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From human nose to objective sensor and MS-based ‘sniff’ detectors

KVCV Studiedag, Belgium | October 12, 2017

Bart Tienpont

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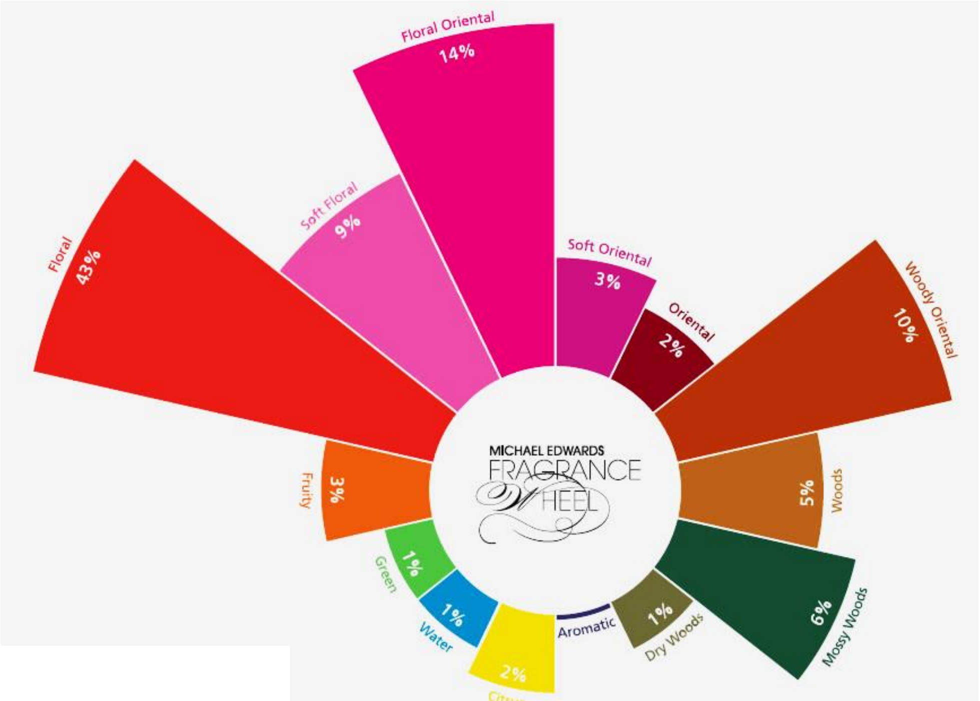
(Off-)Odour Detection
‘Classical Strategies’



Step 1. Sensory panel

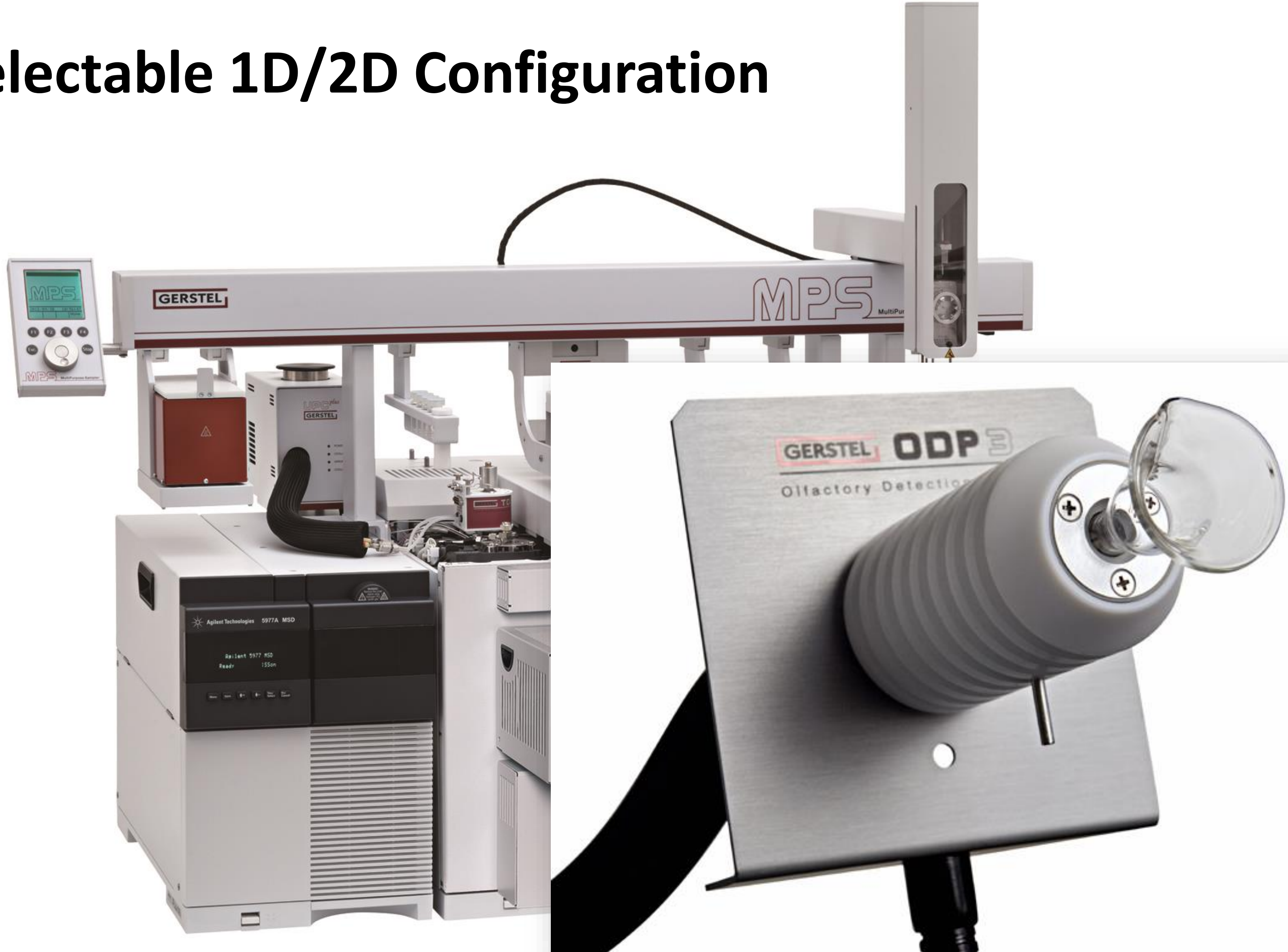
Step 2. Confirmation by HS or

TE-GC-MS/Olfactometry

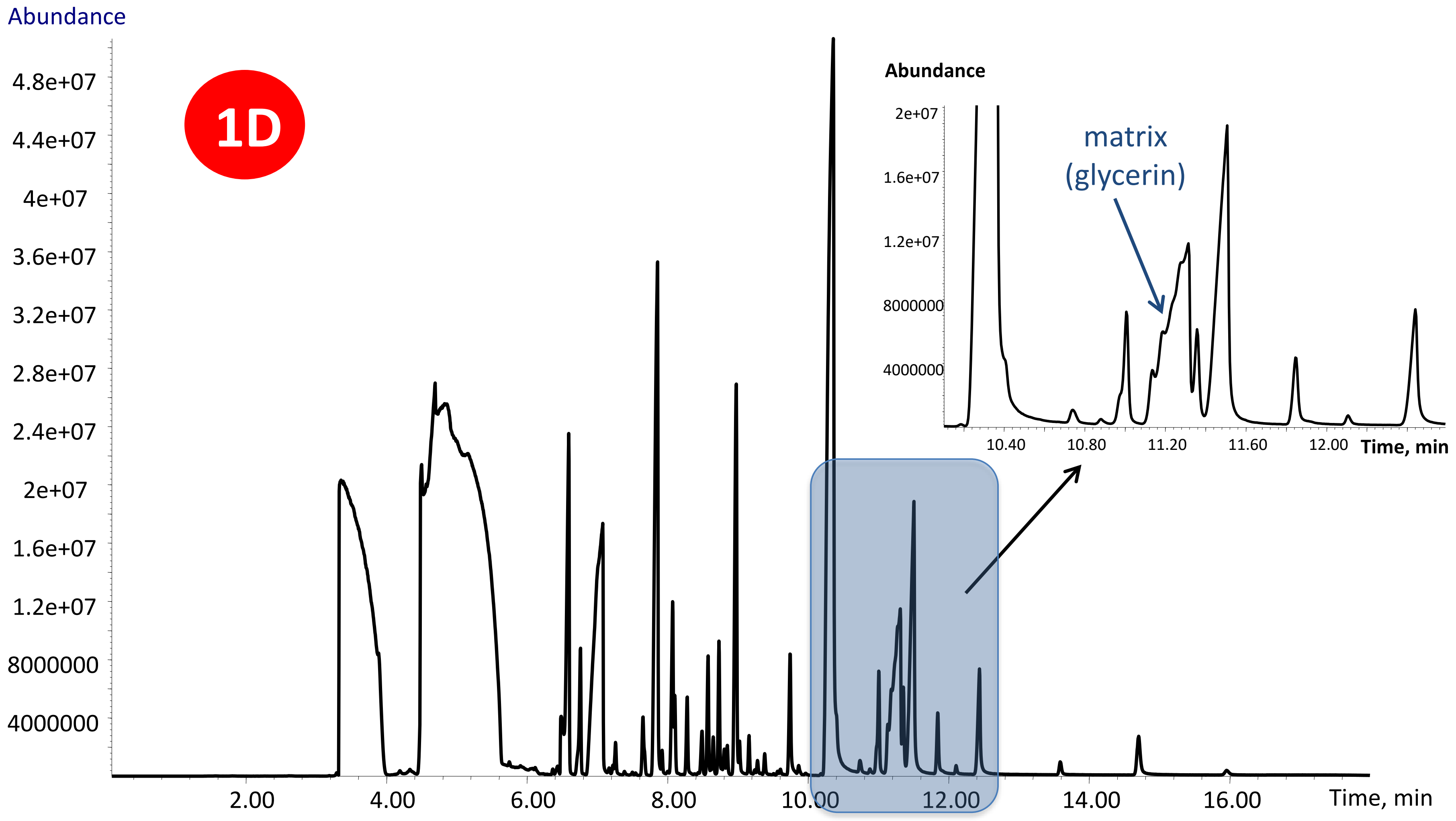
Olfactometric Detection

Human Sensing

Selectable 1D/2D Configuration



1D Analysis – Allergens in Cosmetics



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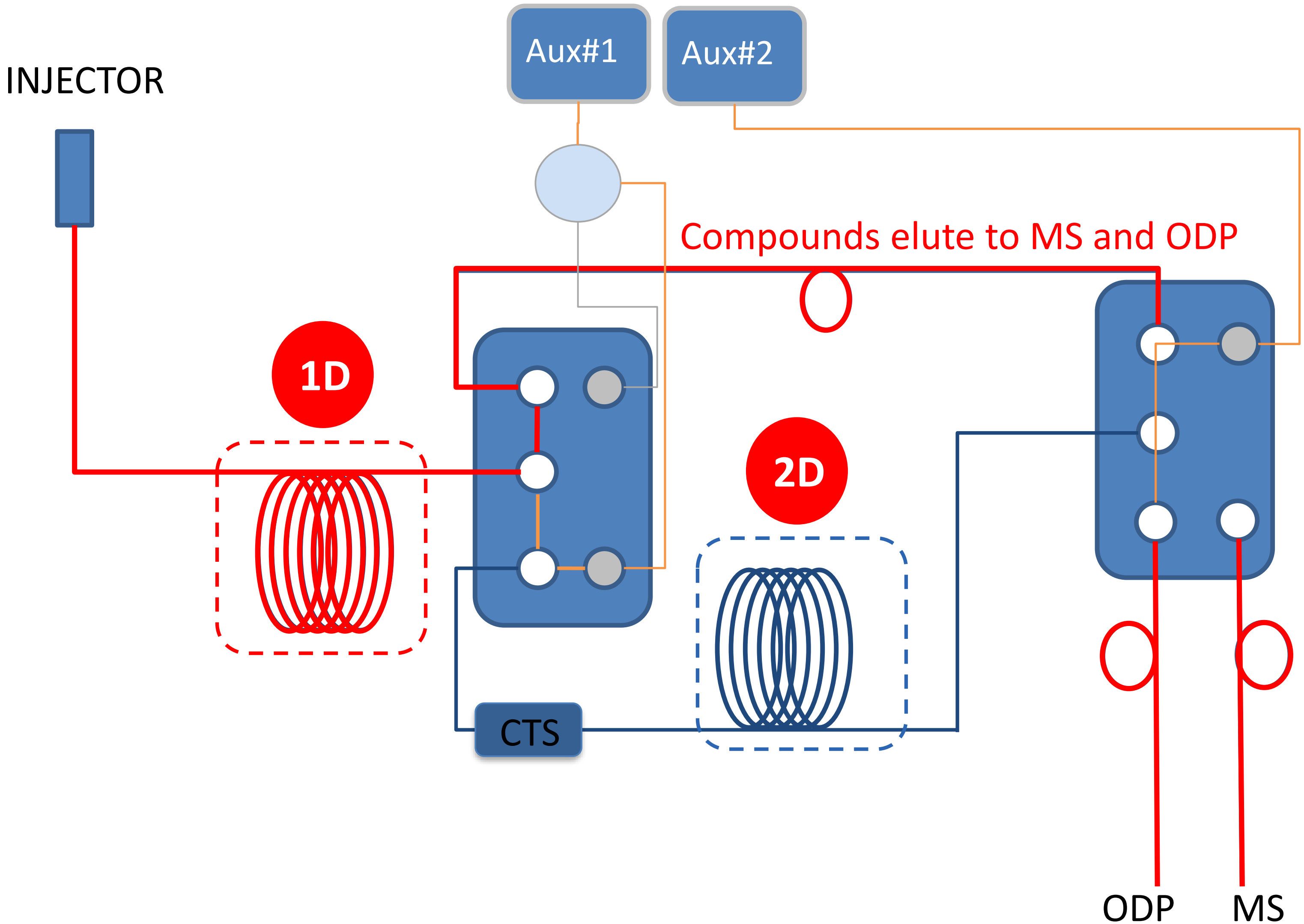
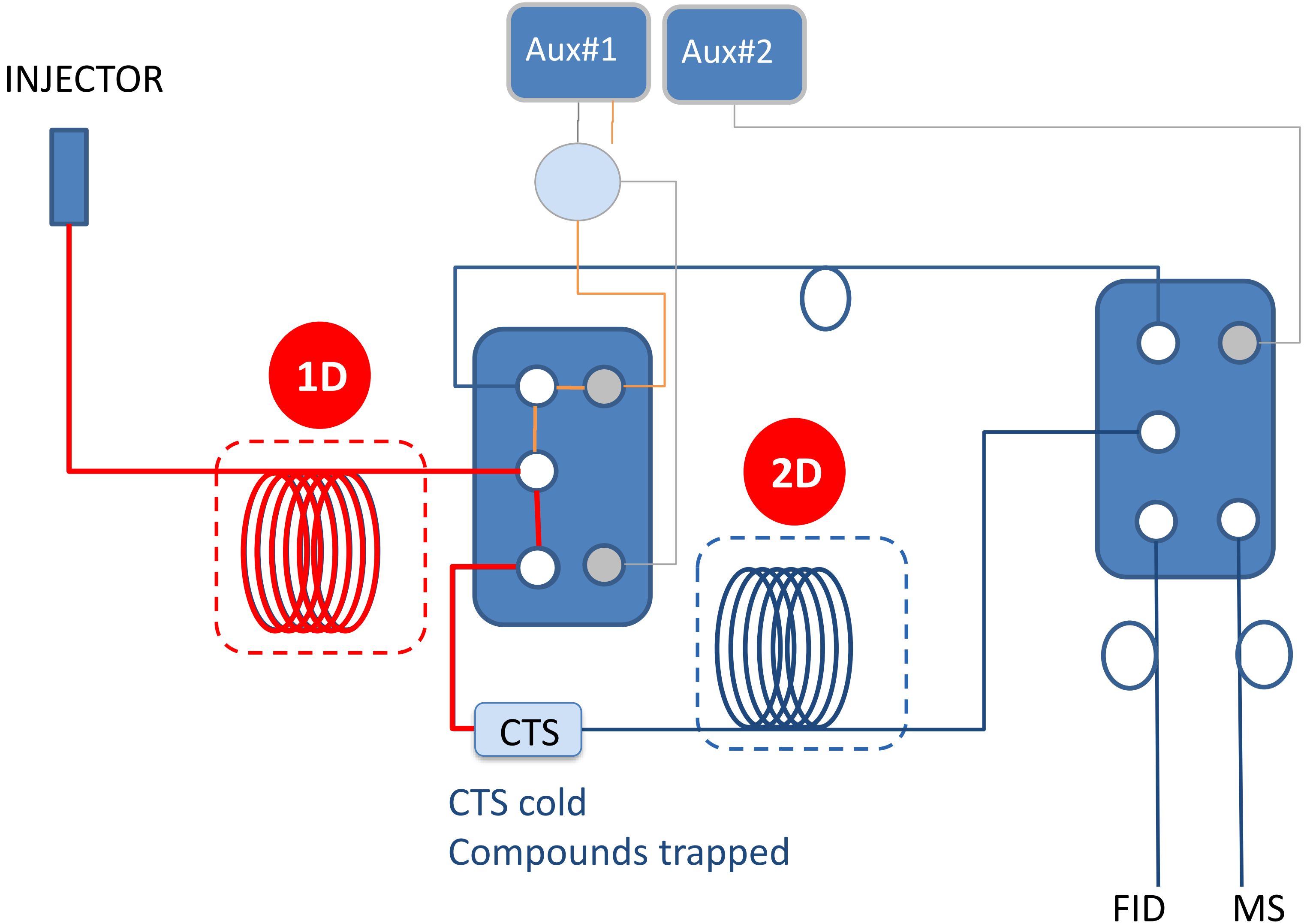
1D Analysis



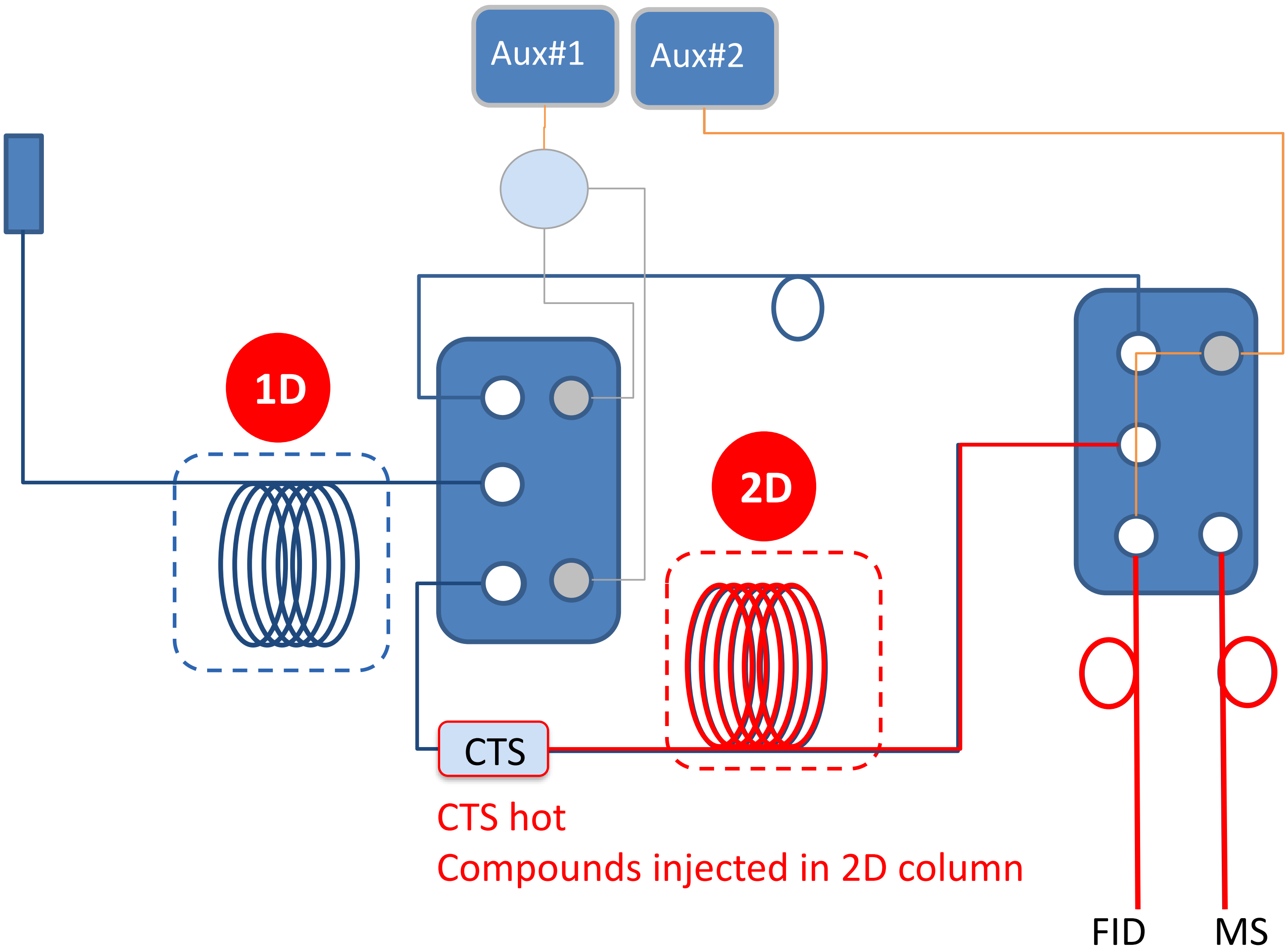
INJECTOR
Aux#1
Aux#2
Compounds elute to MS and ODP
1D
2D
CTS
ODP
MS

2D Analysis – Heart-cut



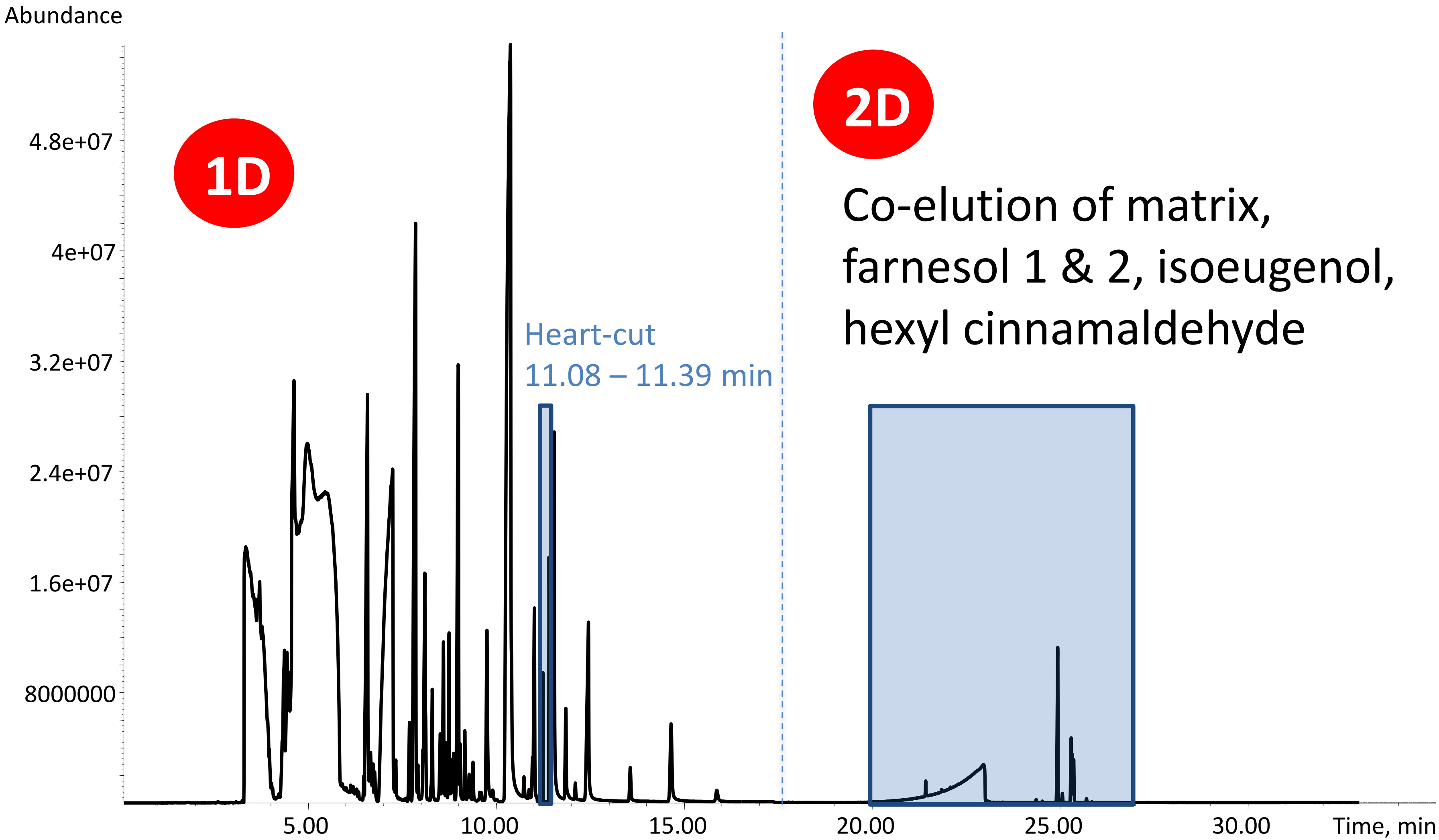
CTS cold
Compounds trapped

2D Analysis – Analysis



CTS hot
Compounds injected in 2D column

2D Analysis – Allergens in Cosmetics



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E-Noses

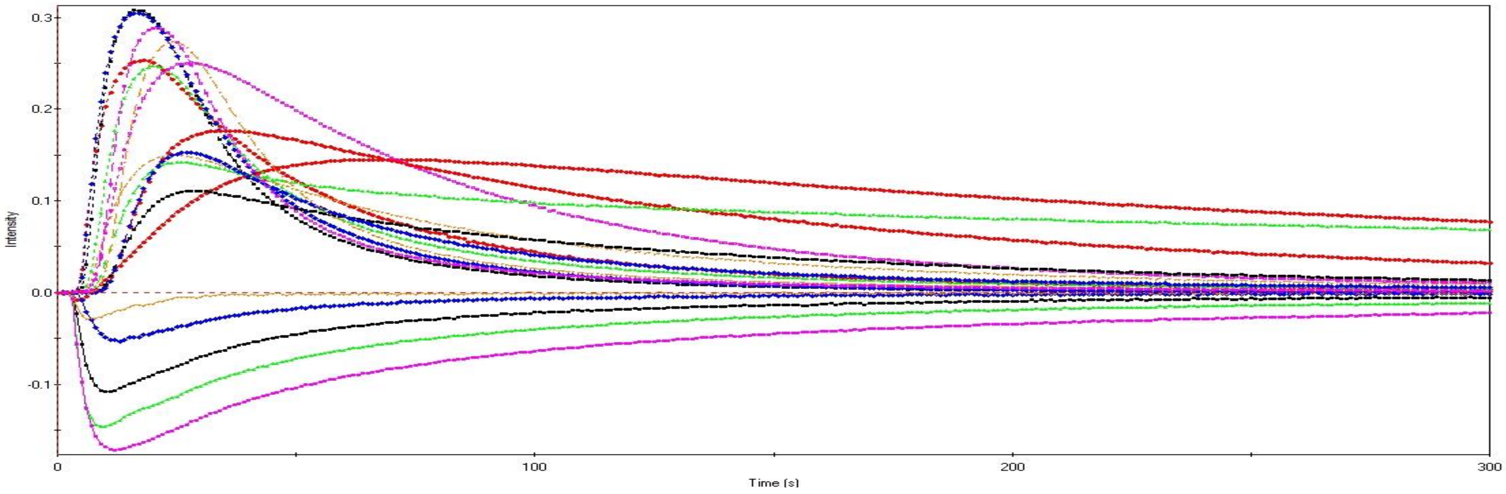
Objective Sensing - Classification

SHS-E-nose: *Objective* approach

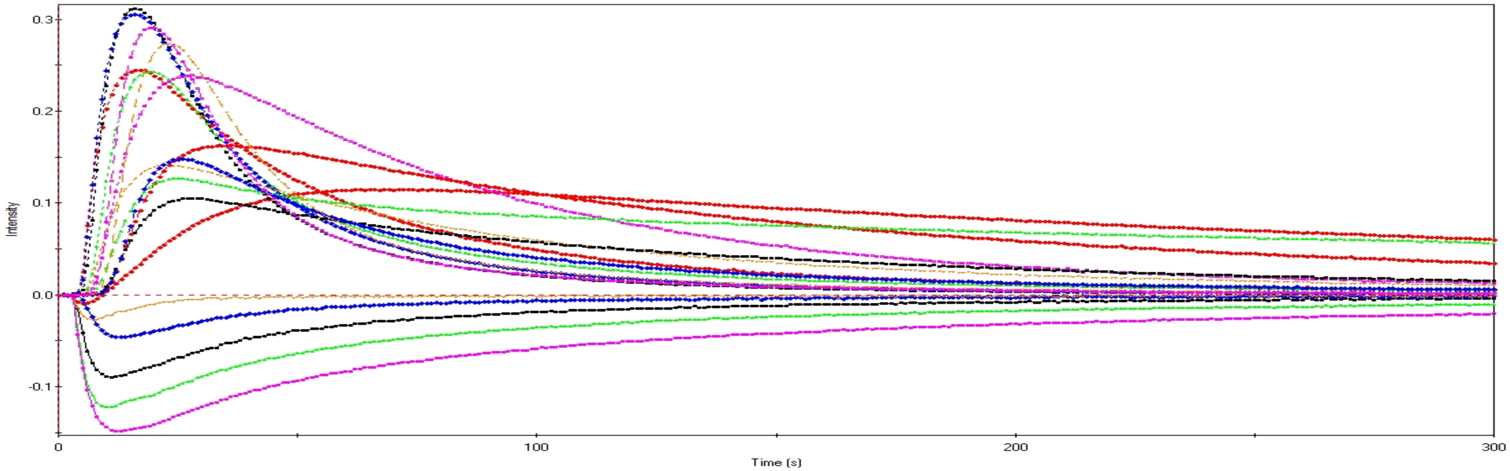
1 g, SHS @ 80°C (20 min)
Injection 2 mL
Enose Fox 4000
Synthetic dry air: 150 mL/min
Acquisition time: 500 s
Acquisition period: 0.5 s

SHS-E-nose responses

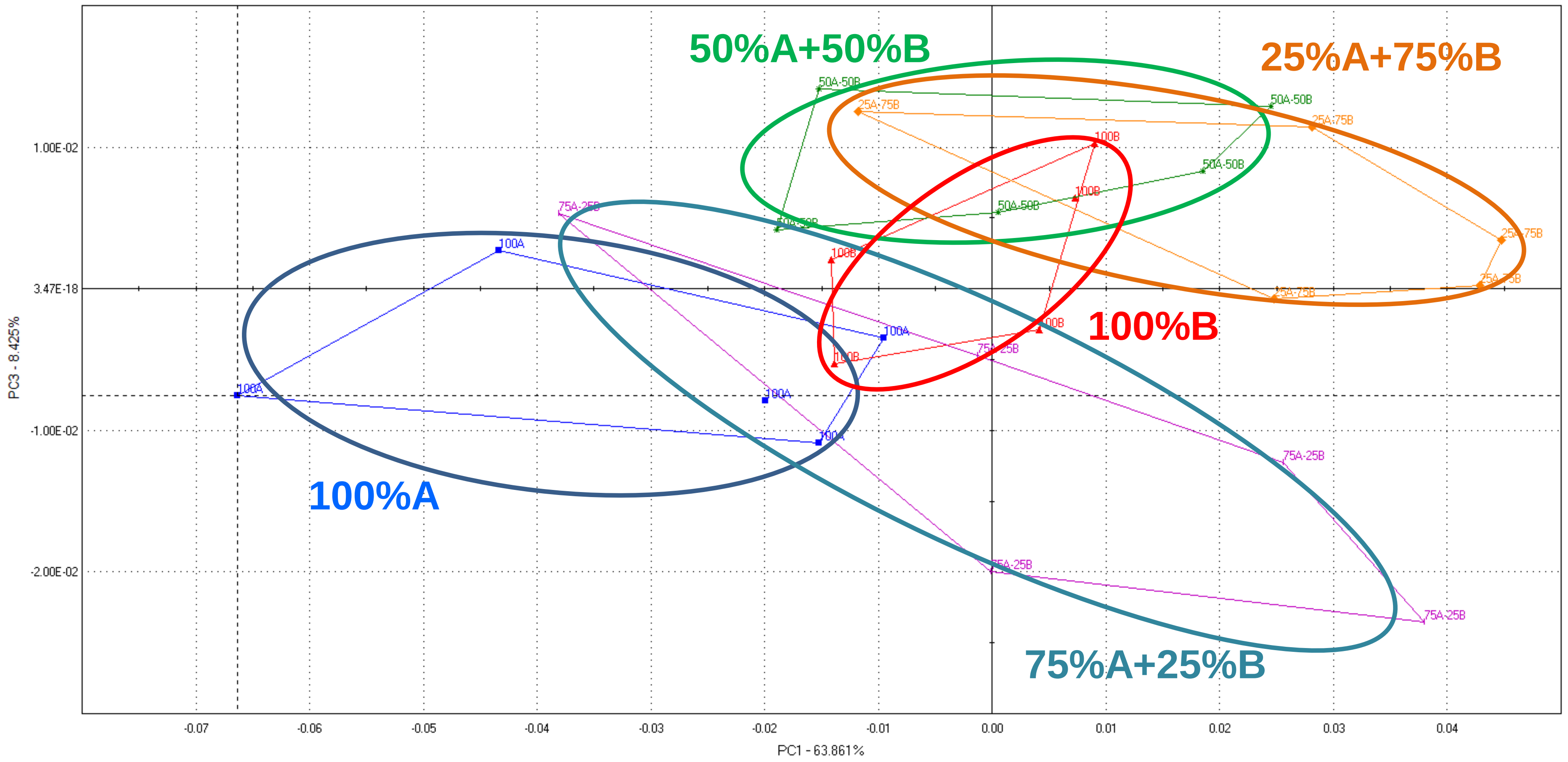
Reference sample (A)



Complaint sample (B)



SHS-E-Nose PCA Plot



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GC-ODP ↔ Sensor panel

- Off-odours often mixture of compounds

  Additive | effects = 'bouquet'
  Synergetic |
  Masking |

- Ghost peaks

- Additional challenge = perception can change in function of *concentration*!

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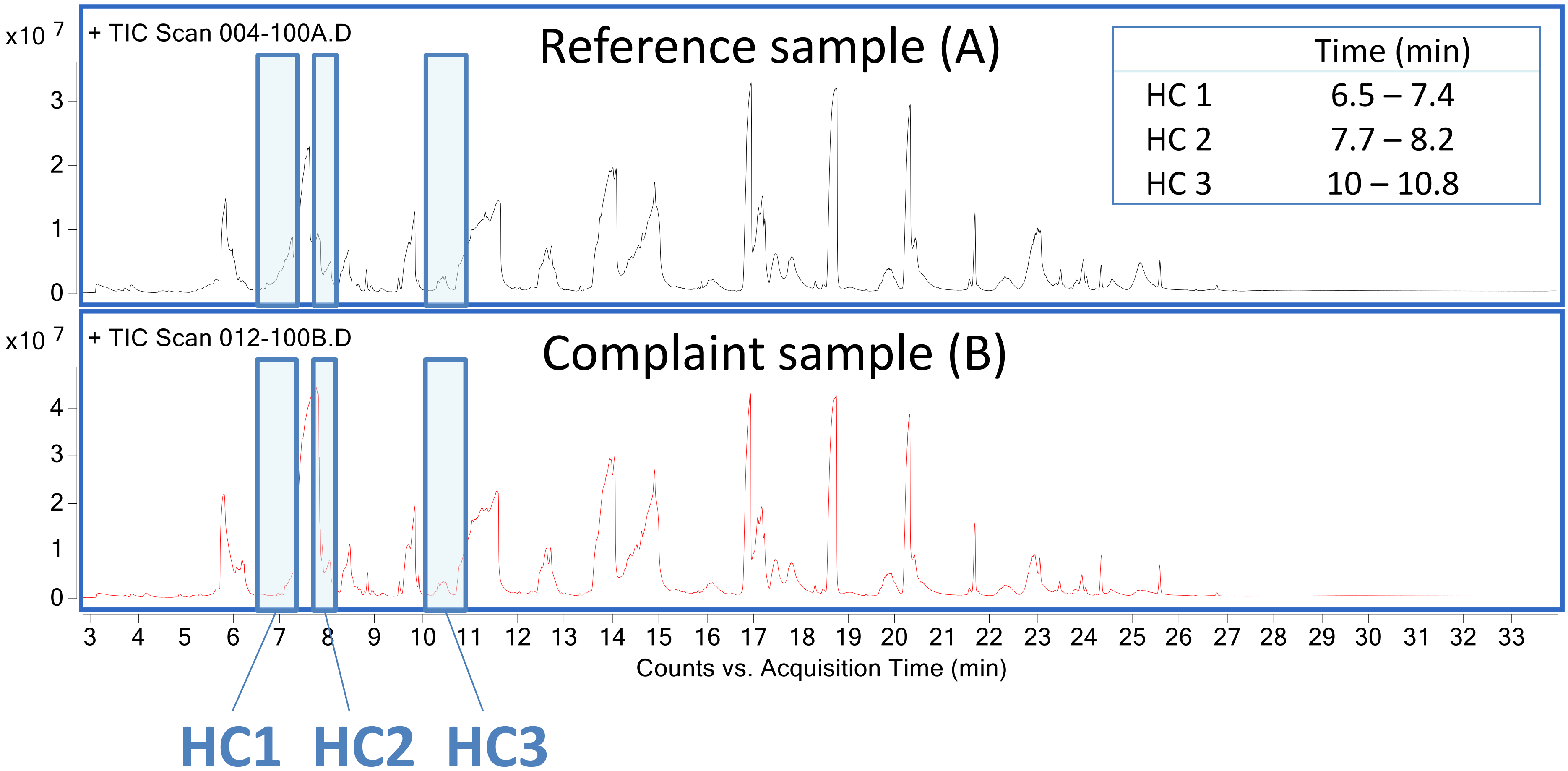
2D- GC-ODP



	Time (min)
HC 1	6.5 – 7.4
HC 2	7.7 – 8.2
HC 3	10 – 10.8

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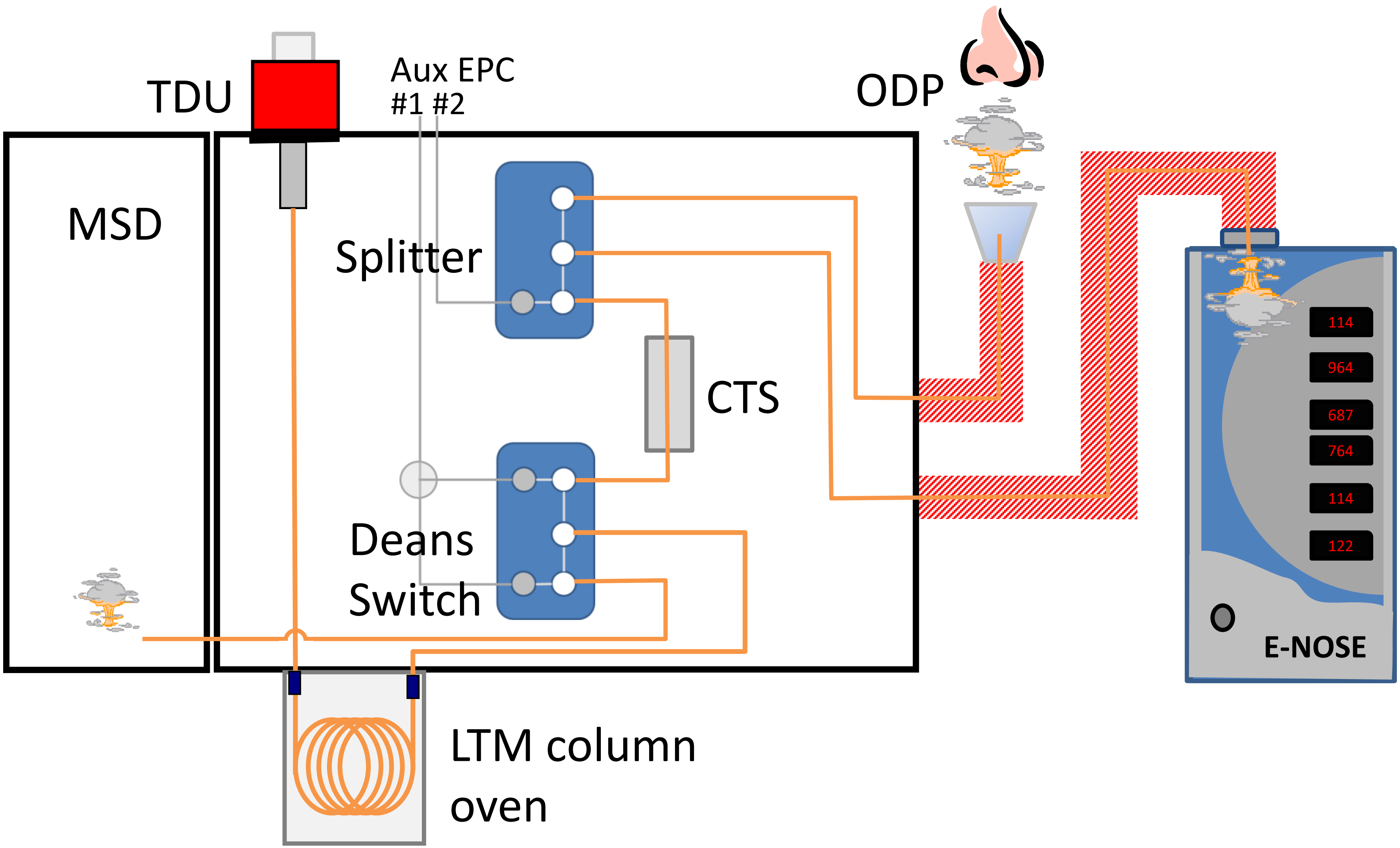
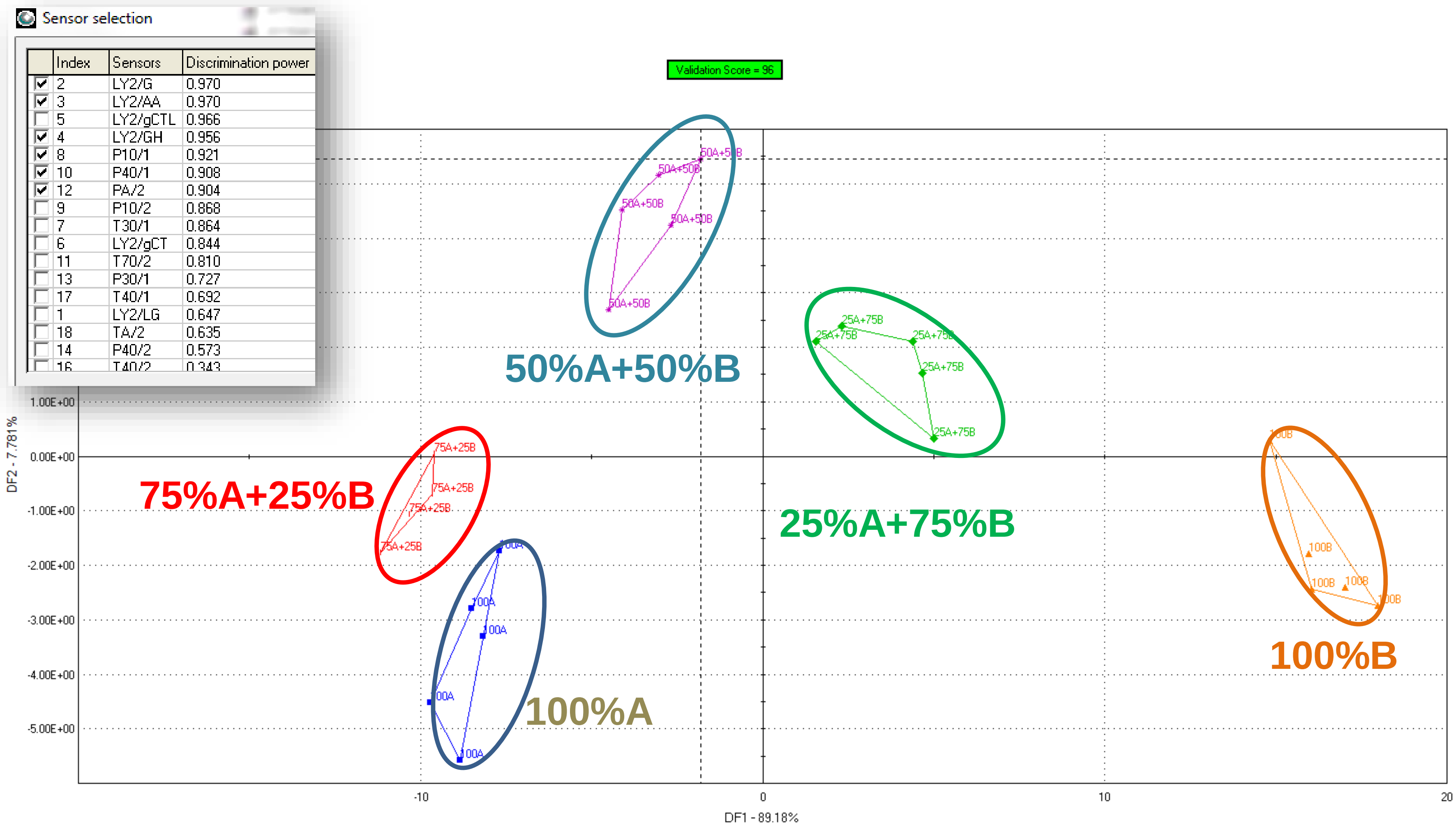
Configuration



Discrimination Function Analysis (DFA) for ∑(HC)

6 Sensors



	Index	Sensors	Discrimination power
✓	2	LY2/G	0.970
✓	3	LY2/AA	0.970
	5	LY2/gCTL	0.966
✓	4	LY2/GH	0.956
✓	8	P10/1	0.921
✓	10	P40/1	0.908
✓	12	PA/2	0.904
	9	P10/2	0.868
	7	T30/1	0.864
	6	LY2/gCT	0.844
	11	T70/2	0.810
	13	P30/1	0.727
	17	T40/1	0.692
	1	LY2/LG	0.647
	18	TA/2	0.635
	14	P40/2	0.573
	16	T40/2	0.343

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MS-based 'Noses'

Objective Sensing – Classification and identification

Proton-Transfer-Reaction – Mass Spectrometry (PTR-MS)

Proton-Transfer-Reaction

- Direct sample injection
- Real-time technology
- Soft and efficient ionization via H_3O^+
- Alternatively NO^+, O_2^+ and Kr^+ can be used as reagent ions, respectively

SRI+

Mass Spectrometry

- Quadrupole
- Time-Of-Flight (TOF)

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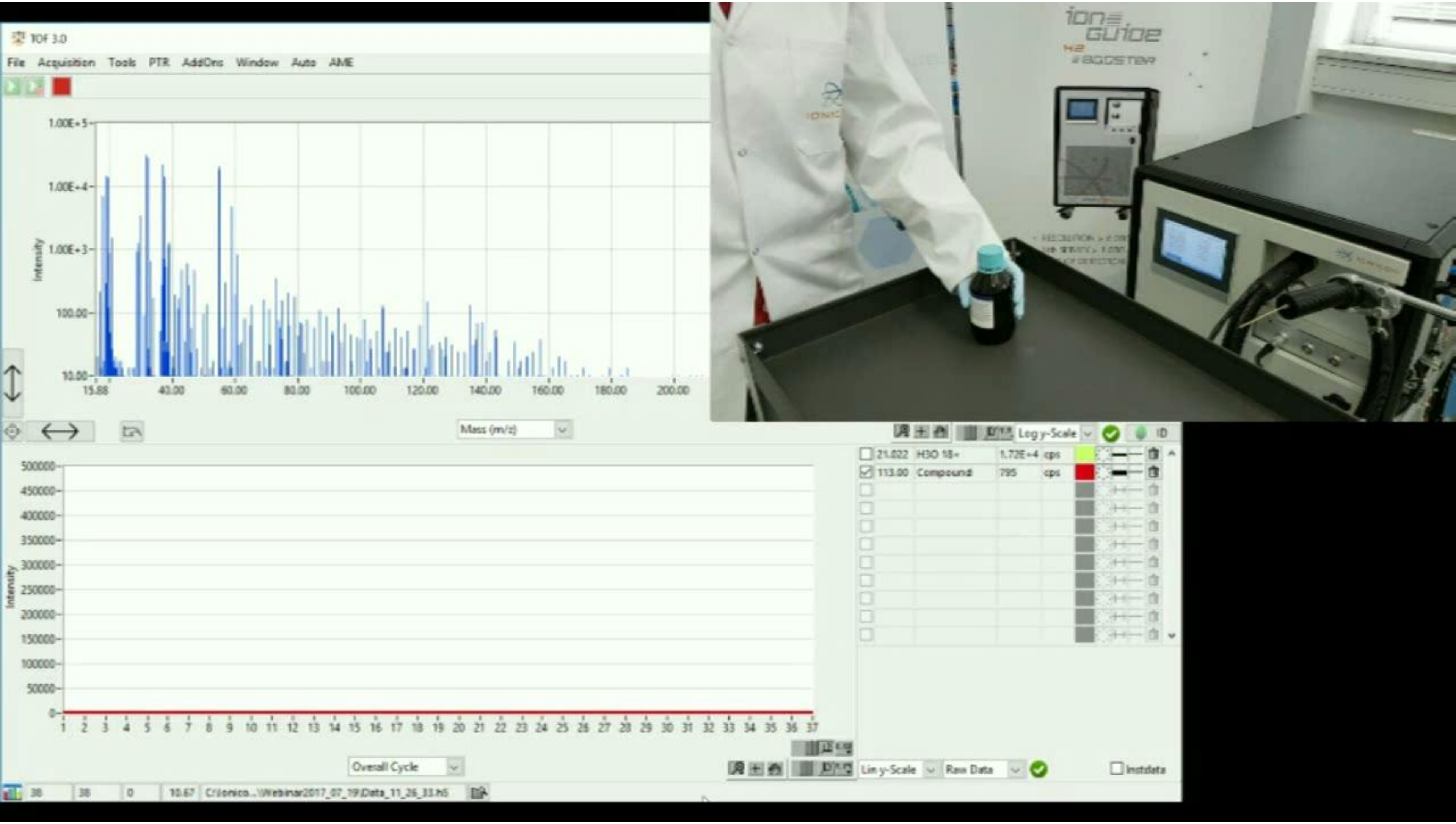
Real-time Analysis



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Proton Transfer Reaction-MS

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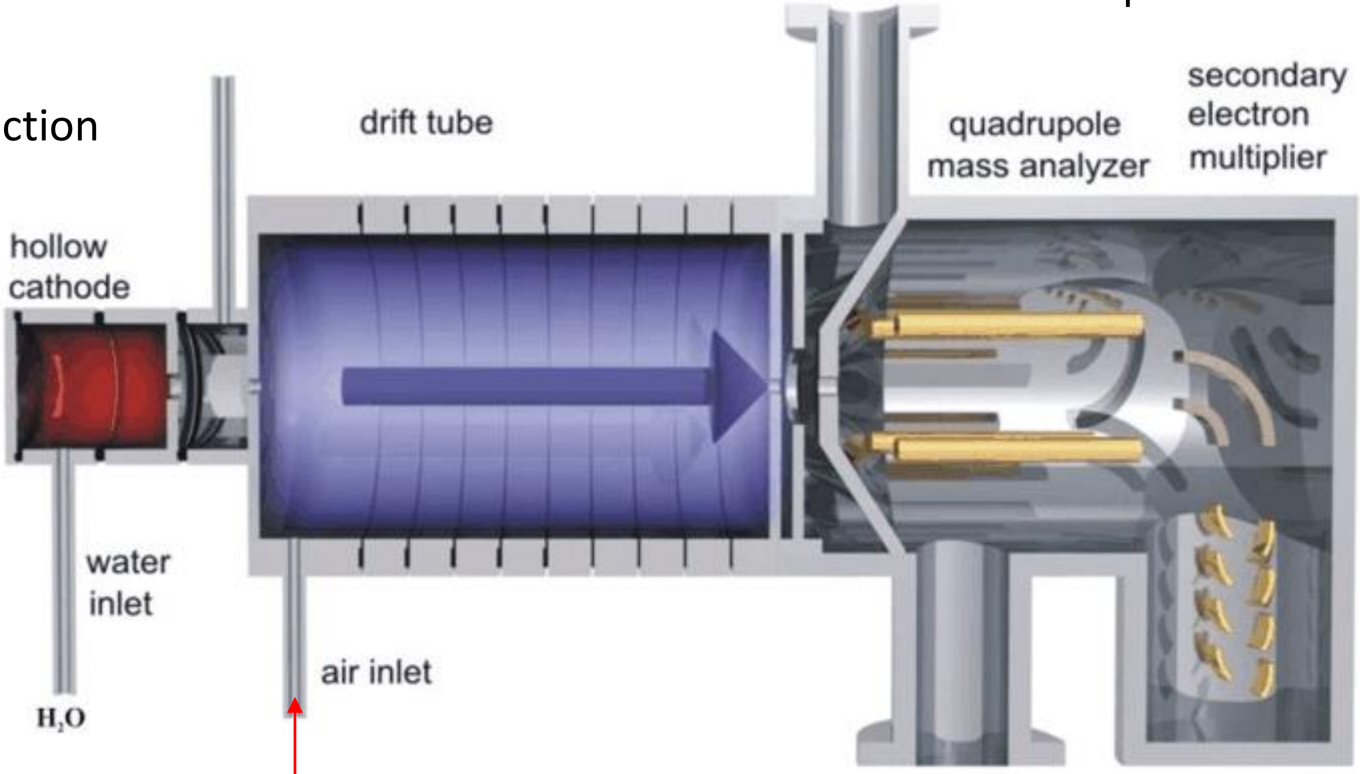
Proton transfer

Mass Spectrometer

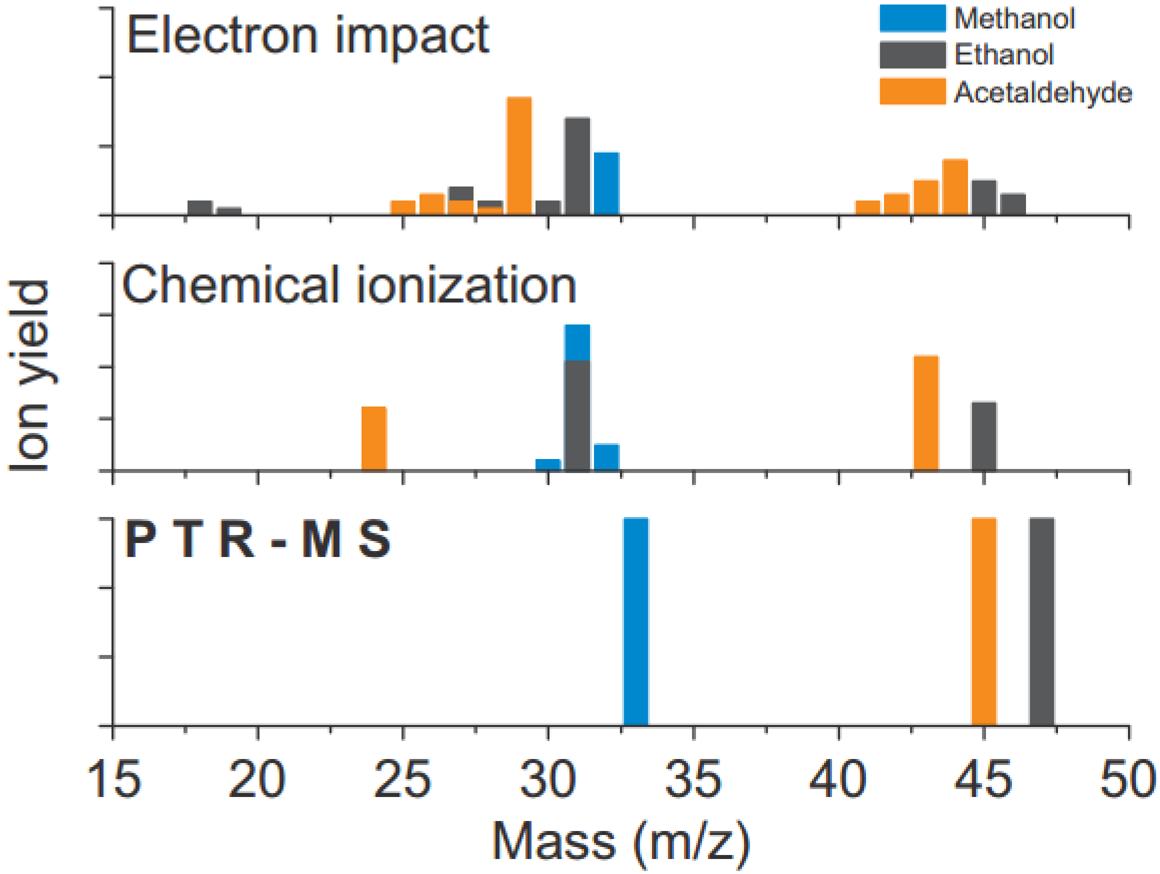
H_3O^+ production



DIRECT AIR SAMPLE ASPIRATION
(heated sampling line)

Soft and efficient Proton Transfer Reaction (PTR) ionization

IONICON



PTR yields only the molecular ion +1

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Sulfur compounds in Syngas

Herbig, J.., R.. Gutmann, K.. Winkler, A.. Hansel, and G.. Sprachmann, "**Real-Time Monitoring of Trace Gas Concentrations in Syngas**", *Oil Gas Sci. Technol. Rev. IFP Energies nouvelles*, vol. 69, pp. 363–372, August, 2014.

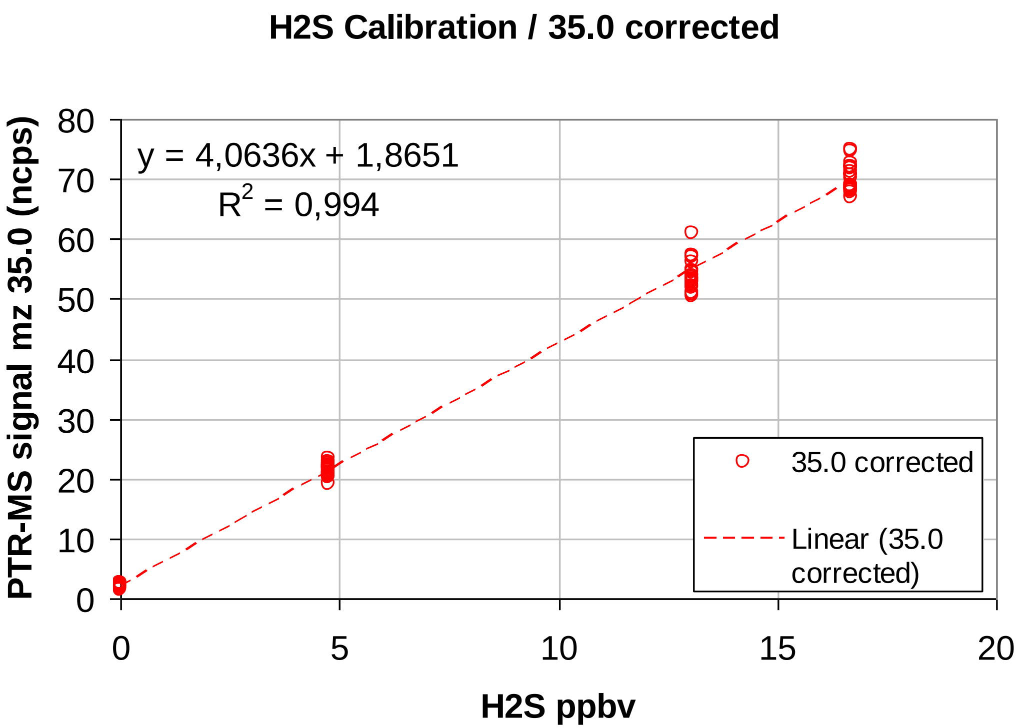
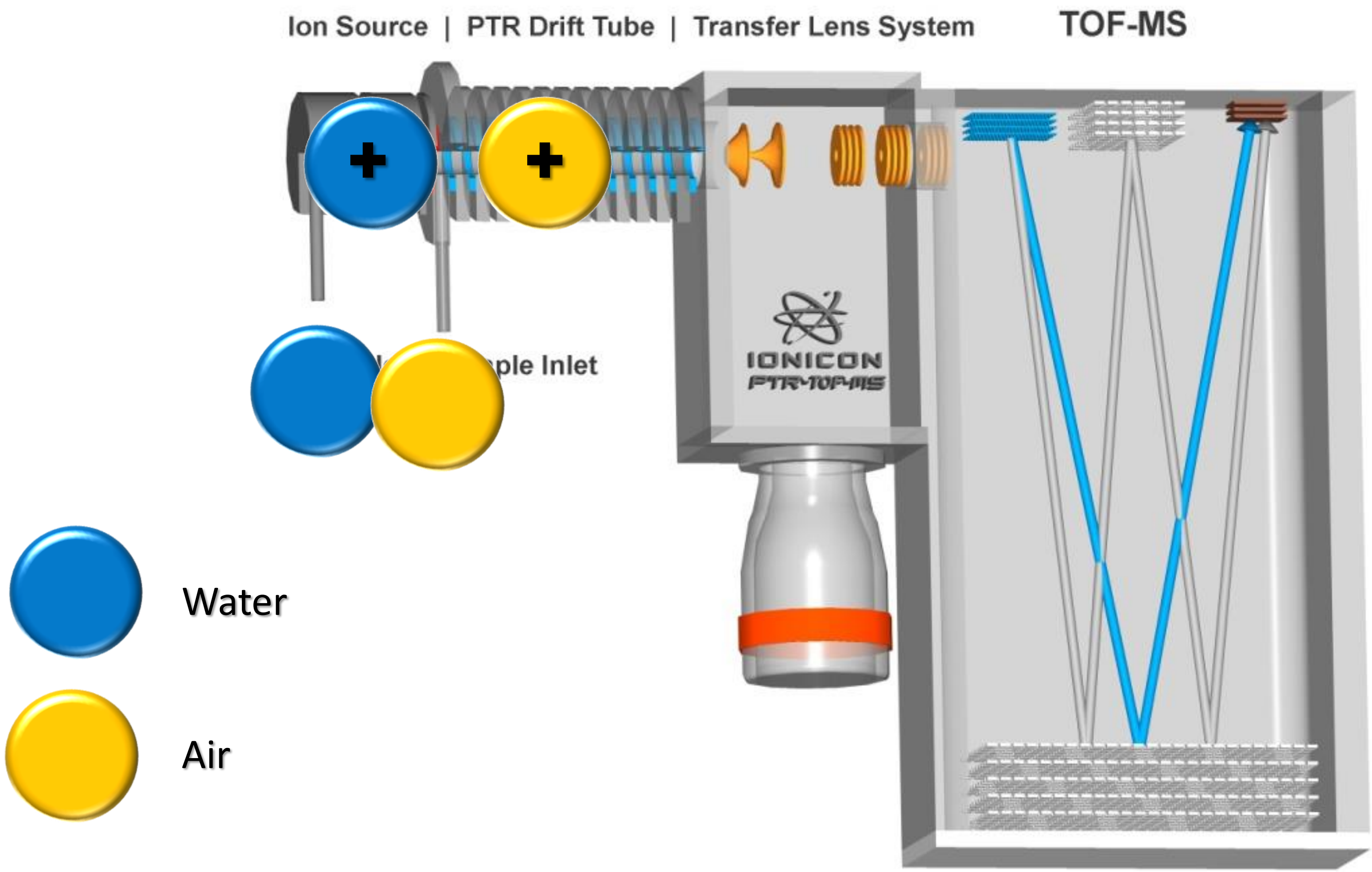


TABLE 1

Listed are *m/z* with prominent signal intensities, mostly we give the tentatively identified compound, typically backed-up by the isotopic ratio. The average concentration ranges observed (over time and over sampling points) are represented by logarithmic categories ranging from o (< 0.3 ppb), oo (< 3 ppb), ooo (< 30 ppb), to ooooo (> 300 ppb range)

m/z (Th)	Concentration range	Potential compound
28	o	HCN
33	ooooo	Methanol
35	ooo	H_2S
42	o	Acetonitrile
43	oo	Acylium fragment (from *e.g.* isopropanol)
47	oo	Formic acid
49	ooo	Methyl mercaptan
51	ooo	Methanol water cluster
57	o	Acroleine
59	o	Acetone
61	ooo	Acetic acid
105	oo	$Ni(CO)H_3O$ + (main fragment of $Ni(CO)_3H^+$)
143	oo	$Ni(CO)_3H^+$
197	oo	$Fe(CO)_5H^+$

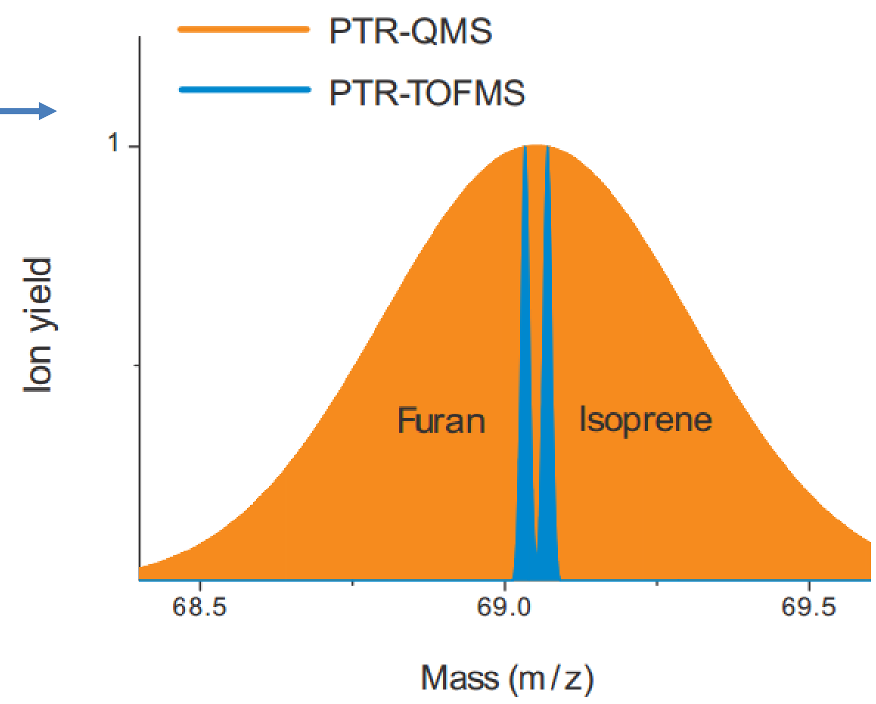
PTR-Time-Of-Flight MS



TOF versus Quadrupole

TOF MS:

- High resolution – better distinction between compounds
- Higher data acquisition frequency
- Data always contains all ions: data is backward interpretable



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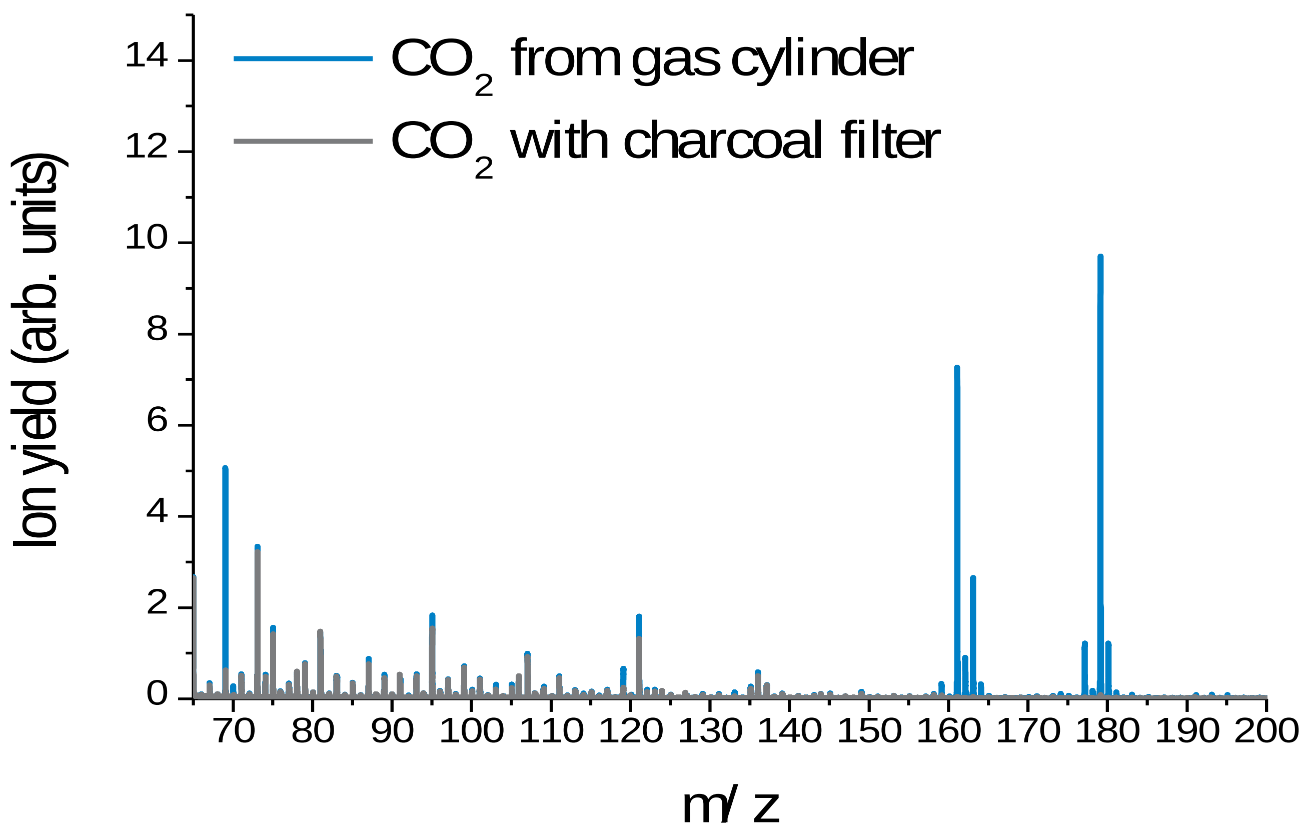
Rapid PTR-MS Analysis

Analysis of impurities in CO_2 cylinder

Rapid PTR-MS Analysis

Analysis of impurities in CO_2 cylinder



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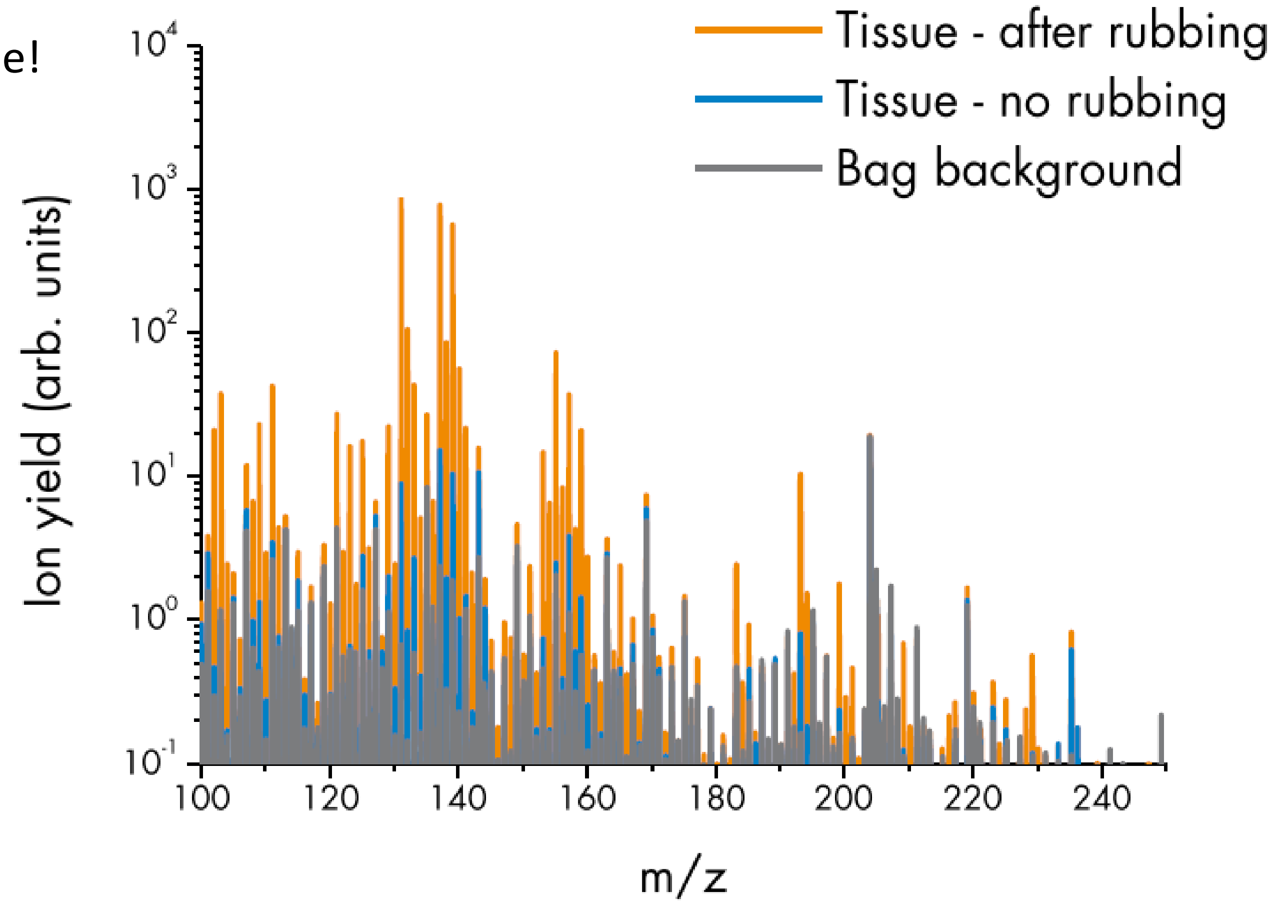
PTR-Time-Of-Flight MS

Untargeted Perfume Analysis from Tissues

Logarithmic scale!



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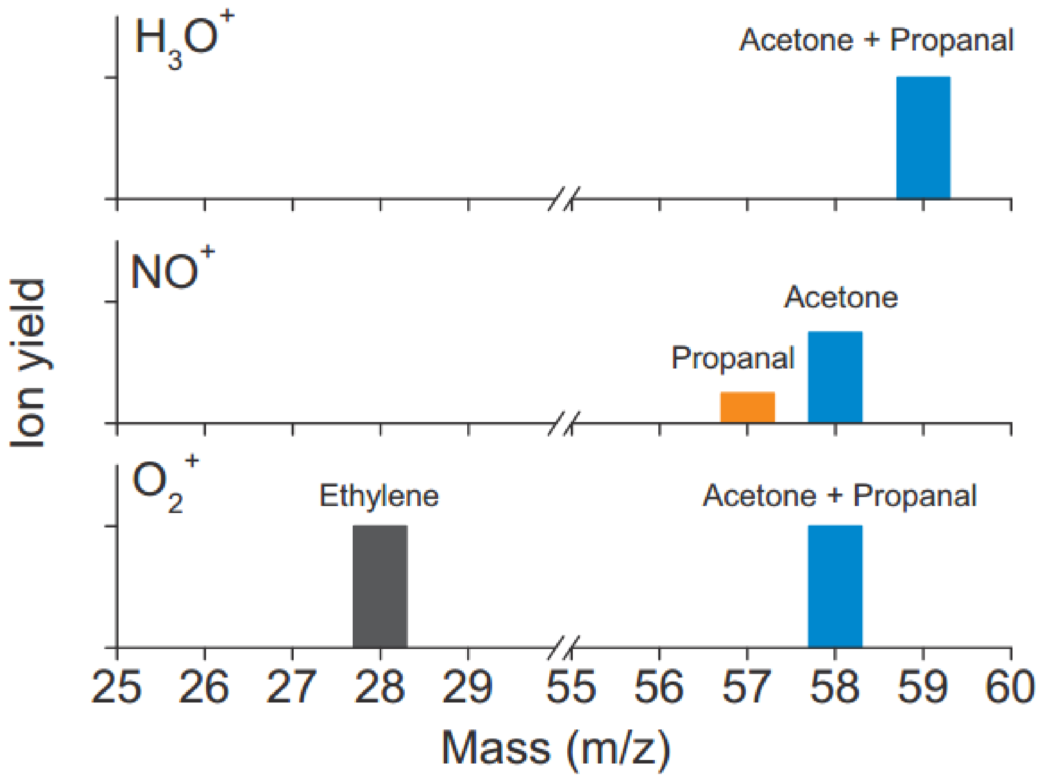
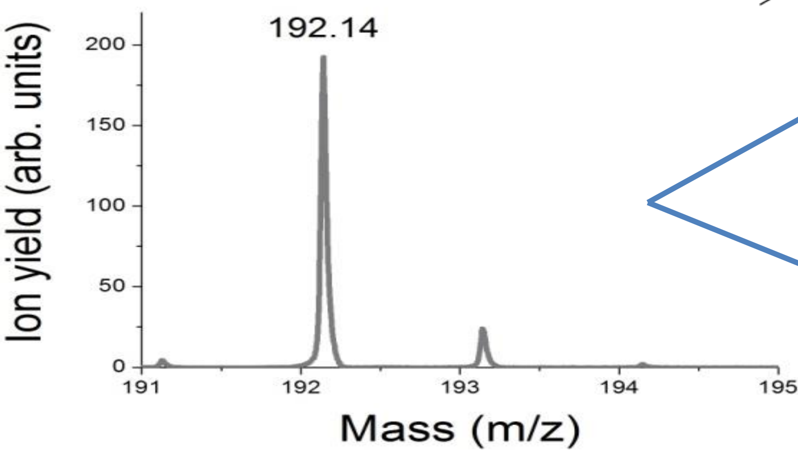
Selective Reagent Ionization-MS

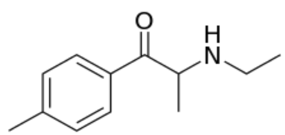
Other gases can be used for soft ionization: NO^+, O_2^+, Kr^+, Xe^+..

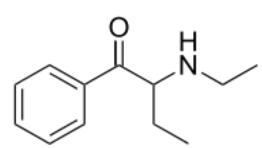


SRI-MS

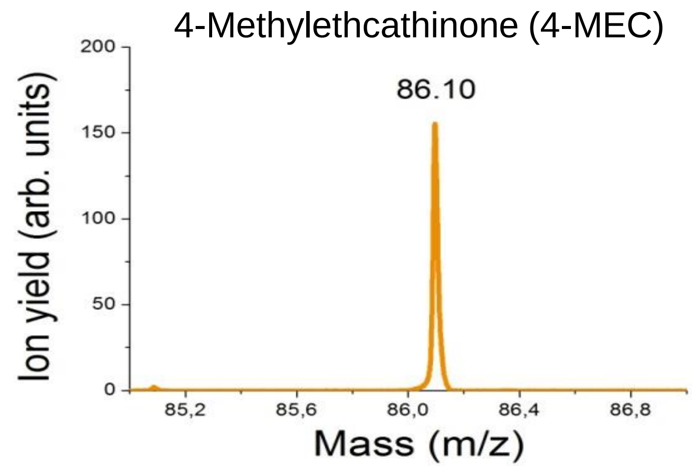
H_3O^+

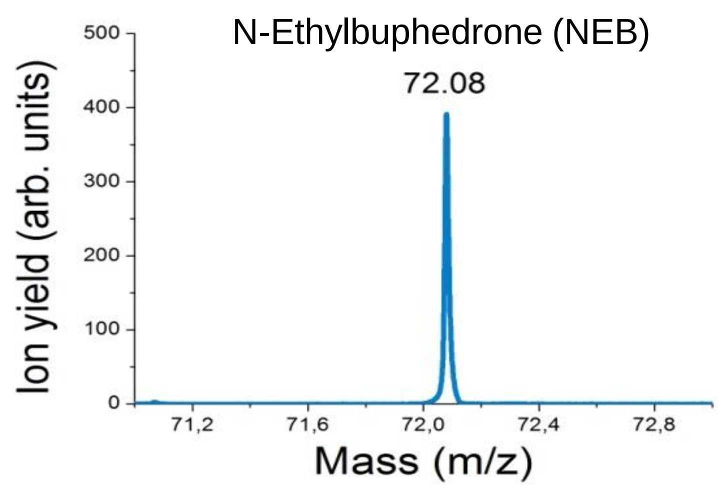






NO^+, O_2^+

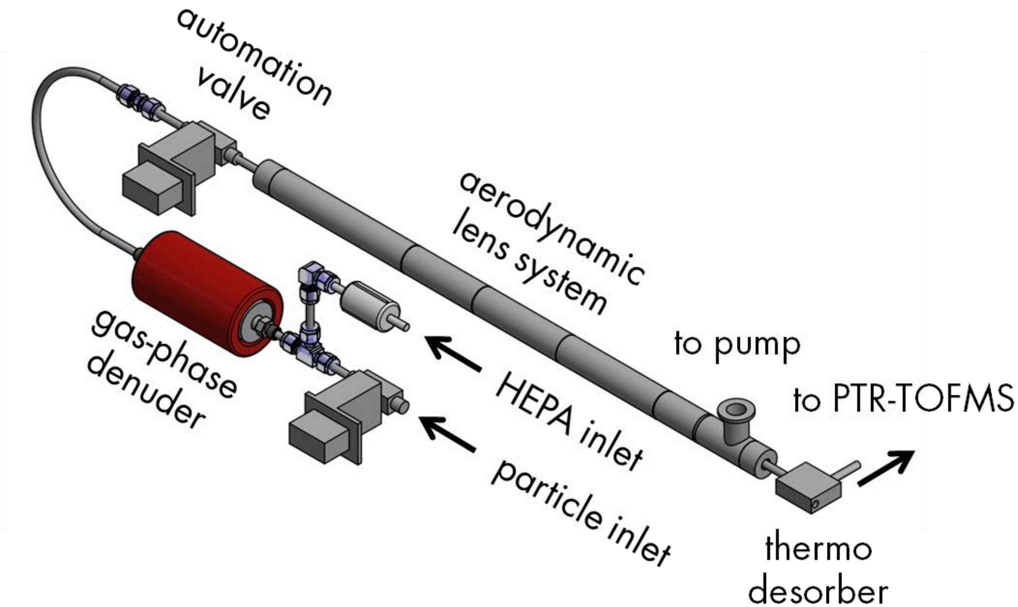




M. Lanza et al.,
J. Mass Spectrom. 48 (2013) 1015-1018.

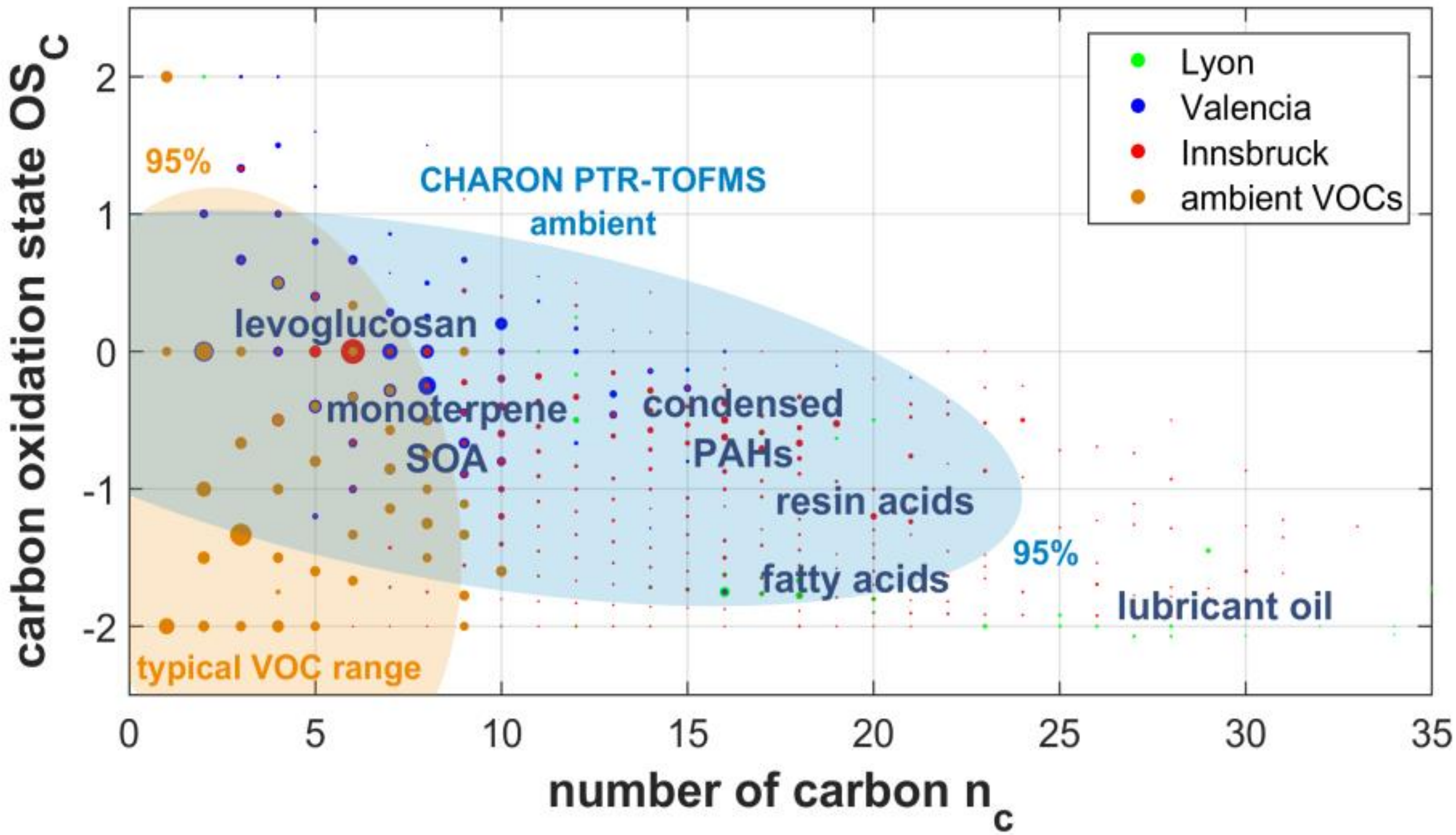
CHARON PTR-TOFMS

Chemical Analysis of *Aerosols* On-line



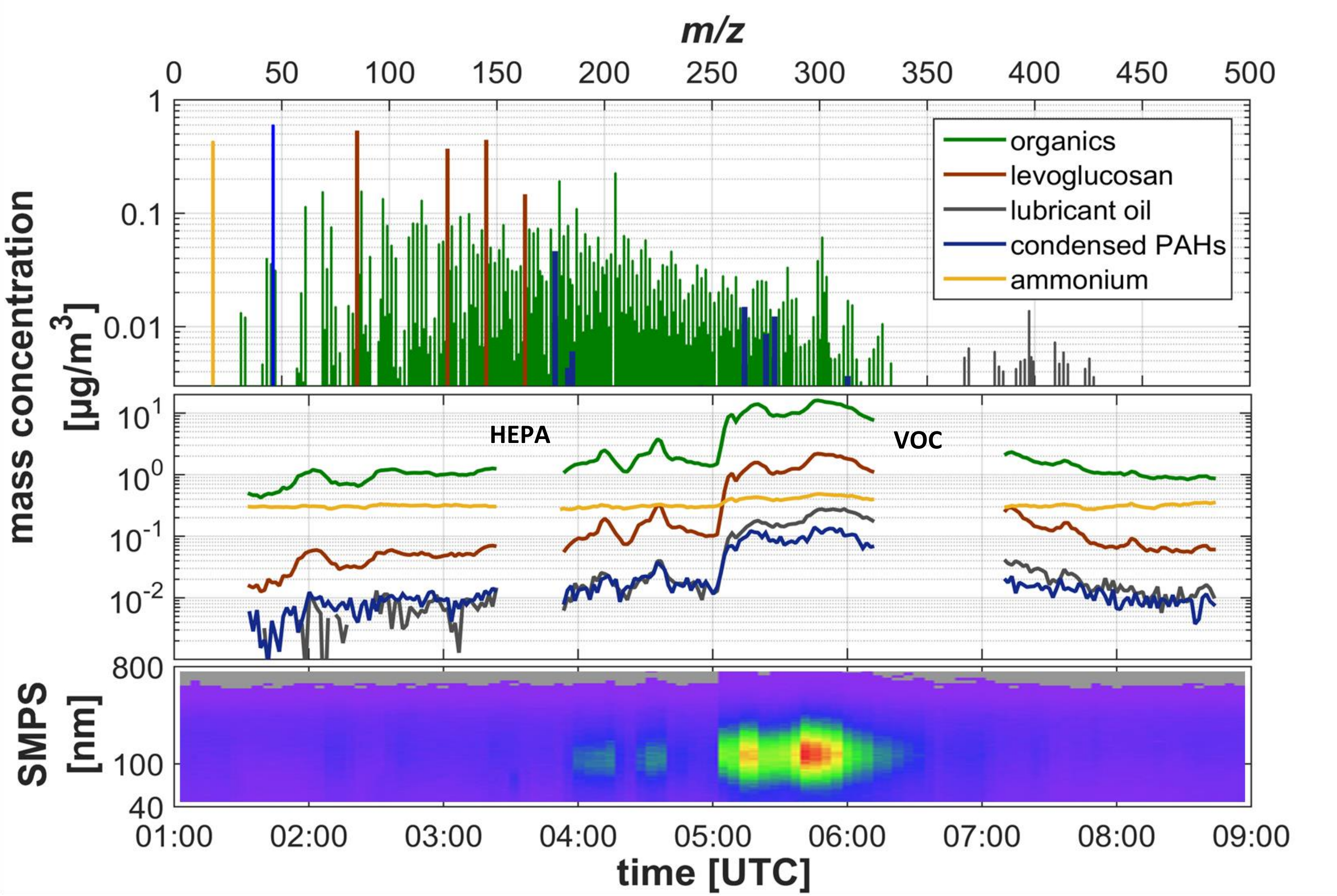
CHARON PTR-TOFMS

From IVOCs to LVOCs



CHARON PTR-TOFMS

Ambient Organic Aerosol in Innsbruck



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Sulfur compounds in meat samples

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Mayr, D., R. Margesin, E. Klingsbichel, E. Hartungen, D. Jenewein, F. Schinner, and TD. Märk, "**Rapid detection of meat spoilage by measuring volatile organic compounds by using proton transfer reaction mass spectrometry**", *Applied and environmental microbiology*, vol. 69, no. 8: Am Soc Microbiol, pp. 4697–4705, 2003

TABLE 2. List of relevant VOCs measured in the headspace of meat during 11 days of storage at 4°C[a]

m+1 (amu)	Compound(s)	Formula	Reference(s)
33	Methanol	CH_4O	2
47	Ethanol	C_2H_6O	1
49	Methanethiol	CH_4S	5
57	1-Butanol (fragment)	C_4H_8	7
57	2-Methylpropan-2-ol (fragment)	C_4H_8	13, 20
63	Dimethylsulfide	C_2H_6S	1, 2, 4, 5
75	Methylacetate	$C_3H_6O_2$	20
91	Diethylsulfide	$C_4H_{10}S$	20
91	Thioacetic acid methyl ester	C_3H_6OS	2
91	2,3-Butanediol	$C_4H_{10}O_2$	5
93	Toluene	C_7H_8	1, 7
95	Dimethyl disulfide	$C_2H_6S_2$	1, 2, 5
113	1-Octanol (fragment), octene	C_8H_{16}	2, 7
127	2,3-Dimethyl trisulfide	$C_2H_6S_3$	2, 5, 7
127	Nonene	C_9H_{18}	7
129	3-Ethyl-4-methyl hexane	C_9H_{20}	2
129	Ethyl tiglate	$C_7H_{12}O_2$	5
129	Nonane	C_9H_{20}	7
129	Octanone	$C_8H_{16}O$	7
131	Isoamyl acetate	$C_7H_{14}O_2$	2, 7
131	1-Octanol	$C_8H_{18}O$	5
143	Dimethyl octane	$C_{10}H_{22}$	2

[a] The VOCs were detected and tentatively identified by PTR-MS based on the protonated masses (*m*+1), fragmentation patterns, isotopic ratios, and published VOC compositions of spoiling meat.

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Sulfur compounds in headspace of fresh truffels

Aprea, E., F. Biasioli, S. Carlin, G. Versini, T. D. Maerk, and F. Gasperi, "**Rapid white truffle headspace analysis by proton transfer reaction mass spectrometry and comparison with solid-phase microextraction coupled with gas chromatography/mass spectrometry.**", *Rapid Commun Mass Spectrom*, vol. 21, no. 16: IASMA Research Center, Agri-Food Quality Department, Via E. Mach 1, 38010 S. Michele all'Adige (TN), Italy. eugenio.aprea@iasma.it, pp. 2564–2572, 2007.

Table 2. List of pure compounds measured by PTR-MS and their fragmentation patterns obtained at E/N = 120 Td. MW: molecular weight; data in parentheses are abundances (%) relative to the most abundant ion

Chemical name	MW	Fragmentation pattern	
dimethyl sulfide	62	63 (100)	
dimethyl sulfoxide	78	79 (100)	
dimethyl disulfide	94	95 (100)	79 (14)
bis(methylthio)methane	108	61 (100)	
2-acetyl-5-methylfuran	124	125 (100)	43 (12.5)
p-cymene	134	93 (100)	135 (9)
benzothiazole	135	136 (100)	
tris(methylthio)methane	154	107 (100)	

Rapid Commun. Mass Spectrom. 2007; **21**: 2564–2572
DOI: 10.1002/rcm

Sulfur compounds in pig production:

Hansen, M. J., A. Peter S. Adamsen, P. Pedersen, and A. Feilberg, "**Prediction of odor from pig production based on chemical odorants.**", *J Environ Qual*, vol. 41, no. 2: Department of Engineering, Aarhus Uninversity, Denmark. michealj.hansen@agrsci.dk, pp. 436–443, 2012.

Table 1. Recovery of odorants measured by proton-transfer-reaction mass spectrometry in Nalophan bags sampled from facilities with growing-finishing pigs ($n = 72$).

Odorants	m/z†	DL‡	OTV§	Recovery¶
		nL L^{-1}	nL L^{-1}	%
Hydrogen sulfide	35	4.9	1.9	90 ± 13
Methanethiol	49	0.06	0.07	94 ± 9
Acetone	59	0.13	13,000	102 ± 6
Trimethylamine	60	0.21	2.1	81 ± 25
Acetic acid	61 + 43	0.9	234	83 ± 17
Dimethyl sulfide	63	0.20	4.1	109 ± 20
C_4–carbonyls (e.g., 2-butanone)	73	0.07	4,500	97 ± 7
Propanoic acid	75 + 57	0.29	25	74 ± 11
2,3-butanedione	87	0.20	0.1	104 ± 15
Butanoic acid	89 + 71	0.22	1.8	85 ± 14
Phenol + dimethyl disulfide	95	0.09	54#	84 ± 28
C_5 carboxylic acids	103 + 85	0.23	1.4	81 ± 10
4-methylphenol	109	0.20	0.3	60 ± 15
Indole	118	0.05	0.4	62 ± 15
4-ethylphenol	123	0.07	1.3††	67 ± 21
Dimethyl trisulfide	127	0.06	1.7††	95 ± 27
3-methylindole	132	0.03	0.09	48 ± 14

† Mass-to-charge ratio.

‡ Detection limit determined as three times the standard deviation on blank samples.

§ Odor threshold values estimated as the geometric mean of detection threshold values reported by van Gemert (2003).

¶ Average recovery based on measurements 4 and 24 h after sampling.

Odor threshold value for phenol.

†† Odor threshold value reported by Devos et al. (1990).

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Sulfur compounds in antarctic ice samples

Jacqueline Stefels, Gauthier Carnat, John W.H. Dacey, Thomas Goossens, J. Theo M. Elzenga, Jean-Louis Tison , "**The analysis of dimethylsulfide and dimethylsulfoniopropionate in sea ice: Dry-crushing and melting using stable isotope additions**", *Marine Chemistry,* vol. 128-129, pp. 34–43, 2012

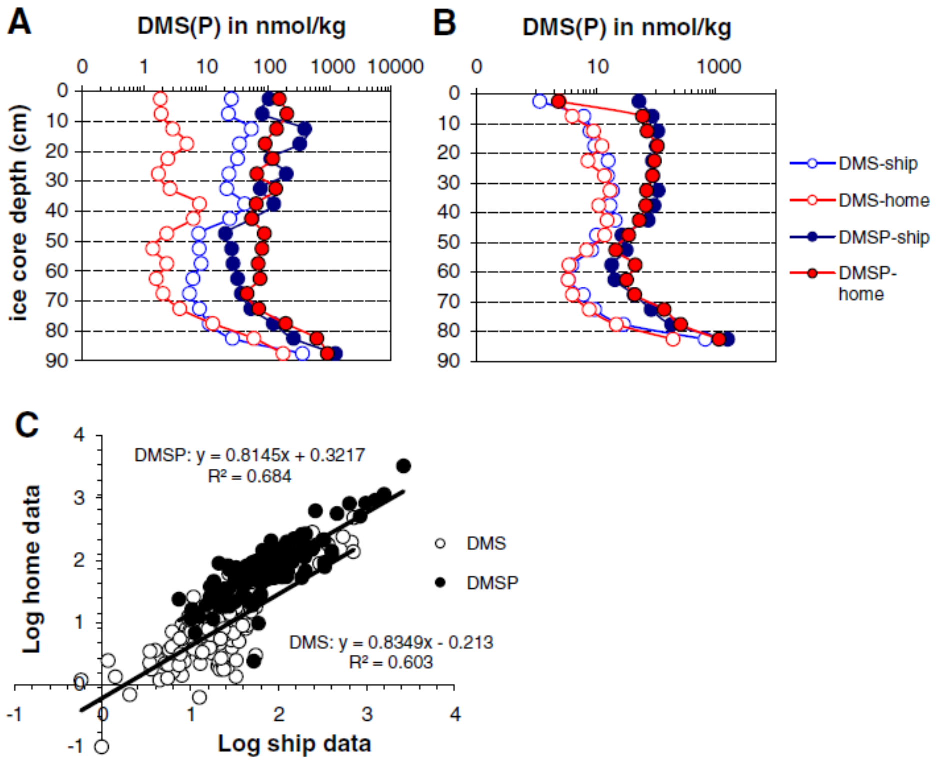

Fig. 4. Comparison between twin ice cores analyzed with the dry-crushing method on board and at home after 2 year of storage. A. Example with largest difference between on-board and at-home analysis of all 7 twin cores used in the comparison; B. Example with smallest difference between on-board and at-home analysis; C. Linear regression of log-transformed data of all paired ice-core samples (n = 120).

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