
Characterization of organic compounds in atmospheric aerosol by

Direct Thermal Extraction

Gas Chromatography - Mass Spectrometry –
Flame Ionization Detection

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Characterization of organic compounds in atmospheric aerosol

Outline:

Direct Thermal Extraction principles

Validation

Examples

Conclusions



Direct Thermal Extraction principles

An off-line technique for the analysis of the organic fraction of particles (sampled on filters or as dust)

Heating of the sample and injection of the thermally releasable compounds onto a gas chromatographic column for separation and detection

Alternative to traditional methods based on solvent extraction



Direct Thermal Extraction principles

Disadvantages:

- filter samples – contamination from the filter material
- compound specific calibration
- large number of compounds
- difficult identification without proper standards
- contamination of the whole instrument – cryo trap, transfer line, mass detector...

Advantages:

- experimentally simple and fast
- no dilution
- smaller amount of sample required
- minimized steps → minimized losses and laboratory contamination



Direct Thermal Extraction principles

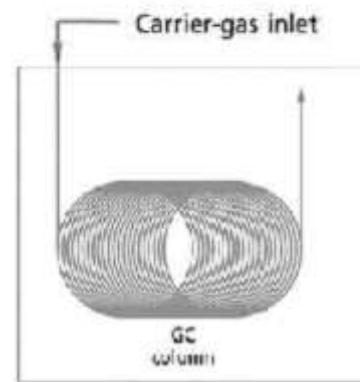
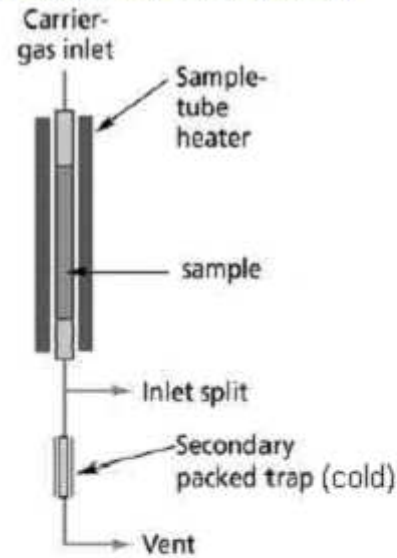
Principle of the two-stage desorption

Primary desorption: Tube

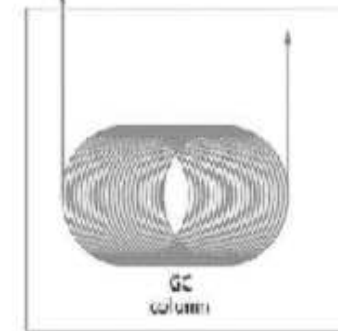
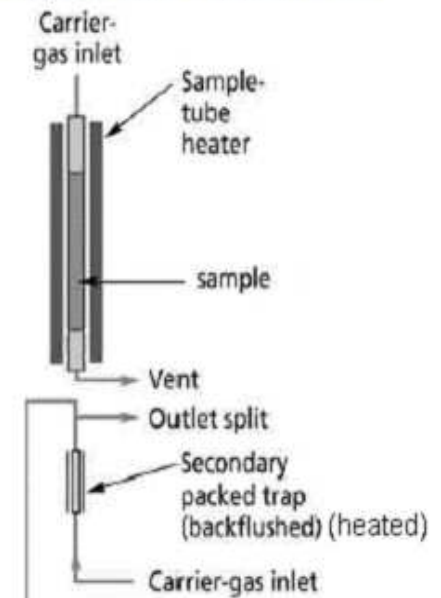
Secondary stage: Trap



PRIMARY DESORPTION



SECONDARY DESORPTION



Direct Thermal Extraction principles

Thermal treatment

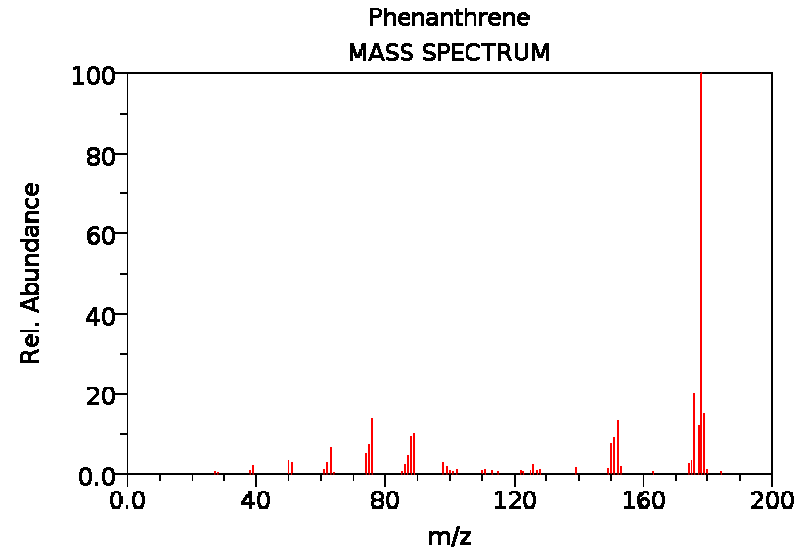
Sample heating

5 – 60 minutes @ 100 – 350 °C

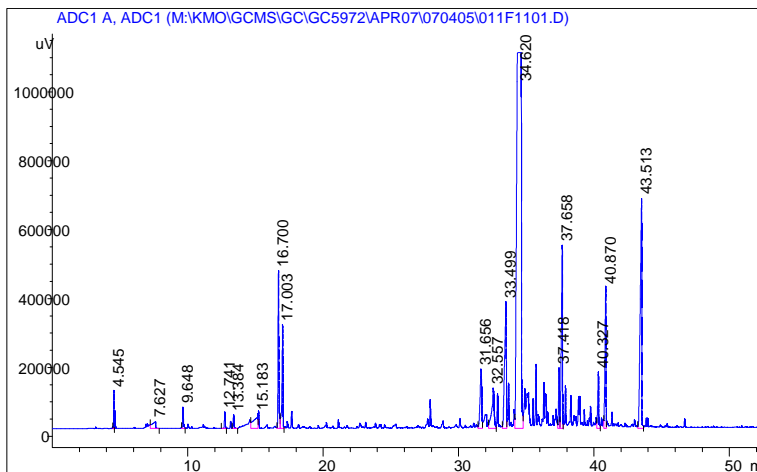
Trap heating

5 – 10 minutes @ 100 – 400 °C

GC column



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)



Two detectors:

MS: mass spectrometer for identification and quantification with specific ions

FID: flame ionization detector for quantification



Direct Thermal Extraction principles



Picture of the thermodesorption tubes with a powder sample (left) and a filter sample (right)

Work with the analyses



Validation

Analysis of selected PAHs in the NIST Standard Reference Material

SRM1649a “Urban Dust”

1 – 5 mg of the sample

between two glass wool plugs (cleaned at 300 °C)

Desorption: 7 minutes @ 275 °C

Trap low: - 30 °C

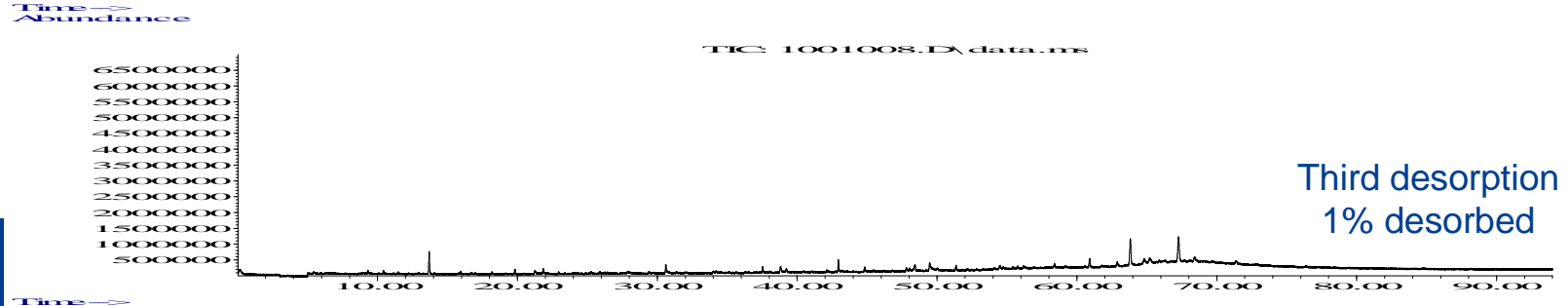
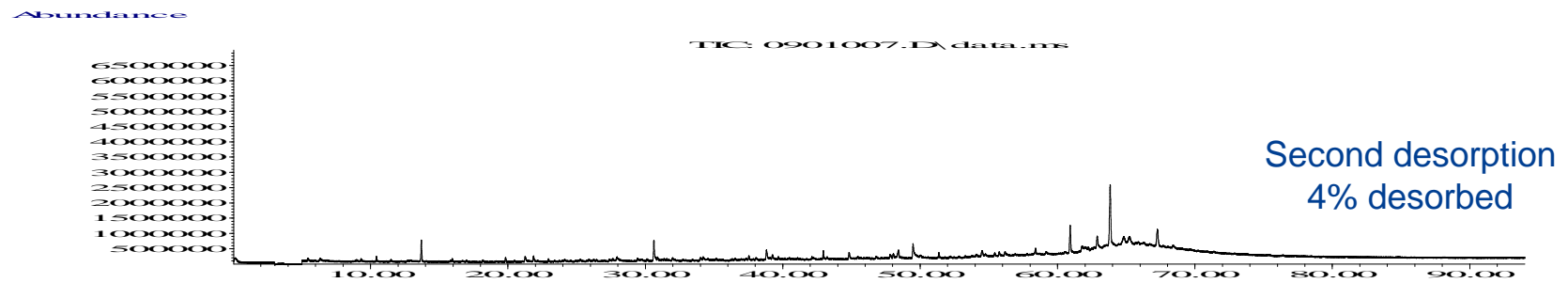
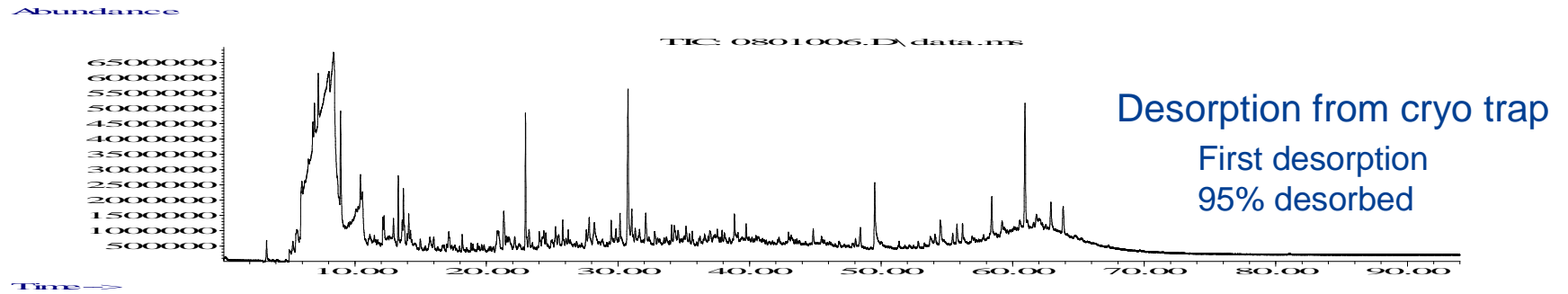
Trap high: 300 °C

GC: 30 °C for 2 minutes → 4 °C/min to 300 °C



Validation

MS chromatogram of the NIST standard Reference material SRM1649a "Urban Dust"



Validation

Analysis of selected PAHs in the NIST Standard Reference Material SRM1649a “Urban Dust”

Concentration (ng/mg)							
Run #	1	2	3	4	5		
Sample weight	1.9 mg	3.8 mg	2.9 mg	2.2 mg	2.1 mg	$M \pm SD$	Certified
Phenanthrene	5.11	4.29	4.49	3.26	3.63	4.16 ± 0.57	4.14 ± 0.37
Anthracene	0.66	0.39	0.29	0.94	1.07	0.67 ± 0.39	0.43 ± 0.08
Fluoranthene	6.73	6.28	5.17	5.45	5.93	5.91 ± 0.49	6.45 ± 0.18
Pyrene	5.00	5.82	5.42	4.81	5.31	5.27 ± 0.41	5.29 ± 0.25



Validation

Analysis of selected PAHs in the NIST Standard Reference Material SRM1649a “Urban Dust”

Concentration ng/mg					
	Waterman et al., 2000	Waterman et al., 2001	Falkovich and Rudich	SP	Certified
Phenanthrene	4.62 ± 0.12	4.56 ± 0.24	4.05 ± 0.13	4.16 ± 0.57	4.14 ± 0.37
Fluoranthene	6.38 ± 0.18	6.4 ± 0.28	n.d.	5.91 ± 0.49	6.45 ± 0.18
Pyrene	5.44 ± 0.20	4.56 ± 0.62	4.61 ± 0.24	5.27 ± 0.41	5.29 ± 0.25
Benz[a]anthracene	n.d.	n.d.	2.20 ± 0.40	n.d.	2.21 ± 0.07



Validation

- Good agreement with certified values, determined ranges all overlap with the certified ranges
- RSD for anthracene is high (58%) → Limit of detection close to 1 ng/mg

Waterman D., B. Horsfield, F. Leistner, K. Hall, S. Smith (2000). *Analytical Chemistry*, 72, 3563-3566. Quantification of Polycyclic Aromatic Hydrocarbons in the NIST Standard Reference Material (SRM 1649A) Urban Dust using Thermal Desorption GC/MS.

Waterman D., B. Horsfield, K. Hall, S. Smith (2001). *Journal of Chromatography. A*, 912, 143-150. Application of micro-scaled sealed vessel thermal desorption – gas chromatography-mass spectrometry for the organic analysis of the airborne particulate matter: linearity, reproducibility and quantification.

Falkovich A.H., Y. Rudich (2001). *Environmental Science and Technology*, 35, 2326-2333. Analysis of semivolatile organic compounds in atmospheric aerosols by direct ample introduction Thermal Desorption GC/MS.

Lavrish R.J., M.D. Hays (2007). *Analytical Chemistry*, 79, 3635-3645. Validation studies of Thermal Extraction-GC/MS applied to source emissions aerosols. 1. Semivolatile analyte - Nonvolatile matrix interactions.



Validation

Analysis of selected monocarboxylic acids in the NIST Standard Reference Material SRM1649a “Urban Dust”

Compounds	ng/mg	ng/mg	ng/mg	M ± SD
Sample weight	3,38 mg	1,52 mg	1,48 mg	ng/mg
	ng/mg	ng/mg	ng/mg	ng/mg
Butanoic acid				
Pentanoic acid				
Hexanoic acid	23	27	18	22.7 ± 4.5
Heptanoic acid	11	13	9	11.0 ± 2.0
Octanoic acid	17	19	13	16.3 ± 3.1
Nonanoic acid	10	17	11	12.7 ± 3.8
Decanoic acid	16	12	8	12.0 ± 4.0
Undecanoic acid				
Dodecanoic acid				
Tetradecanoic acid				
Hexadecanoic acid				
Octadecanoic acid				

Monocarboxylic acids:

- No certified values
- Characteristic ion
m/z = 60
- RSD between 20 - 30%



Examples

Examples of application:

DTE-GC/MS/FID of SOA from sabinene/ozone reaction

Fine and coarse particles sampled on Teflon filters during a field campaign GÖTE2005 (Gothenburg) with respect to monocarboxylic acids

Fine and coarse urban particles sampled on Teflon filters Cork, Ireland in March 2006) with respect to the identification of individual compounds and quantification of the organic content



DTE-GC/MS/FID of SOA from sabinene/ozone reaction

L Chiappini, E. Perraudin, R. Durand-Jolibois, J.F. Doussin, 2006. Anal Bioanal Chem 386(6), 1749-1759.

“Development of a **supercritical fluid extraction** – gas chromatography – mass spectrometry method for the identification of highly polar components in secondary organic aerosol formed from biogenic hydrocarbons in smog chamber experiments”.

LISA = Laboratoire Interuniversitaire des Systèmes Atmosphériques

Ozone/sabinene reaction

Highly oxidized products

Chemical structures from mass spectra

Quantification using structurally similar compounds

Samples for SP: collected on cleaned glass microfibre filters

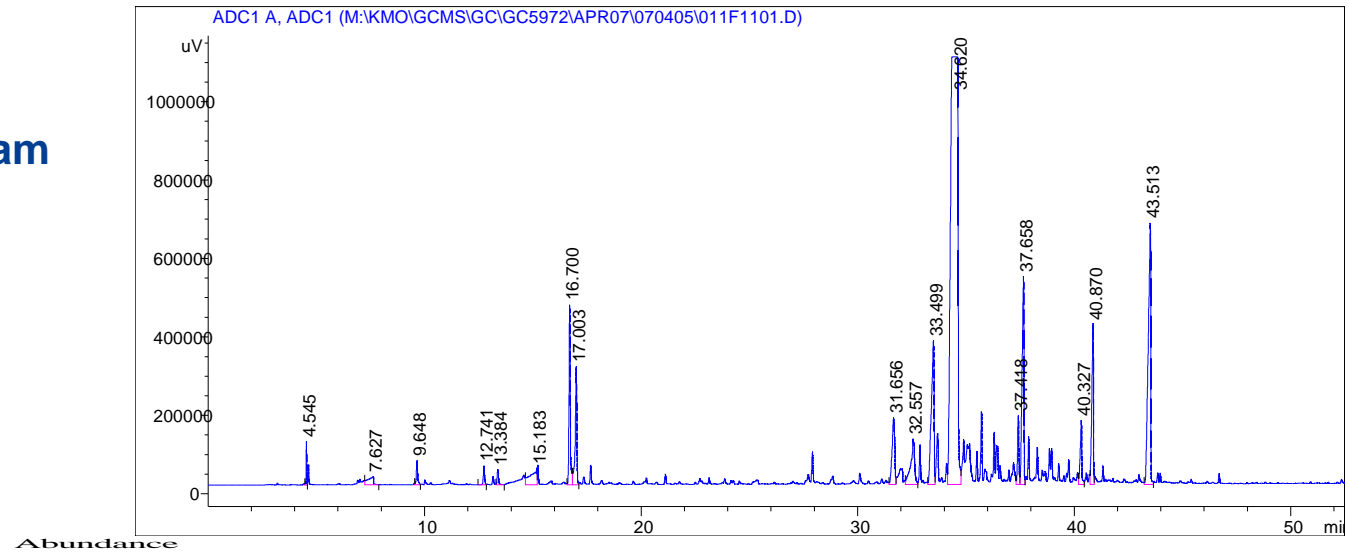
¼ of a filter analyzed

5 samples

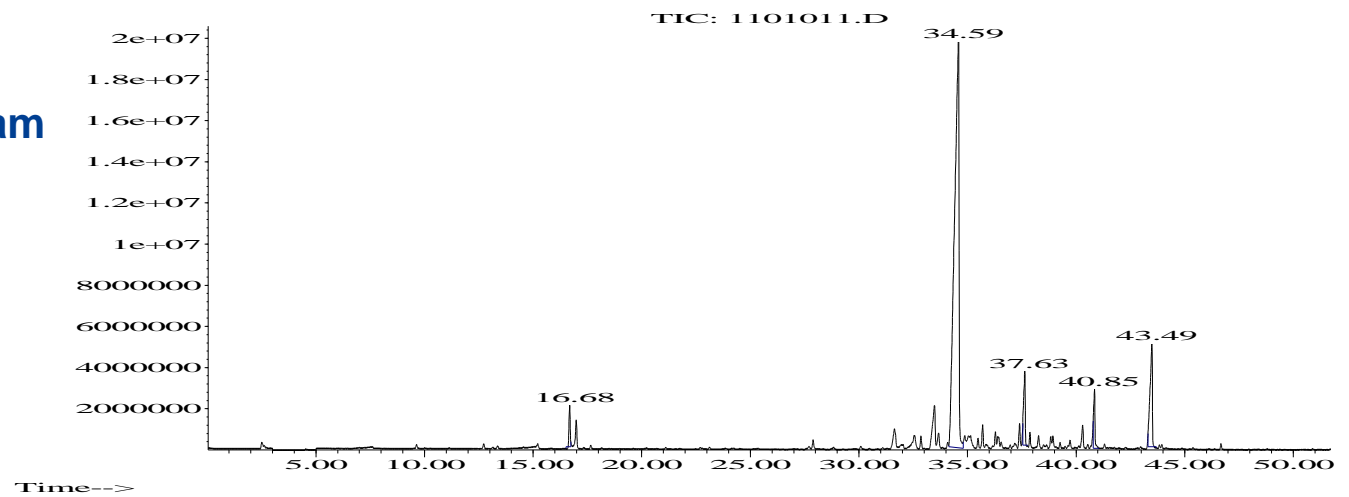


DTE-GC/MS/FID of SOA from sabinene/ozone reaction

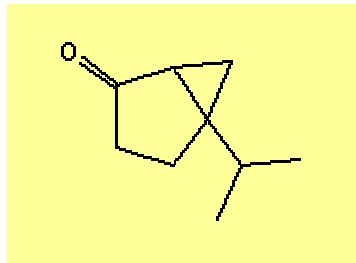
FID chromatogram



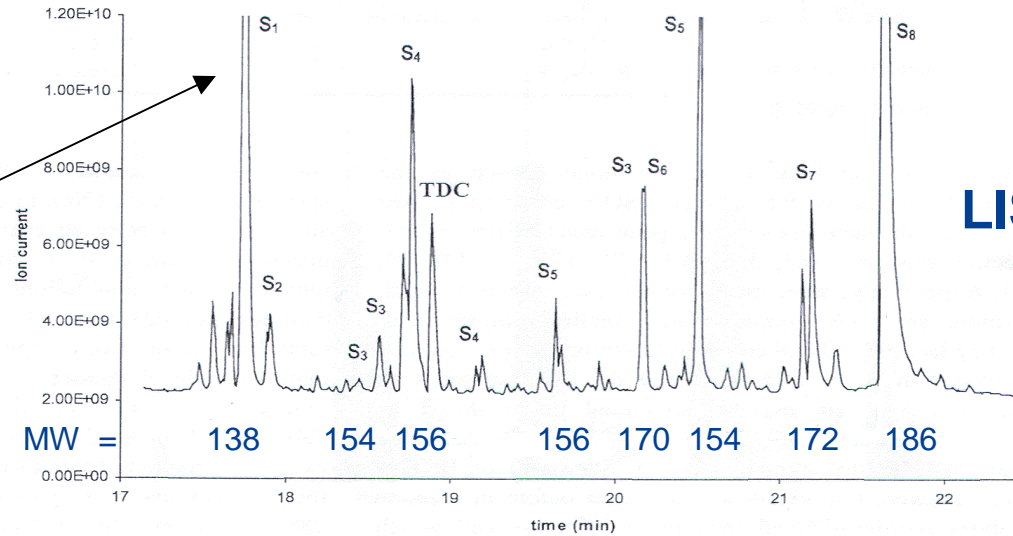
MS chromatogram



DTE-GC/MS/FID of SOA from sabinene/ozone reaction

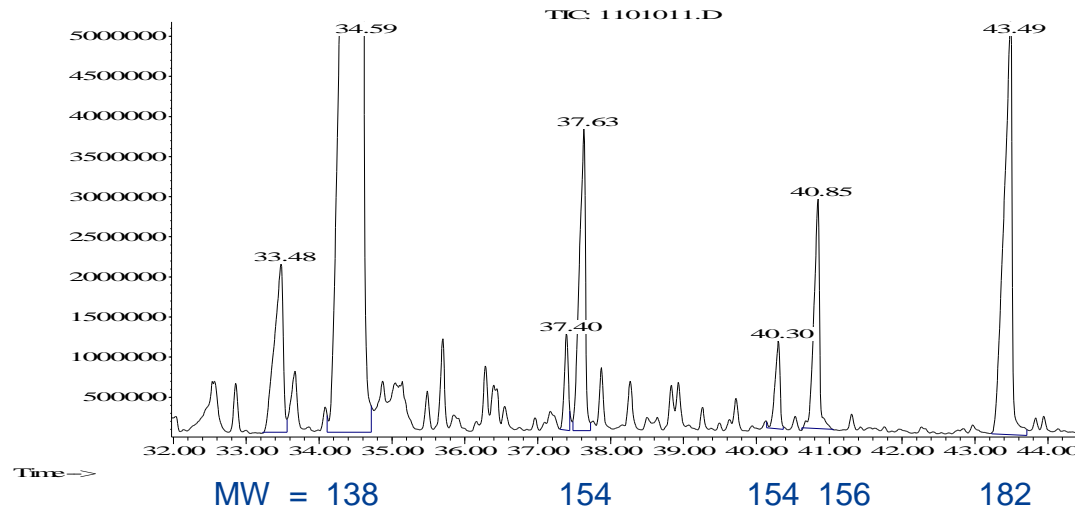


Sabinaketone



LISA

Abundance



SP



DTE-GC/MS/FID of SOA from sabinene/ozone reaction

Identification: using NIST mass spectral database

Quantification: toluene equivalents in accredited procedure

Particle mass sampled on filters: calculated from maximum size and number concentration – approx. 300 µg/filter

Compound quantifications: oxygenated compounds approx. 50% of the response factor for toluene

Identified compounds “before”; no good identification “after” sabinaketone

Compound yields in SOA calculated given the above assumptions



DTE-GC/MS/FID of SOA from sabinene/ozone reaction

Compound yields in particles from ozone/sabinene reaction in % of SOA

RT (min)	Compound	mean	stddev	RSD %
4,54	Formic acid	0,4	0,1	17,5
4,64	Isopropanol	0,1	0,01	9,9
7,57	Acetic acid	0,6	0,04	6,4
9,64	2-Butanone, 3-methyl-	0,3	0,02	5,6
12,73	Ethanone, 1-(2-furanyl)-	0,2	0,02	8,5
13,38	1-Penten-3-one, 4-methyl-	0,2	0,01	5,5
15,14	Propanoic acid, 2-methyl-	1,4	0,1	4,0
15,22	4,4-Dimethyl-2-cyclopenten-1-one	0,2	0,0	9,8
16,69	1,3-Cyclohexadiene, 5,6-dimethyl-	1,9	0,2	10,5
16,99	Cyclopentadiene, 2,5,5-trimethyl-	1,5	0,2	10,5
20,23	2(3H)-Furanone, 5-methyl-	0,1	0,02	22,6
21,11	2-Cyclopentene-1,4-dione	0,1	0,01	13,6
27,90	3-Hepten-2-one, 3-methyl-	0,4	0,04	12,3
31,62	2,4,4-Trimethylbut-2-enolide	1,4	0,2	11,9
32,58	Bicyclo[3.1.0]hex-3-en-2-one, 5-(1-methylethyl)-	1,0	0,5	49,2
32,87	Thujone	0,4	0,05	11,2
33,47	2-Cyclopenten-1-one, 3-(1-methylethyl)-	2,9	0,6	21,0
33,67	1,3-Cyclopentanedione, 2,2-dimethyl-	0,8	0,1	10,0
34,60	Sabinaketone	29,3	1,8	6,1



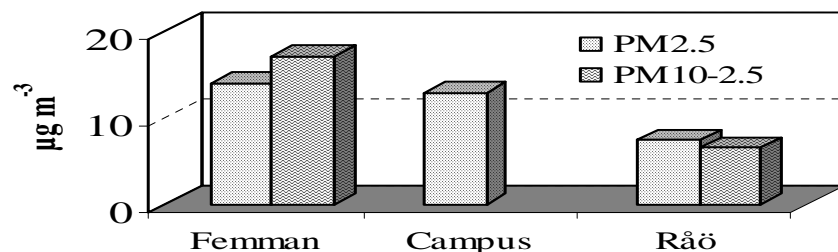
DTE-GC/MS/FID of SOA from sabinene/ozone reaction

Compound yields in particles from ozone/sabinene reaction in % of SOA

RT (min)	Compound	mean	stddev	RSD %
34,60	Sabinaketone	29,3	1,8	6,1
35,49	5-Acetyl-2-furanmethanol	0,3	0,05	13,9
36,28	Phenol, 2,3,6-trimethyl-	0,5	0,1	20,8
37,40	??? m/z = 154	0,7	0,1	14,9
37,62	??? m/z = 154	3,0	1,0	32,9
40,29	??? m/z = 154	0,9	0,1	7,5
40,84	??? m/z = 156	2,0	0,2	10,1
41,31	1(3H)-Isobenzofuranone	0,2	0,04	15,8
42,98	2H-1-Benzopyran-2-one	0,2	0,1	34,4
43,48	??? m/z = 182	5,7	0,7	11,7
43,84	Isopropyl phenyl ketone	0,1	0,01	8,8
43,95	2-Isopropyl-5-methyl-6-oxabicyclo[3.1.0]hexane-1-carboxaldehyde	0,1	0,02	18,0
	sum of identified/attempted identification	57	3	5
	TVOC	71	4	5



GÖTE2005



Femman: Urban site heavy traffic

Campus: Urban site

Råö: rural site outside of Göteborg

Concentration of PM2.5 and PM10-2.5 during Göte2005

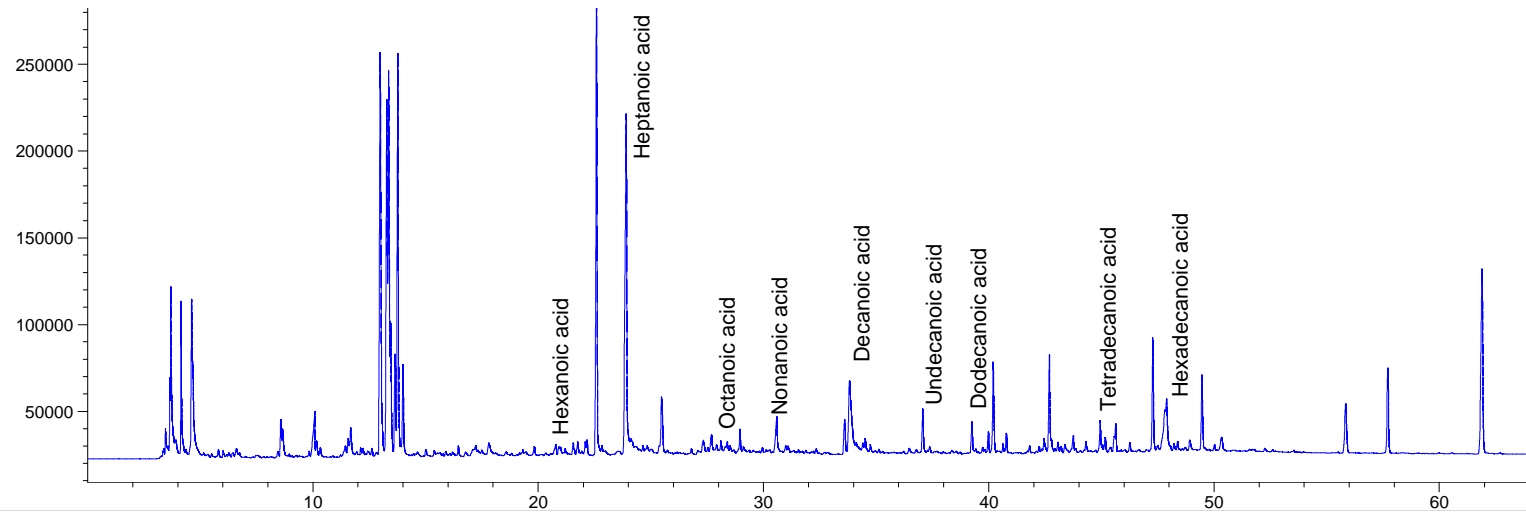
Campaign focuses on two particle sizes: PM_{2.5} and PM_{10-2.5}

Three locations: two urban sites and one rural site during February 2005

Ardhendu S. Shannigrahi, Mattias Hallquist, Sarka Langer, Karine Arrhenius, Magnus Hagström, Sara Janhäll. "Direct Thermal Desorption GC/MS Method for Analysis of n-Alkanoic Monocarboxylic Acids in PM_{2.5} and PM_{2.5-10} Samples", **2007**, manuscript for *Atmospheric Chemistry and Physics*.



GÖTE2005

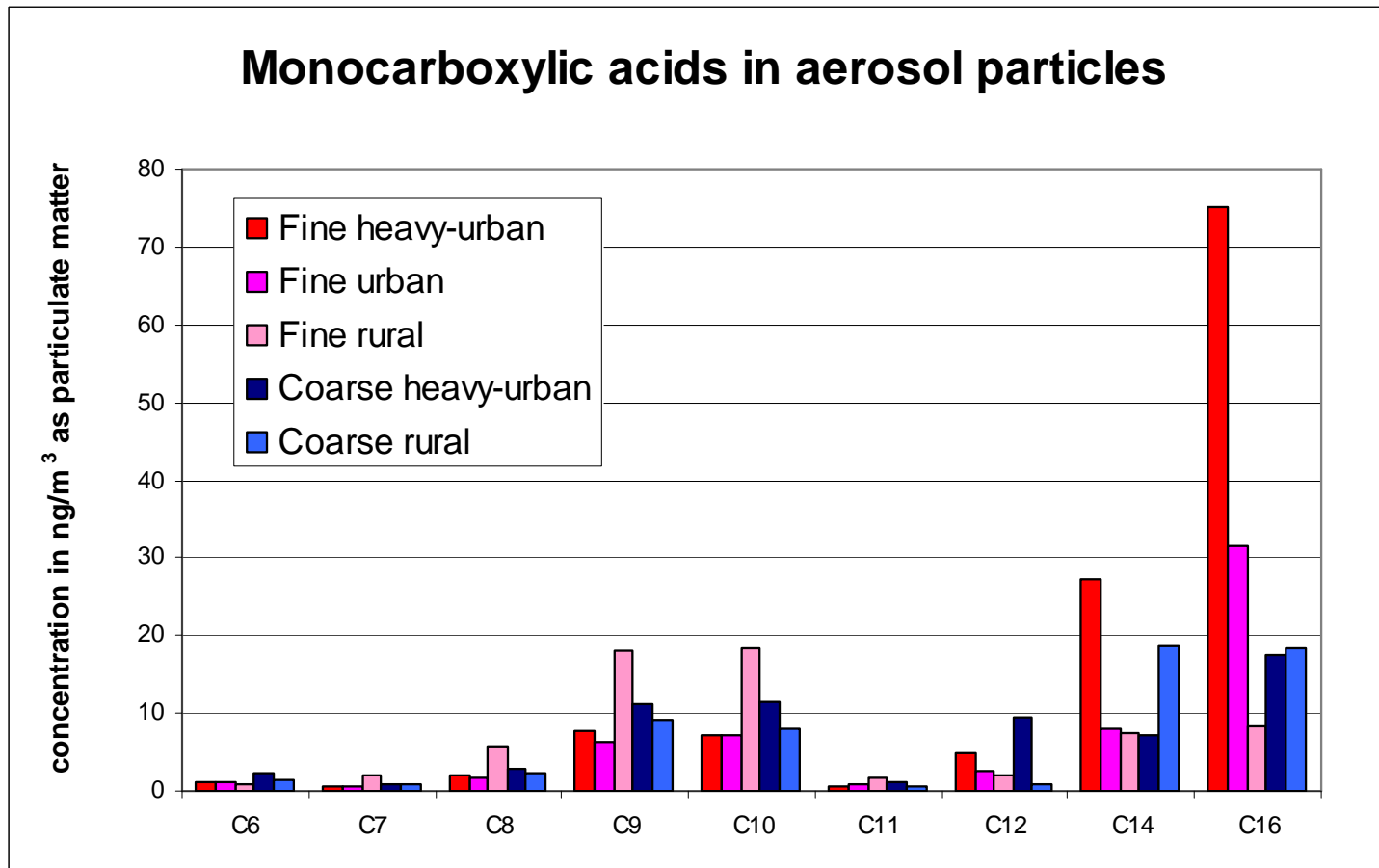


Example of a chromatogram recorded from an ambient sample during GÖTE-2005. The peaks of monocarboxylic acids (C_6 - C_{16}) are indicated.

Quantification was performed using extracted ion $m/z = 60$ using gravimetrically prepared standards of the acids in methanol.



GÖTE2005

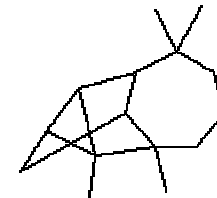
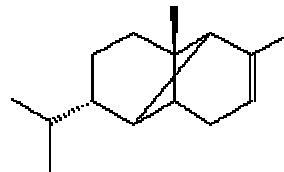
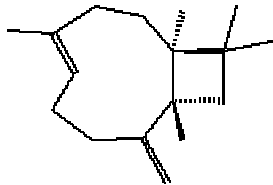


Cork, Ireland

Urban air samples – fine and coarse particles

Compounds identified in the particles:

Small oxygenated (2-Pentanone, 3-Hexen-2-one), branched alkanes > C₁₂, phthalates, 1-Octanol, 2-butyl-, 1-Hexadecanol, n-Hexadecanoic acid
Unknowns, special compounds such as α -Ylangene, Longicyclene, Beta-caryophyllene (C₁₅H₂₄)

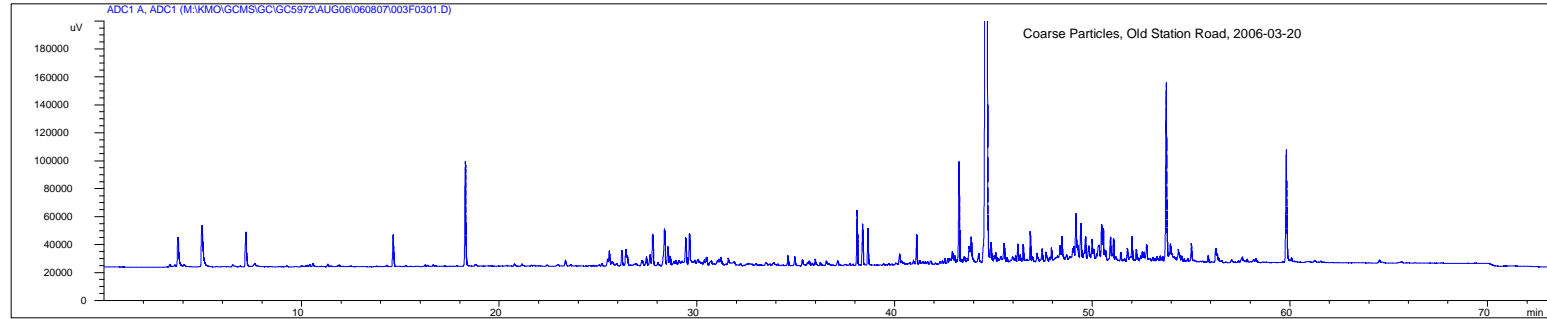


Organic content C₆ – C₃₀ as toluene equivalents

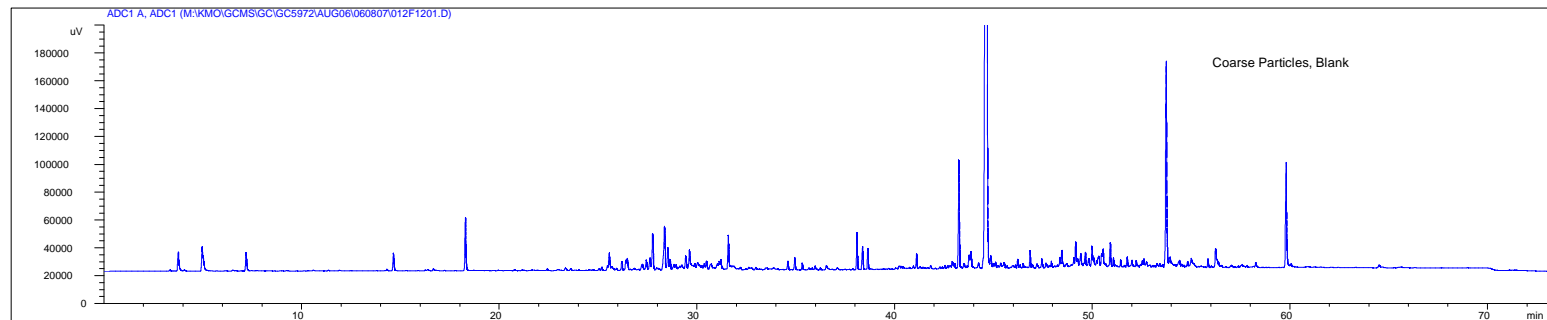
Plans: Polycyclic Aromatic Hydrocarbons
TDEGCMS (SIM) vs. soxhlet GCMS



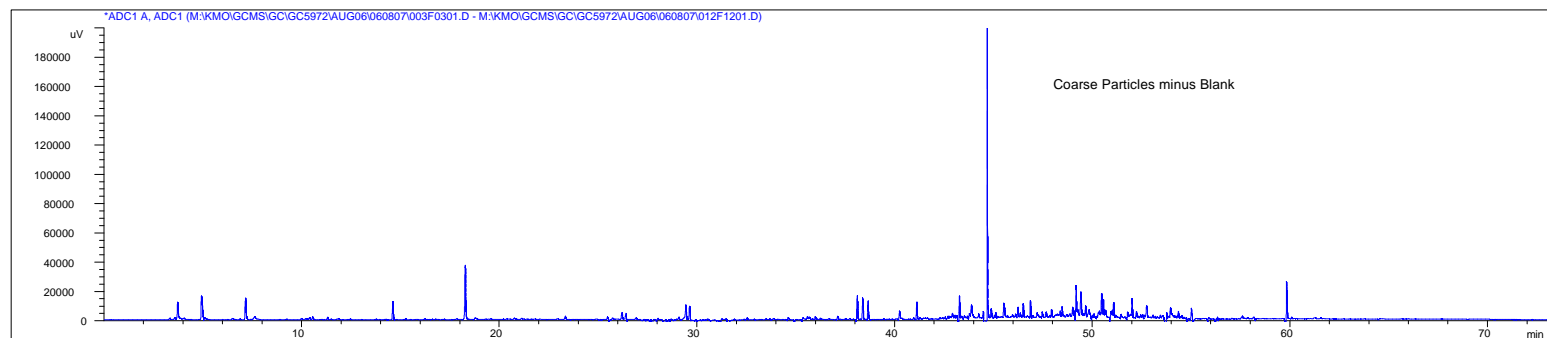
Cork, Ireland



Particles
+ filter



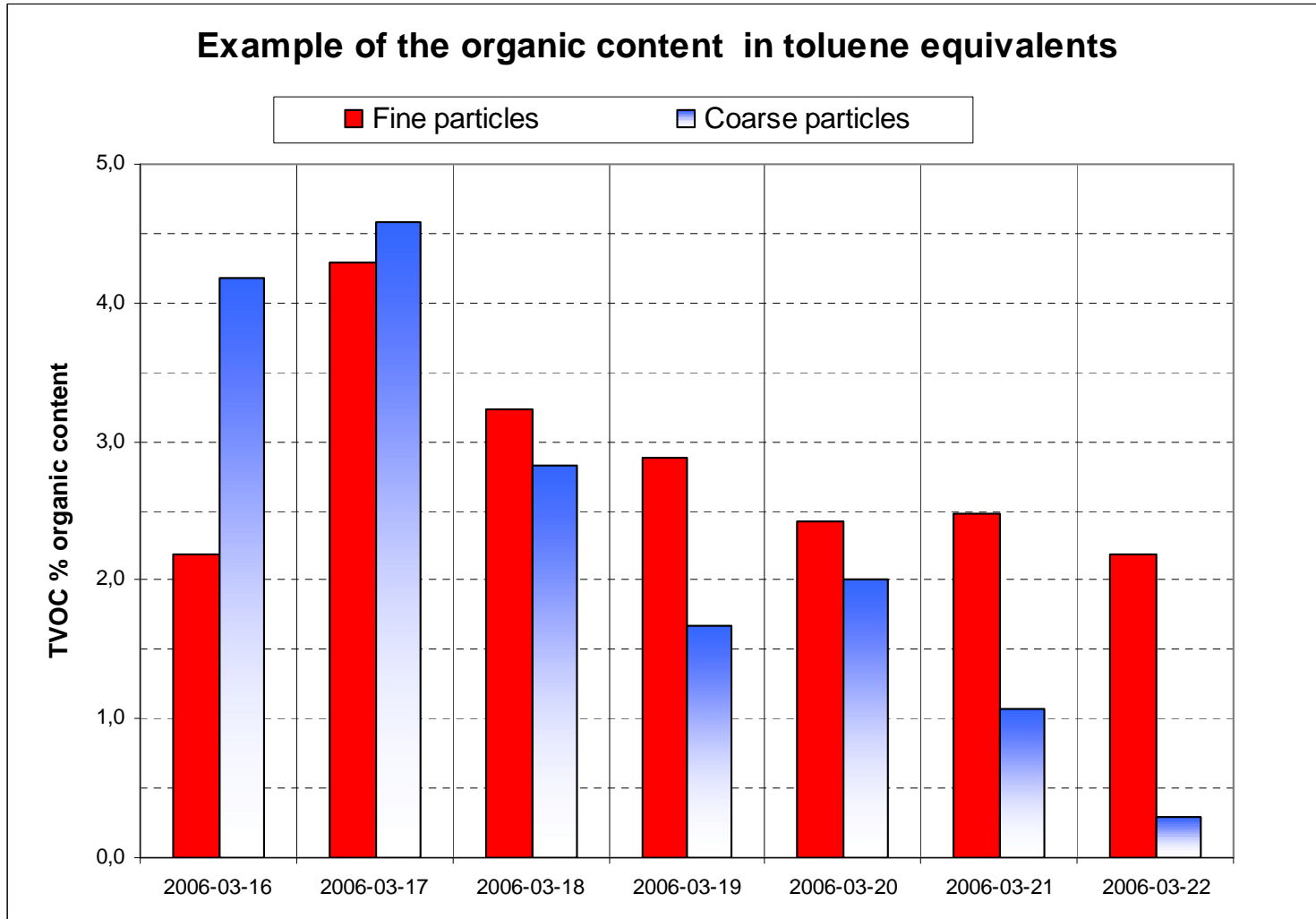
Filter



Substraction



Cork, Ireland



Conclusions

Next steps:

- Determination and creating a list compound specific response factors in FID for target compounds; quality assurance routine
- Database of compounds analysable by this technique: limitation by the thermal desorption AND chromatography
- Testing various filter materials? Sampling of other particle sizes ? What kind of filters?

Intercomparison with other techniques!!

Planned within EUROCHAMP – one experiment, three chambers, three techniques

LISA Paris – supercritical fluid extraction + GCMS

UCC Cork – denuder sampling + GCMS

SP Borås – Direct Thermal Extraction GCMSFID

