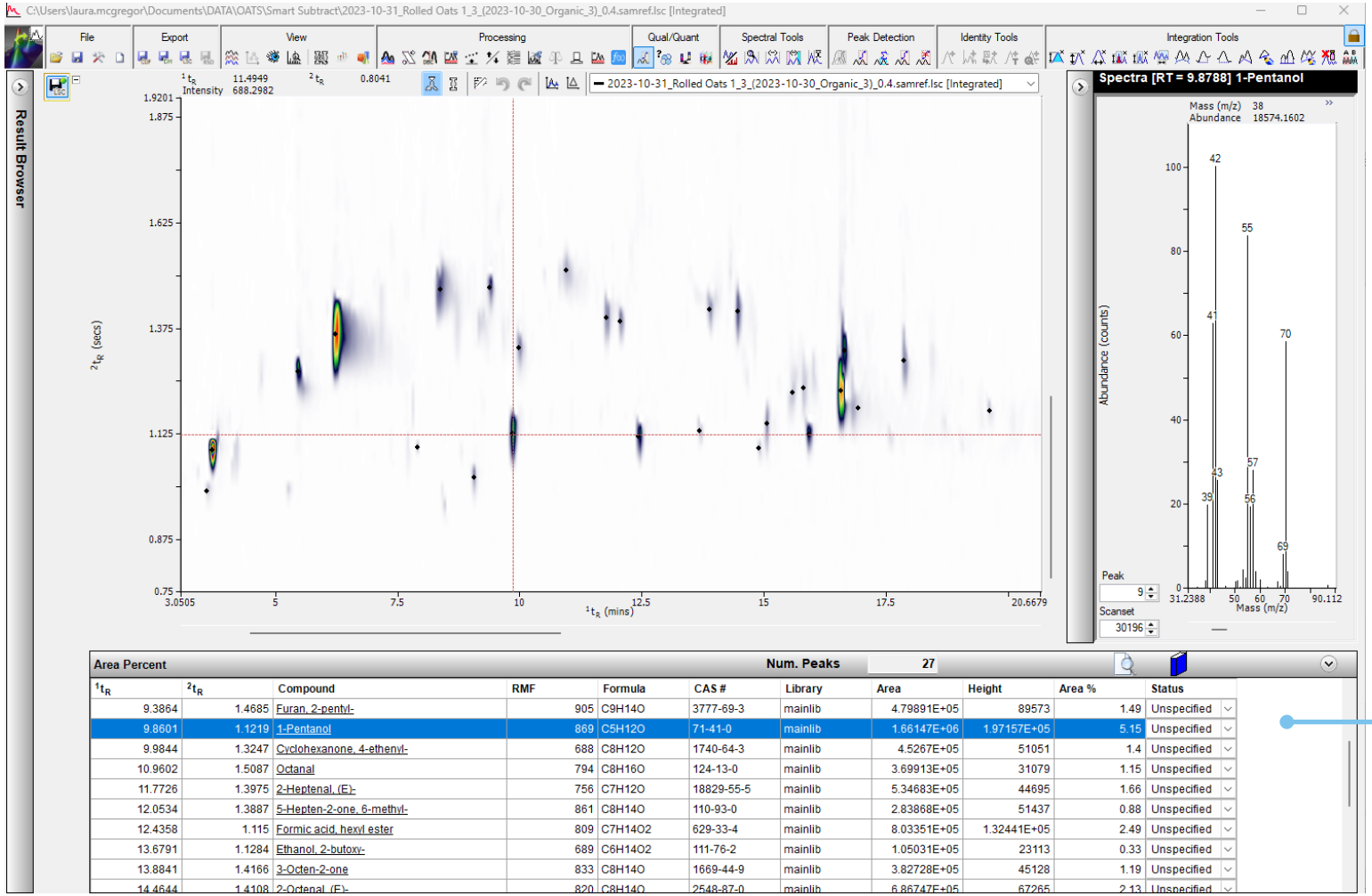
Smart Subtract®





Comparing two plastic-packaged oats

Smart Subtract®



^1t_R	^2t_R	Compound	RMF	Formula	CAS #	Library	Area	Height	Area %	Status
9.3864	1.4685	Furan, 2-pentyl-	905	C9H14O	3777-69-3	mainlib	4.79891E+05	89573	1.49	Unspecified
9.8601	1.1219	1-Pentanol	869	C5H12O	71-41-0	mainlib	1.66147E+06	1.97157E+05	5.15	Unspecified
9.9844	1.3247	Cyclohexanone, 4-ethenyl-	688	C8H12O	1740-64-3	mainlib	4.5267E+05	51051	1.4	Unspecified
10.9602	1.5087	Octanal	794	C8H16O	124-13-0	mainlib	3.69913E+05	31079	1.15	Unspecified
11.7726	1.3975	2-Heptenal, (E)-	756	C7H12O	18829-55-5	mainlib	5.34683E+05	44695	1.66	Unspecified
12.0534	1.3887	5-Hepten-2-one, 6-methyl-	861	C8H14O	110-93-0	mainlib	2.83868E+05	51437	0.88	Unspecified
12.4358	1.115	Formic acid, hexyl ester	809	C7H14O2	629-33-4	mainlib	8.03351E+05	1.32441E+05	2.49	Unspecified
13.6791	1.1284	Ethanol, 2-butoxy-	689	C6H14O2	111-76-2	mainlib	1.05031E+05	23113	0.33	Unspecified
13.8841	1.4166	3-Octen-2-one	833	C8H14O	1669-44-9	mainlib	3.82728E+05	45128	1.19	Unspecified
14.4644	1.4108	2-Octenal, (E)-	820	C8H14O	2548-87-0	mainlib	6.86747E+05	67265	2.13	Unspecified

Subtracted chromatograms can be integrated & library-searched to generate peak tables of differences

Summary

- Understanding and reducing the migration of volatile compounds from packaging into food is crucial for food safety and consumer satisfaction.
- The complexity of volatile profiles necessitates advanced analytical tools.
- Headspace sorptive extraction and GC×GC–TOF MS offer:
  - Enhanced resolution and sensitivity.
  - Reliable identification of both aroma-related volatiles and packaging contaminants.
  - Comprehensive, non-target screening.
- Smart Subtract streamlines pairwise comparisons for faster resolution of product quality issues or complaints in industrial settings.

Acknowledgements

- James Ogden, SepSolve Analytical

- Meriem Gaida, Luzi AG

SepSolve Analytical

Thanks for listening!

Any questions?