

Identification of non-regulated polycyclic aromatic compounds (PACs) and other markers of urban pollution in road tunnel particulate matter (PM)

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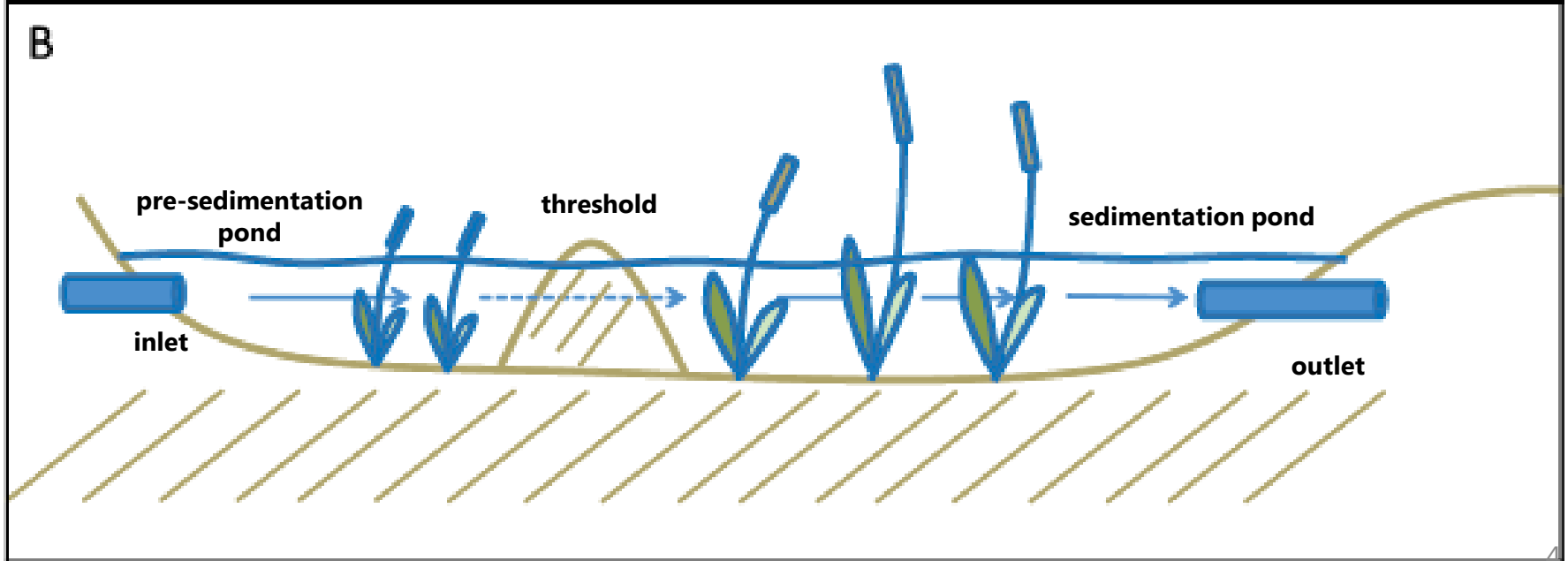
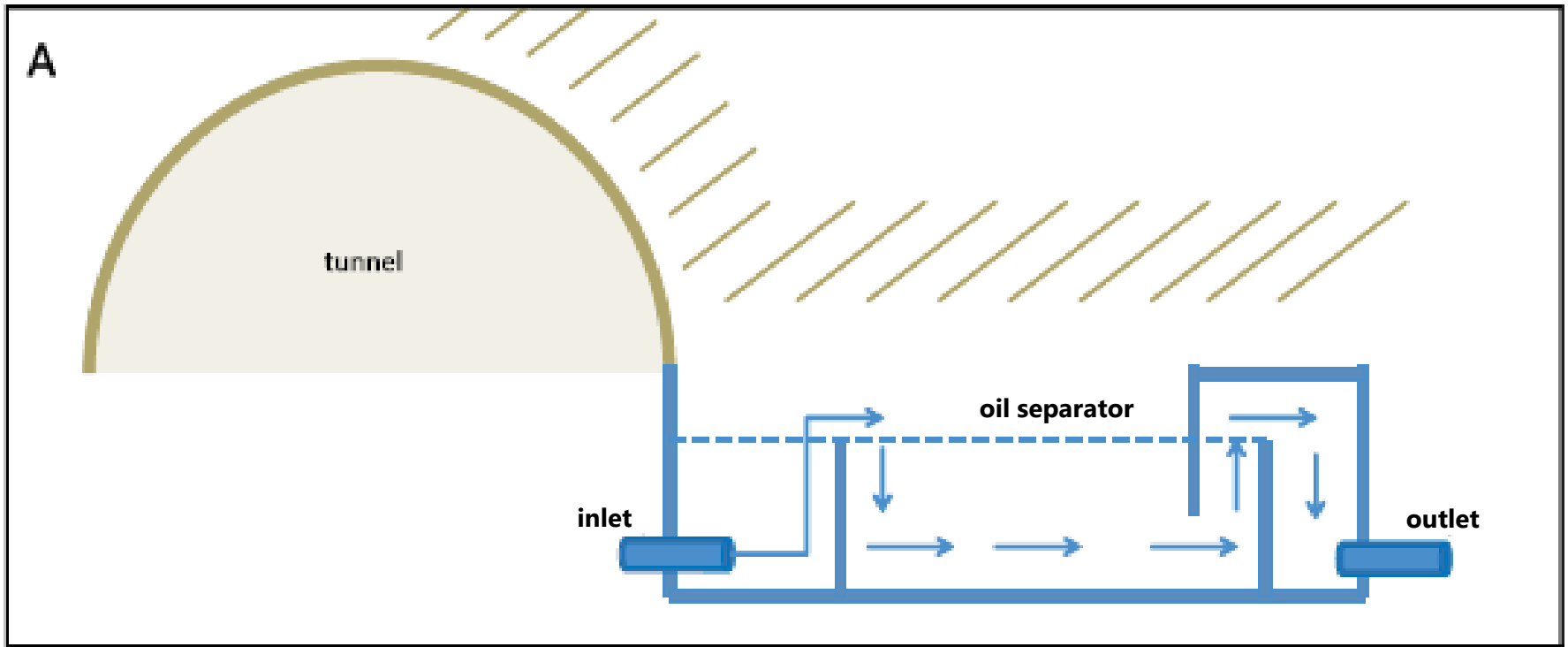
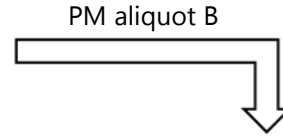
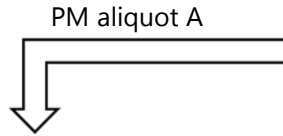
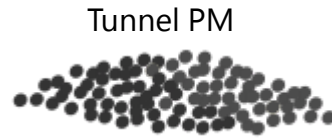




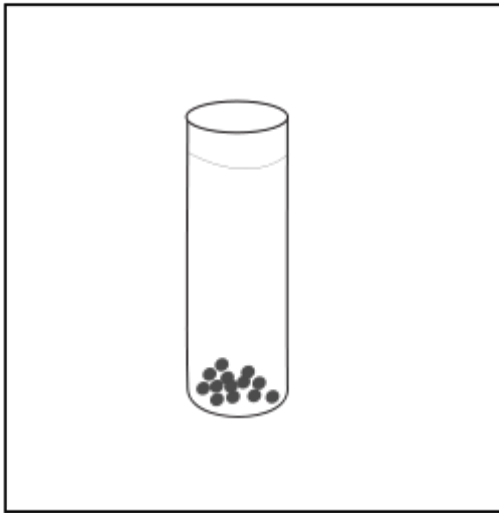




Photo: Max Lotternes, NIVA

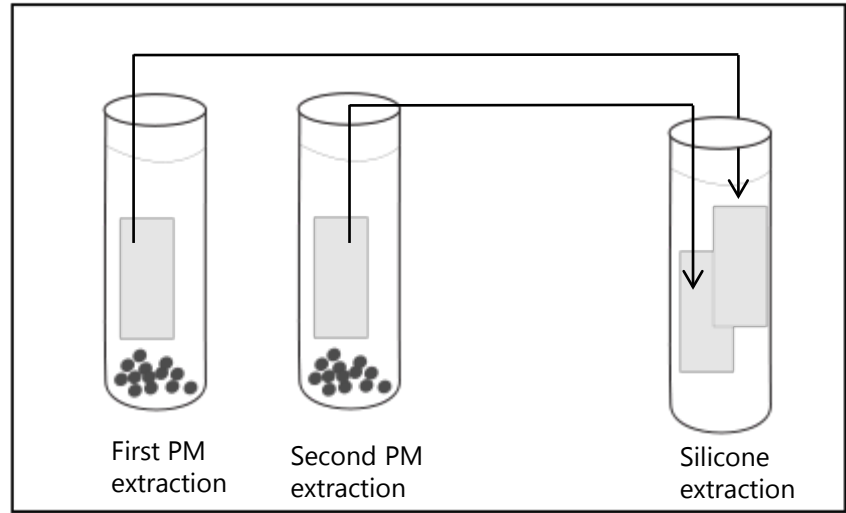


Solvent extraction



1. Non-target analysis GC/MS-ToF - 49 peaks with tentative identifications detected

Passive sampling extraction (silicone rubber)



1. Non-target analysis GC/MS-ToF
358 peaks tentative identifications
2. Selected groups suspect screening (n=19)
3. Suggested compounds (n=71)
4. Co-chromatography with standards (n=16)
5. (Clean-up of extract and target analysis
(Allan et al. ES&T, 10.1021/acs.est.6b00504))

Comparison extraction methods

(nw-XIC 20 mDa)

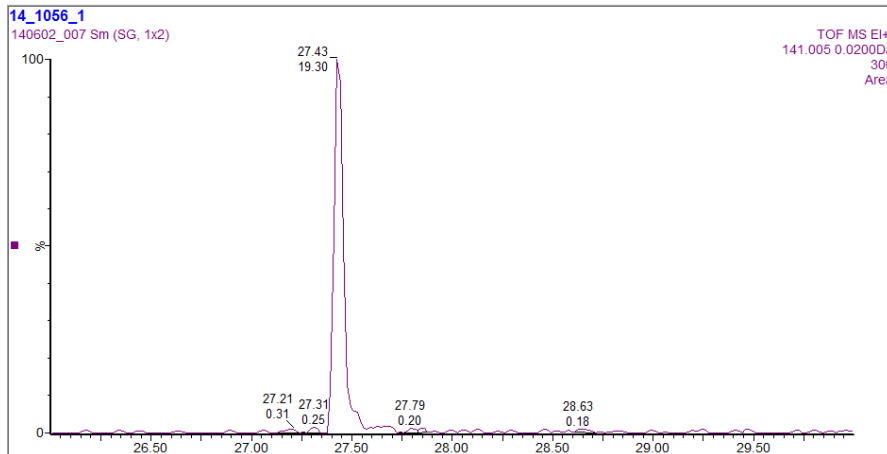
Compound	Silicone (Area)	Solvent (Area)	Silicone/ Solvent
N-butyl benzene sulfonamide	19	0,44	43
9,10-Anthracenedione	61	3,2	19
Anthrone	170	15	11
Galaxolide	33	6,2	5
Benzothiazole	480	140	3

Comparison extraction methods

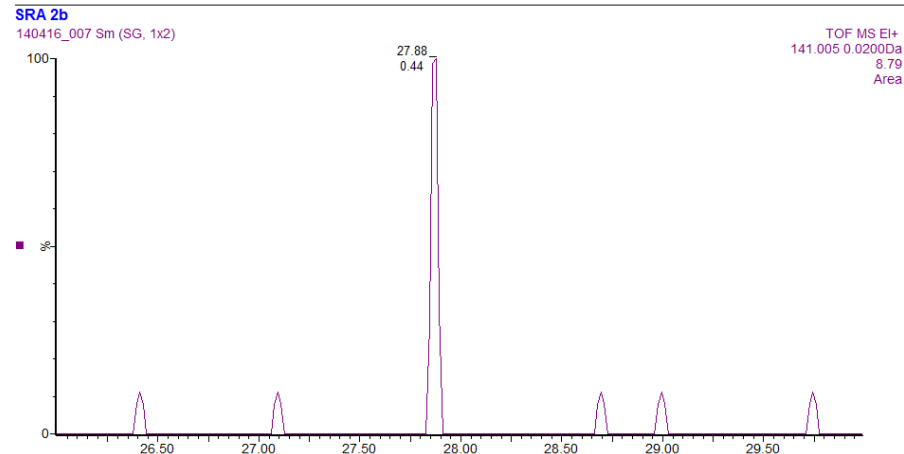
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Silicone



Solvent

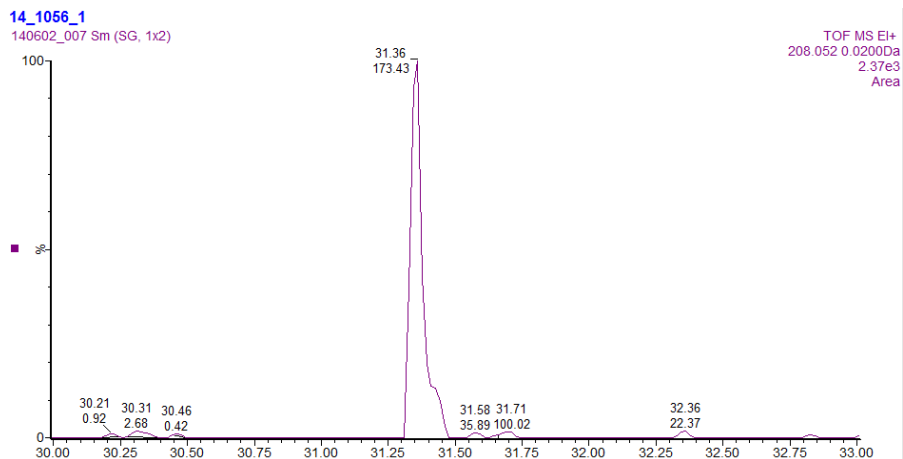


Comparison extraction methods

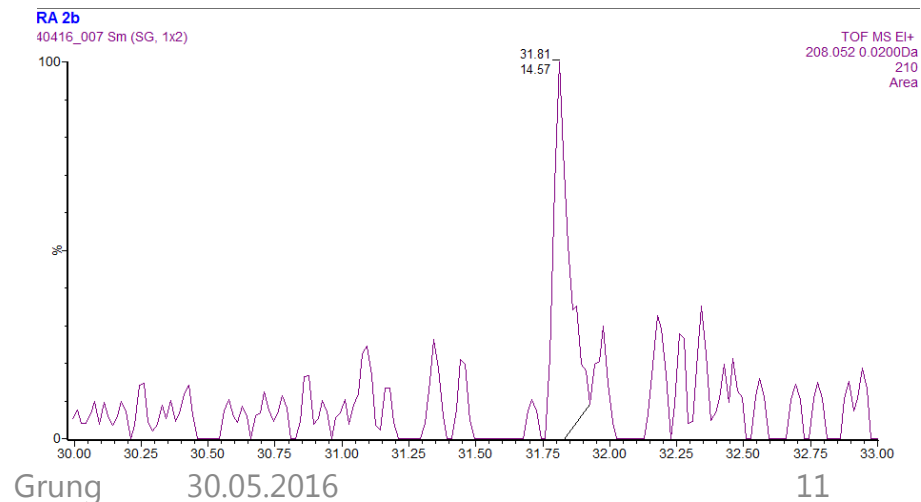
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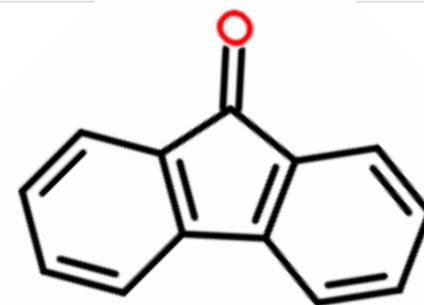
Silicone



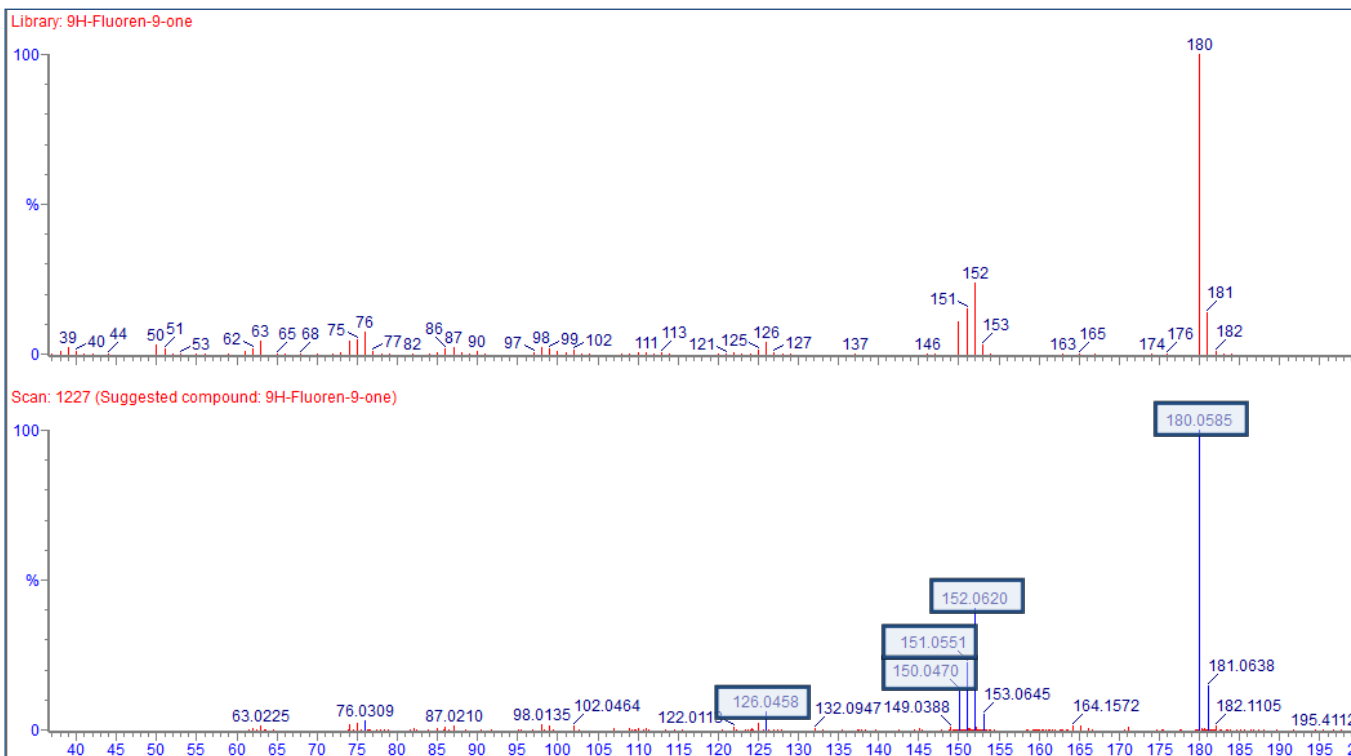
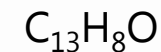
Solvent



Non-target identification



9-fluorenone



Frags. Pattern fit:

Forward: **930**

Reverse: **956**

Acc. mass (Δ mDa)

$C_{13}H_8O$ **1.0**

$C_{12}H_8$ **-0.6**

$C_{12}H_7$ **0.3**

$C_{12}H_6$ **0.0**

$C_{10}H_6$ **-1.2**

Retention index:

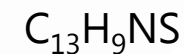
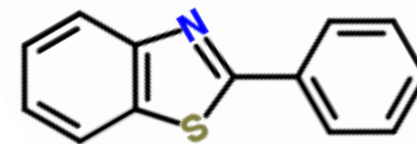
1782 **1.1%**

1863

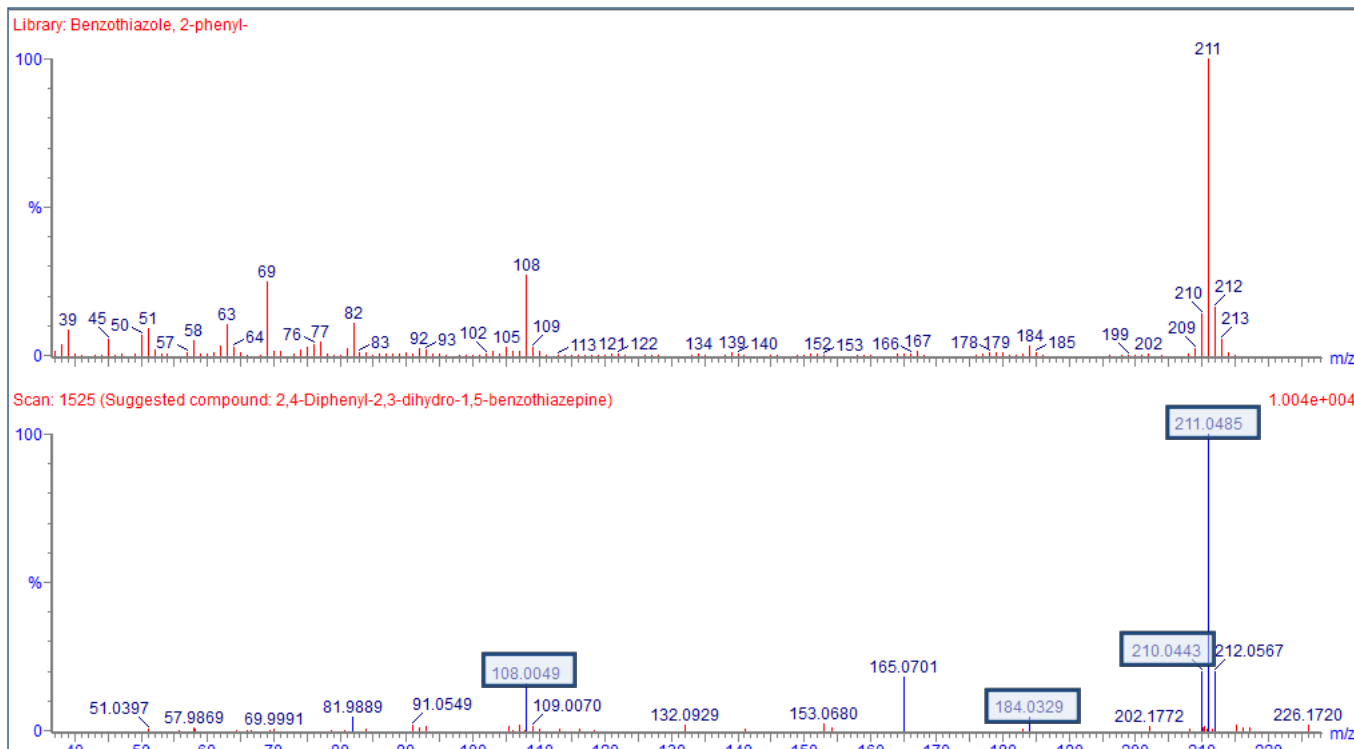
Hit probability:

0.60

Non-target identification



2-phenyl benzothiazole



Fragn. Pattern fit:

Forward: 673

Reverse: 722

Acc. mass (Δ mDa)

$C_{13}H_9NS$ 2.9

$C_{13}H_8NS$ 6.6

$C_{12}H_8S$ 1.2

C_6H_4S 1.5

Retention index:

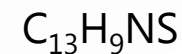
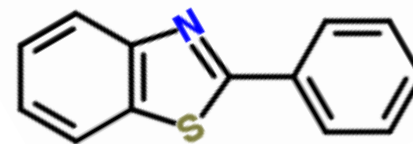
2584 7.3 %

(2437 \pm 757)

Hit probability:

0.37

Non-target identification



2-phenyl benzothiazole

Fragm. Pattern fit:

Forward: 673

Reverse: 722

Acc. mass (Δ mDa)

C₁₃H₉NS 2.9

C₁₃H₈NS **6.6**

C₁₂H₈S 1.2

C₆H₄S 1.5

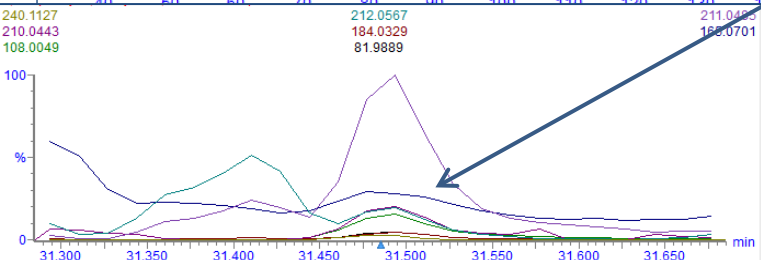
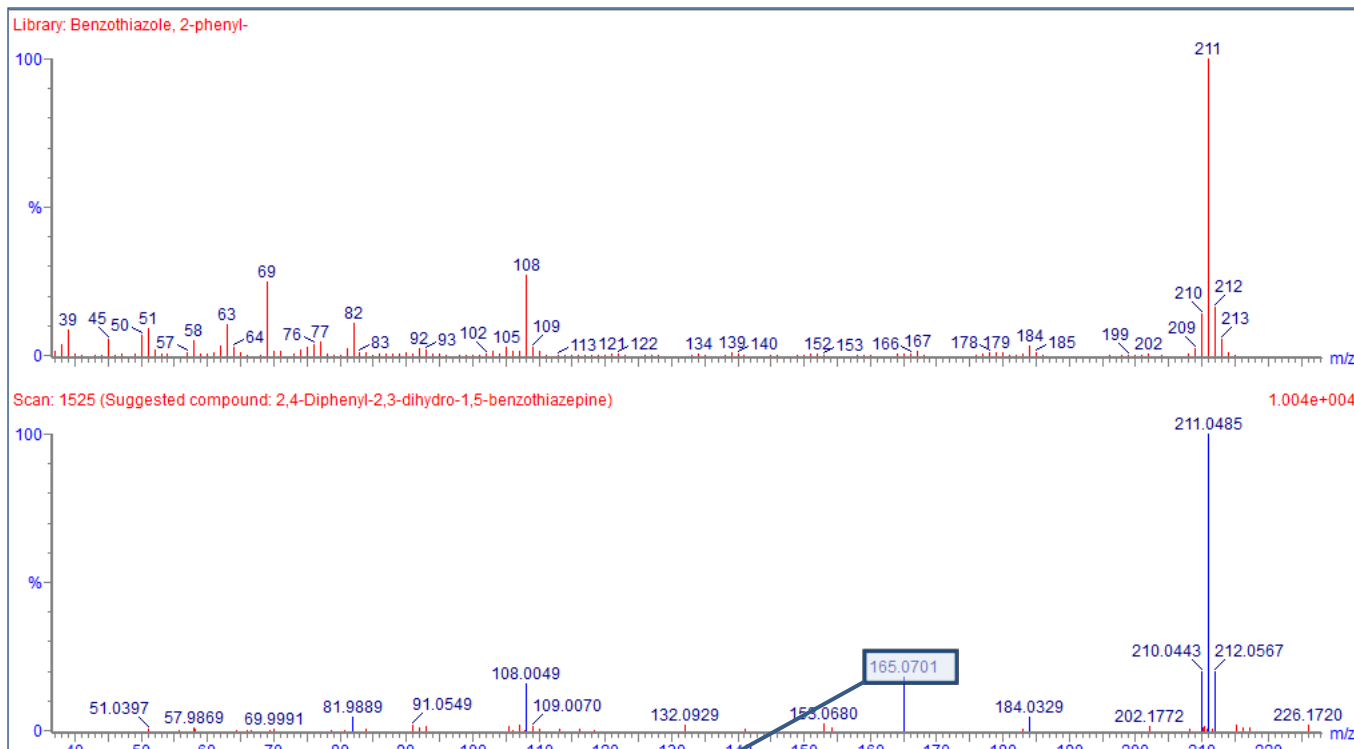
Retention index:

2584 **7.3 %**

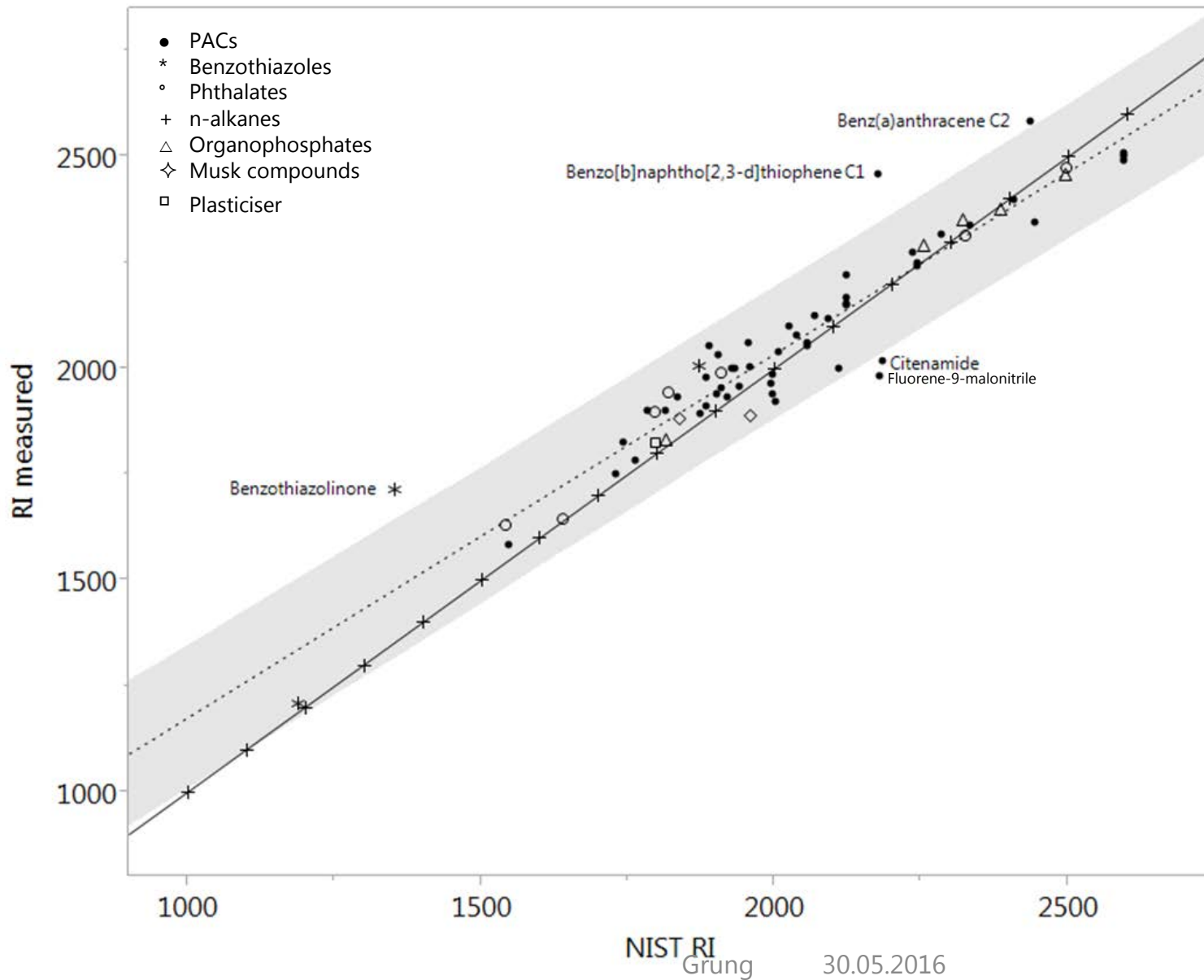
(2437 ± 757)

Hit probability:

0.37



Retention index



PACs identified by non-target analysis

Group	Suggested Compound	Confidence ^a	Group	Suggested Compound	Confidence
5 EPA PAH16	Phenanthrene	1^b	19 Heteroatom PAC	9H-Fluoren-9-one	1
	Fluoranthene	1^b		Dibenzothiophene C1	2a
	Pyrene	1^b		Anthrone	1
	Chrysene	1^b		Xanthone	1
	Benzo[a]pyrene	1^b		Benzo[c]cinnoline C1	2b
23 Alkylated EPA PAH16	Naphthalene C3	2b		Phenanthrenol	2b
	Fluorene C1	2b		Dibenzothiophene C1	2b
	Anthracene C1	2b		Benzo[c]cinnoline C2	2b
	Phenanthrene C1, C2, C3, C4	2b		9H-Fluoren-9-one, 1-hydroxy-	1
	Anthracene C1	2b		Fluorene-9-malononitrile	3
	Anthracene dihydro C2	2b		Fluorenylmethoxycarbonyl chloride	3
	Pyrene C1	2a		9,10-Anthraquinone	1
	Chrysene C1	2b		Citenamide	3
3 Other	Pyrene C3	2b		5H-Dibenzo(a,d)cyclohepten-5-ol	1
	Benz(a)anthracene C2	3		Cyclopenta(def)phenanthrenone	2b
	Phenyl-naphthalene	2b		9,10-Anthraquinone	2a
	7H-Benzo[c]fluorene	2b		1-Pyrene-carbaldehyde	2a
	Cyclopenta[cd]pyrene	2a		Benzo[b]naphtho[2,1-d]thiophene	1
				Benzo[b]naphtho[2,3-d]thiophene C1	3

^a According to Schymanski et al., ES&T (2014)

^b Confirmation from target analysis (Allan et al. ES&T (submitted))

Selected group suspect screening

Group	Name	Scr. m/z	Conf. m/z	Conf. m/z	%Diff. RI/ NIST RI
PAC	Benzo[c]cinnoline	180.069	152.063	126.047	3.4
7 Phthalates	DEP	149.024	177.055	105.034	5.6
	DIPP	149.024	209.081	167.034	0.3
	DPP	149.024	223.097	209.081	5.5
	DIBP	149.024	223.097	205.087	6.7
	DBP	149.024	208.101	208.110	4.1
	Benzylbutylphthalate	149.024	91.055	206.094	-0.6
	DEHP	non-target			-1.0
Benzo- thiazoles	Benzothiazole	non-target			2.0
	Benzothiazolinone	151.009	123.014	96.003	-27.0
	2-Phenyl-Benzothiazole	non-target			7.3
6 Organo- phosphate compounds	T CPP	125.004	201.008	277.016	1.0
	TDCP	190.943	378.899	380.896	1.6
	TPhP	non-target			1.3
	EHDPP	251.047	362.165		-0.3
	2-Isopropylphenyl diphenyl phosphate	251.047	368.118	118.078	-1.5
	Cresyl Diphenyl Phosphate	340.086	339.087		
Musk compounds	Galaxolide	243.175	213.129		2.4
	Tonalide	243.175	258.198		-3.5
Plasticiser	N-butyl-benzenesulfonamide	non-target			1.5

Co-injection mixtures

Mixture	Compound	Conc. ng mL ⁻¹	Response std.	Response extract
A	N-butyl-benzenesulfonamide		281	2 317
	Benzothiazole	250	689	1 377
	TPhP		263	31
B	2-Phenyl-Benzothiazole		3 889	2 582
	9H-Fluoren-9-one		3 680	3 150
	Anthrone	1 250	2 025	73
	9H-Fluoren-9-one, 1-hydroxy-		98	45
	5H-Dibenzo(a,d)cyclohepten-5-ol		153	56
C	Xanthone		3 128	995
	9,10-Anthracenedione		1 169	1 058
	Benzo[c]cinnoline	1 250	1 416	75
	Naphtho[1,2-b]thianaphthene		3 948	882
	EHDPP		1 238	22
D	DEHP	1 250	2 250	1 871
E	Galaxolide	250	732	333
	Tonalide		758	179

Co-chromatography

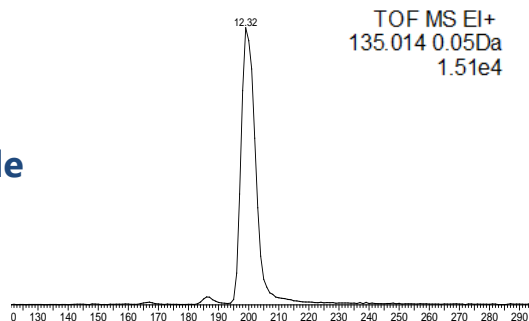
Compound	RI diff NIST (%)	Conc. std. in mix (ng mL ⁻¹)	Δ Rt min	Increase peak area	Q ion conf.	Estim. amount (ng)
N-butyl-benzenesulfonamide	-1.0	2 000	0.00	x	x	520
Benzothiazole	-2.0	2 000	0.00	x	x	130
TPhP	-1.3	80	0.06	x		7
2-Phenyl-Benzothiazole	-7.3	80	0.00	x	o	210
9H-Fluoren-9-one	-1.1	80	0.00	x	x	270
Anthrone	-6.3	80	0.05	x		11
9H-Fluoren-9-one, 1-hydroxy-	-5.0	80	0.00	x		140
5H-Dibenzo(a,d)cyclohepten-5-ol	-6.8	80	0.01	x		110
Xanthone	-4.7	80	0.00	x	x	100
9,10-Anthracenedione ^b	-3.8	80	0.02	x	x	280
Benzo[c]cinnoline	-1.5	80	-0.05	x		17
Naphtho[1,2-b]thianaphthene	-0.2	80	0.05	x		70
EHDPP	0.3	80	0.01	x		6
DEHP	1.0	400	0.04	x	x	260
Galaxolide	2.4	60	0.00	x	o	30
Tonalide	-3.5	60	0.02	x		20

NIST estimated RI

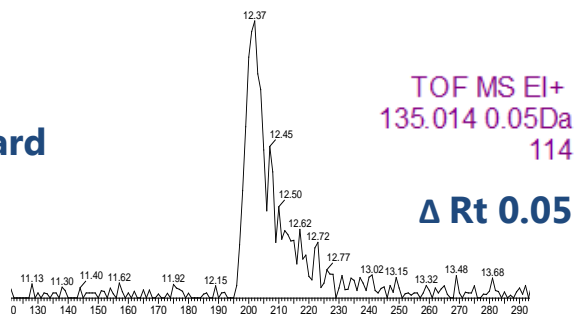
NIST measured RI

Co-chromatography benzothiazole

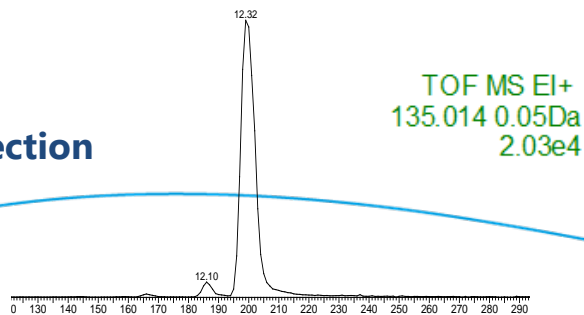
Sample



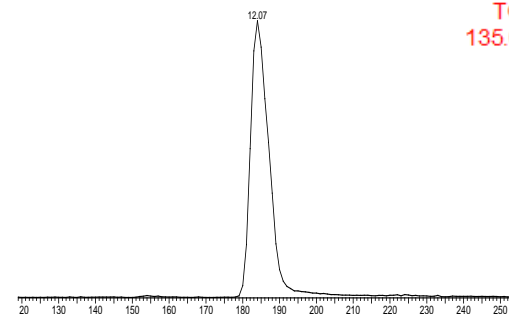
Standard



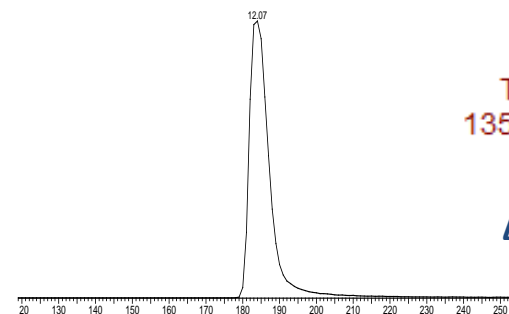
Co-injection



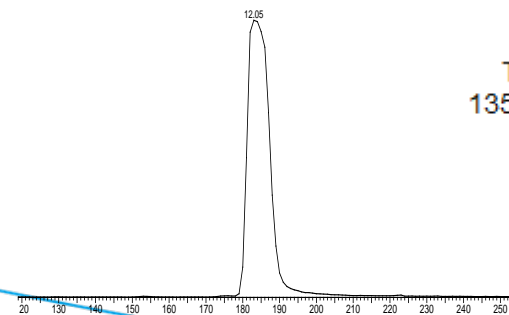
TOF MS EI+
135.014 0.05Da
1.57e4



TOF MS EI+
135.014 0.05Da
4.91e4

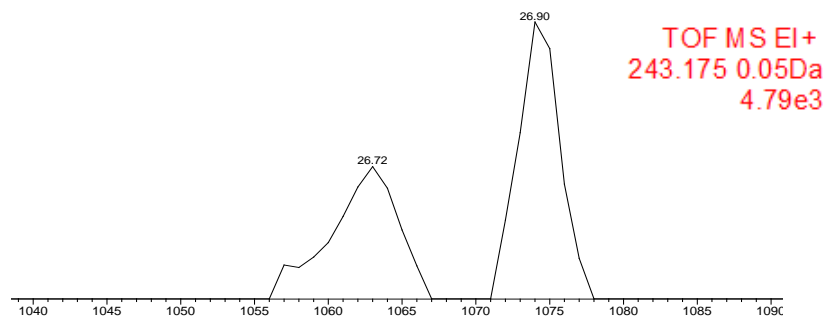
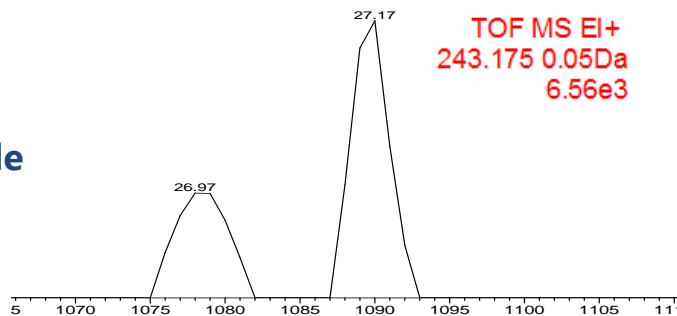


TOF MS EI+
135.014 0.05Da
5.22e4

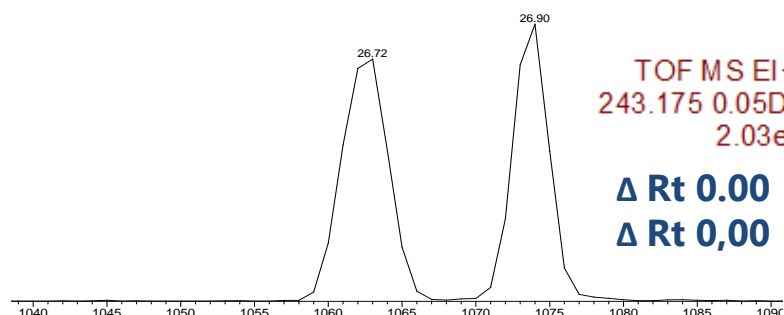
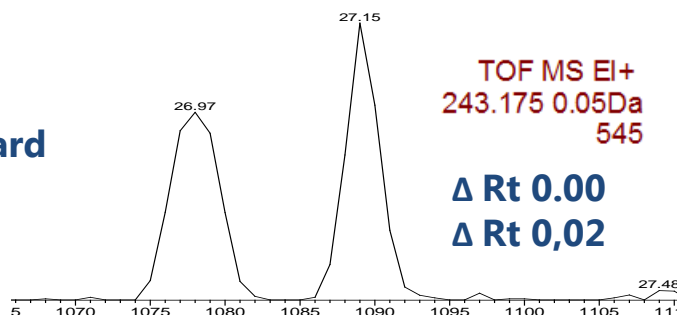


Co-chromatography galaxolide and tonalide

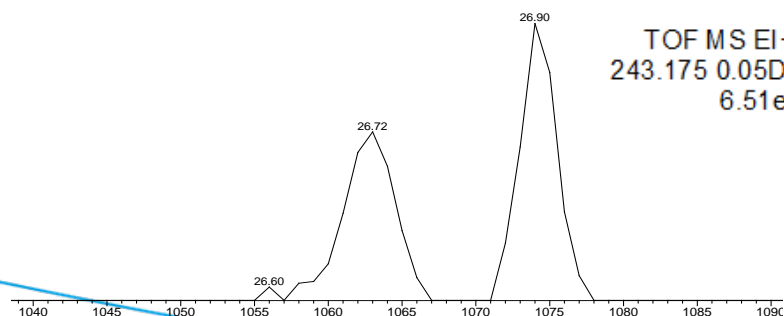
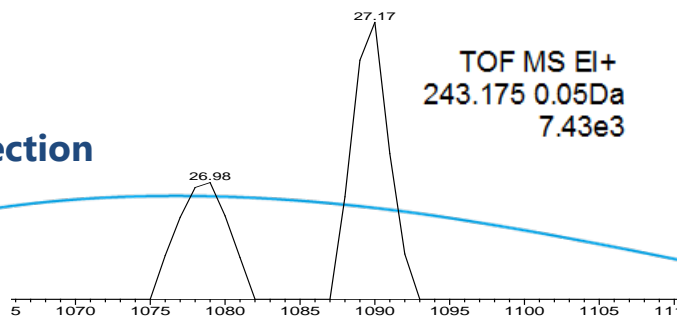
Sample



Standard



Co-injection



Conclusions

- **Silicone rubber** extracted a **broad range** of compounds from road tunnel PM
- **90%** of the compounds identified by non-target screening were **PACs**
- A major portion of the **PACs** were **alkylated** and/or contained a **heteroatom**
- **Urban markers** were also **identified** by non-target and suspect screening
- **Co-chromatography** with authentic standards confirmed the identity of **16 compounds**

Acknowledgement:

NORWAT

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Administration

www.vegvesen.no/norwat

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