Off-line chemical analysis of organic aerosols

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Overview

- Introduction
- Sampling of aerosols
- Extraction
- Chemical analysis
  - GC-MS
  - LC-MS
- Examples of investigations
- Conclusions

GEOPHYSICAL RESEARCH LETTERS, VOL. 32, L18809, doi:10.1029/2005GL023831, 2005

A large organic aerosol source in the free troposphere missing from current models

Colette L. Heald,[1] Daniel J. Jacob,[1] Rokjin J. Park,[1] Lynn M. Russell,[2] Barry J. Huebert,[3]
John H. Seinfeld,[4] Hong Liao,[4] and Rodney J. Weber[5]

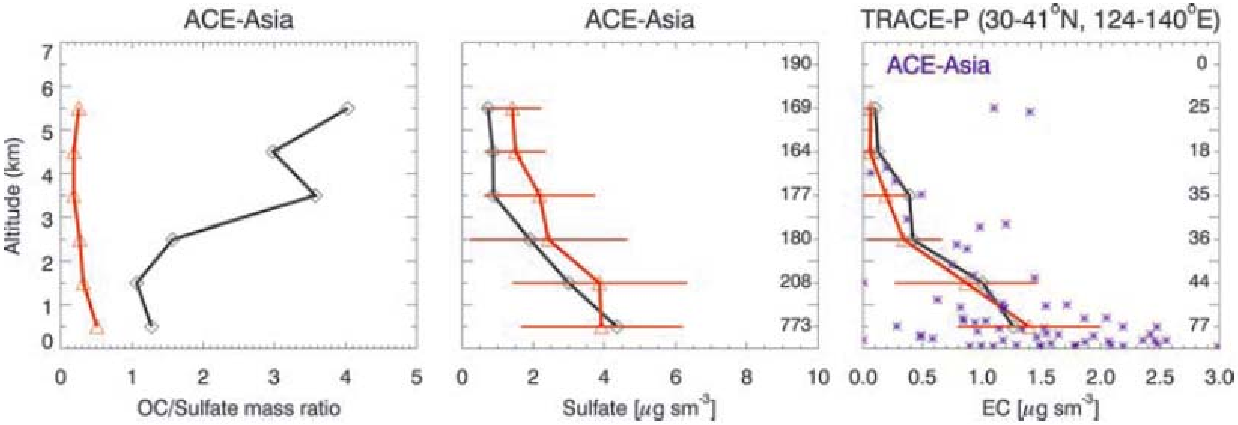

Figure 2. Mean vertical profiles of OC/sulfate mass ratio (left) and sulfate concentrations (center) from the ACE-Asia campaign, and elemental carbon (EC) aerosol concentrations from the TRACE-P campaign (right). Observations are shown in black. GEOS-Chem model results are shown in red, with standard deviations of concentrations for each altitude interval. Individual EC observations from the ACE-Asia campaign are shown as blue symbols. The number of observations in each averaging interval is shown at the right of each panel. Model values are sampled along the flight tracks.

Which types of organic compounds are found in particles?

- Semivolatile / particulate organic compounds
  - Condensed
  - e.g. polycyclic aromatic hydrocarbons with high affinity to soot
- Oligomeric or humic-like substances
  - Large, oligomeric substances
- Water-soluble and water-insoluble compounds

Analysis of organic compounds in particles

- OC - thermal oxidation
  - relatively cheap, but limited information
- Identification of compound classes
  - based on solution properties followed by thermal oxidation or ^{1}H-NMR
- Detailed chemical analysis
  - identification of hundreds of compounds
  - tracer molecules

Fourier Transform MS

app. 450 compounds!

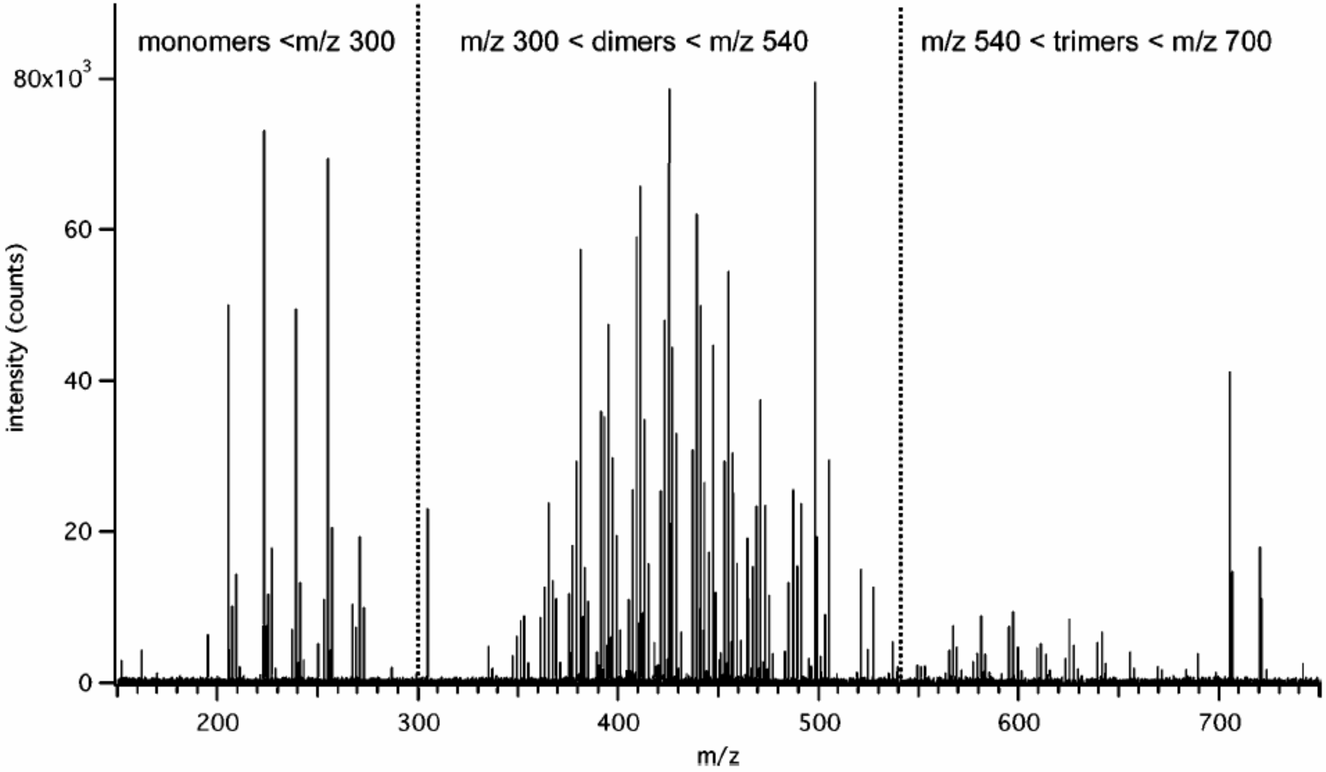

Figure 2. FTICR mass spectrum of α-pinene SOA generated in an ozonolysis experiment in a smog chamber.

Reinhart et al., Analytical Chemistry, 2007

Molecular organic tracers

- PAH are combustion tracers
  - specific compound patterns differ between sources
- Some compounds are specific tracers of different particle sources
  - Levoglucosan - specific tracer of cellulose combustion
  - Hopanes and stearanes - specific tracers of (mainly) lubricating oil
  - BSOA tracers?

Aerosol sampling

Aerosol sampling

1. Choose filter material based on type of analysis
    - quartz / glass fibre, teflon (impregnated), cellulose, nucleopore / polycarbonate
2. Determine flow, volume of air and time resolution
    - ➢ Type of sampler
3. Investigate artefacts

Aerosol sampling

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Sampling of marine particles The Galathea III expedition

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Department of Chemistry

Marianne Glasius

Sampling of marine particles

P. Konggaard

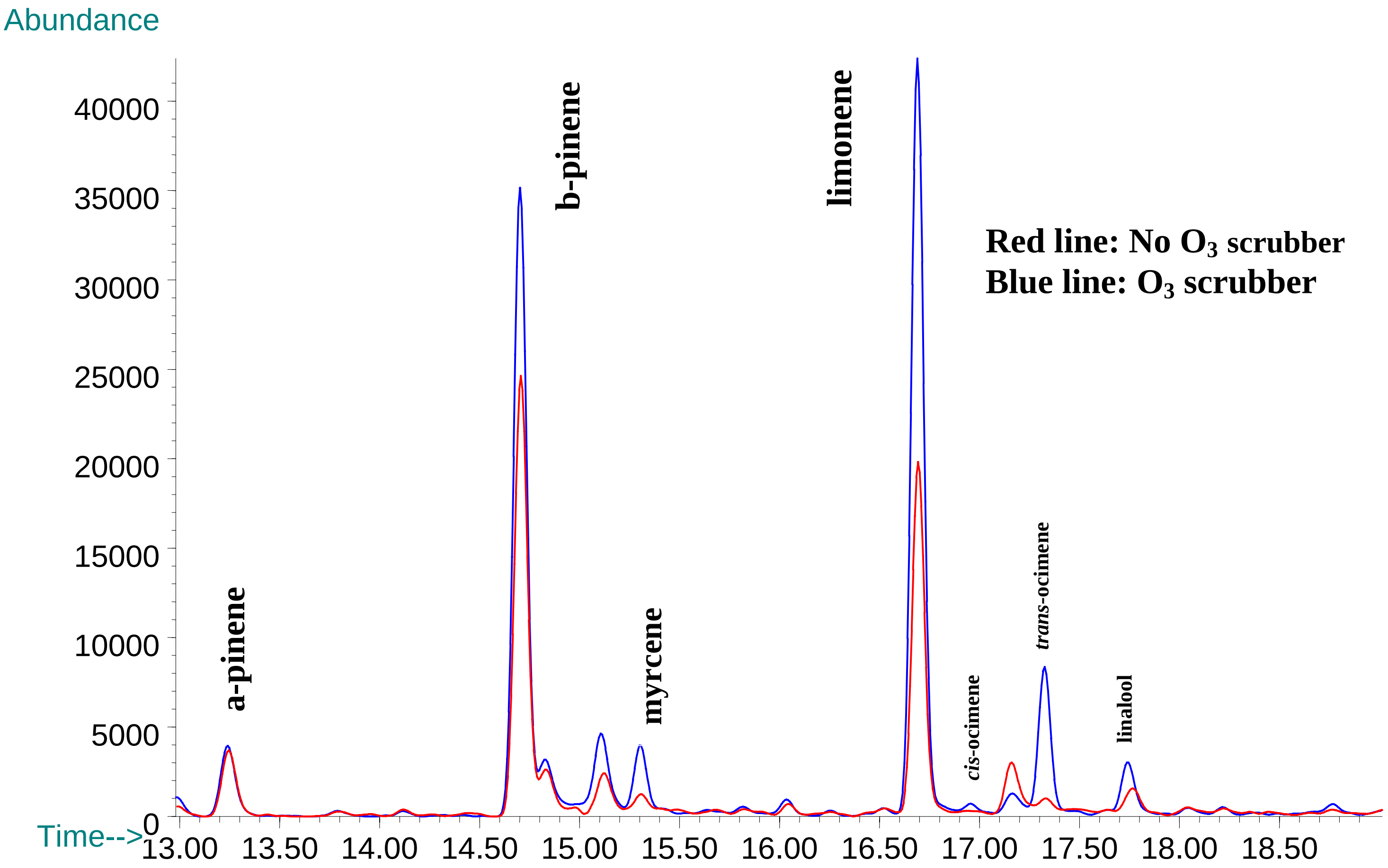
Aerosol sampling

1. Choose filter material based on type of analysis
    - quartz/glass fibre, teflon impregnated, cellulose, nucleopore
2. Determine flow, volume of air and time resolution
    - ➢ Type of sampler
3. Investigate artefacts

Possible artefacts in aerosol sampling

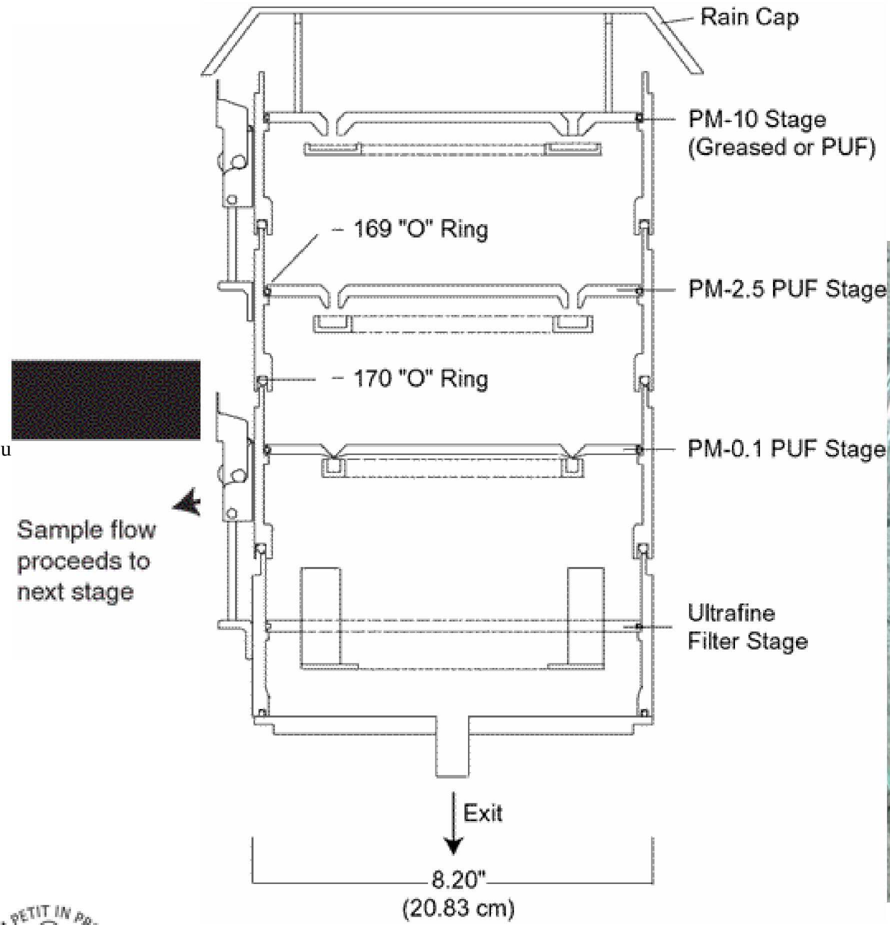
- Positive artefact
  - adsorption of gas-phase SVOC
- Negative artefact
  - desorption of particle-phase SVOC
- Reactions during sampling
  - with reactive compounds (ozone, NO_2)
  - with filter surface – quartz fibre
  - ?

Oxidation of terpenes during sampling



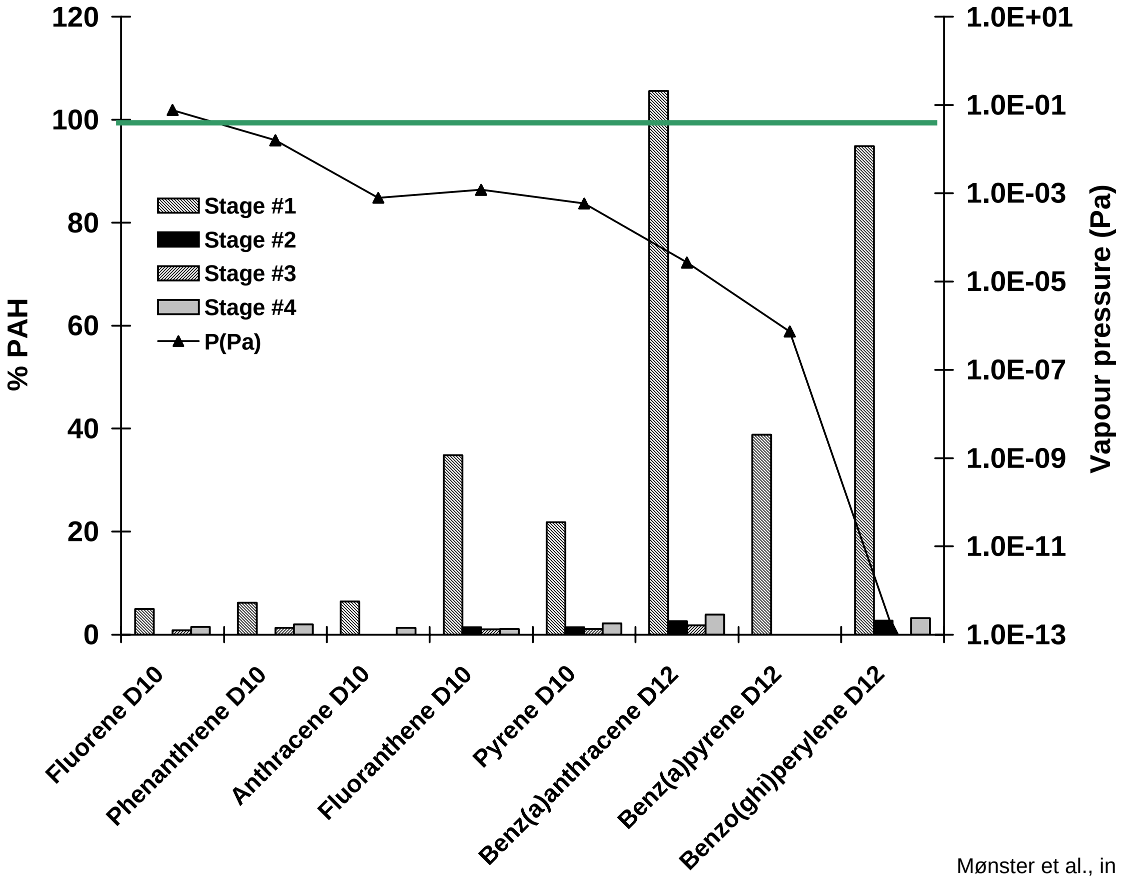
Selected-ion chromatograms of two air samples collected simultaneously: one with ozone scrubber before sorbent cartidge (upper line) and the other without ozone scrupper (lower line). From Christensen et al. (Atmos Environ, 2000).

Evaporation during sampling with an impactor



Sou [redacted]

Evaporation during sampling with an impactor



Mønster et al., in prep.

Solutions

- Positive artefact
  - Gas-phase denuder
  - Back-up filter
- Total sample
  - Filter + VOC sampling
    - absorbants: XAD / polyurethane foam
- Removal of reactive compounds e.g. ozone
  - denuder

Atmos. Chem. Phys., 7, 5711–5725, 2007
www.atmos-chem-phys.net/7/5711/2007/

Atmospheric Chemistry and Physics

Elemental and organic carbon in PM_{10}: a one year measurement campaign within the European Monitoring and Evaluation Programme EMEP

K. E. Yttri[1], W. Aas[1], A. Bjerke[1], J. N. Cape[7], F. Cavalli[6], D. Ceburnis[2], C. Dye[1], L. Emblico[3], M. C. Facchini[3], C. Forster[1], J. E. Hanssen[1], H. C. Hansson[4], S. G. Jennings[2], W. Maenhaut[5], J. P. Putaud[6], and K. Tørseth[1]

Table 3. Magnitude of the positive artefact reported for various European sites obtained using tandem filter sampling.

References	Location and season	Site category	Size fraction	Sampling time	Correction/FFV ($cm\,s^{-1}$)	Positive artifact (%)	OC ($\mu g\,m^{-3}$)
Viidanoja et al. (2002)	Helsinki (FI), 1 year	Urban	$PM_{2.5}$	24 h	QBQ/22 $cm\,s^{-1}$	17±6	3.0 (1.0–8.5)
Salma et al. (2004)	Budapest (HU), Spring	Kerbside	$PM_{2.5}$	12 h (day)	QBQ/22 $cm\,s^{-1}$	15±2%^{1}	6.8 (3.5–14) (Median)
				12 h (night)	QBQ/22 $cm\,s^{-1}$		6.9 (3.6–15) (Median)
			PM_{10}	12 h (day)	QBQ/22 $cm\,s^{-1}$	10±2%^{1}	11 (5.9–24) (Median)
				12 h (night)	QBQ/22 $cm\,s^{-1}$		11 (4.6–23) (Median)
Viana et al. (2006a)	Ghent (BE), Summer	Urban backgr.	$PM_{2.5}$	24 h	QBQ/22 $cm\,s^{-1}$	6%	2.7±0.9 (Mean)
Maenhaut et al. (2003)	Ghent (BE), Winter	Urban backgr.	$PM_{2.5}$	48–72 h	QBQ/22 $cm\,s^{-1}$	10%	5.6 (5.4–12.6) (Median)
Viana et al. (2006b)	Barcelona (ES), Summer	Urban backgr.	$PM_{2.5}$	24 h	QBQ/22 $cm\,s^{-1}$	14%	3.6±1.4 (Mean)
	Barcelona (ES), Winter					10%	6.9±2.2 (Mean)
Putaud and Cavalli, 2006	Ispra (IT), Winter	Rural backgr.	$PM_{2.5}$	24 h	QBT/22 $cm\,s^{-1}$	22±12%^{2}	7.5 (Mean)
	Ispra (IT), Summer			24 h	QBT/22 $cm\,s^{-1}$	22±7%^{2}	5.5 (Mean)

(1) Both for day and night
(2) Positive artefact as a function of TC

Extraction in solvent

- Simple
  - ultrasound
- More complicated – and time-consuming
  - soxhlet
  - accelerated solvent extraction
- Evaporation of solvent / redissolve
- Derivatisation?

Which artefacts may the extraction cause?

Chromatographic analysis

Chromatographic separation

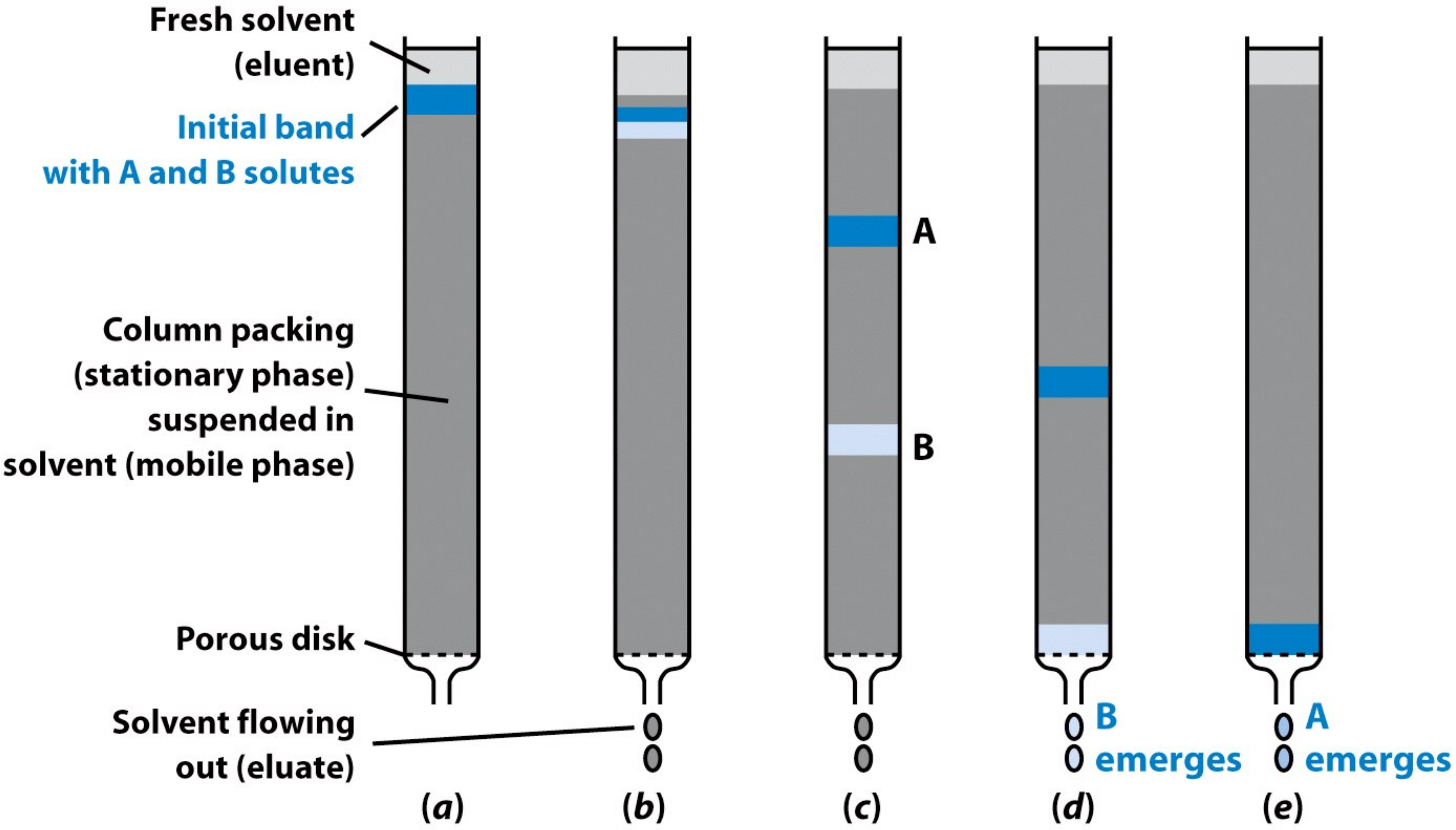


Figure 23-5
Quantitative Chemical Analysis, Seventh Edition

High Performance liquid chromatography

Solvents

Pump

Sample injection

Column oven

UV-detector

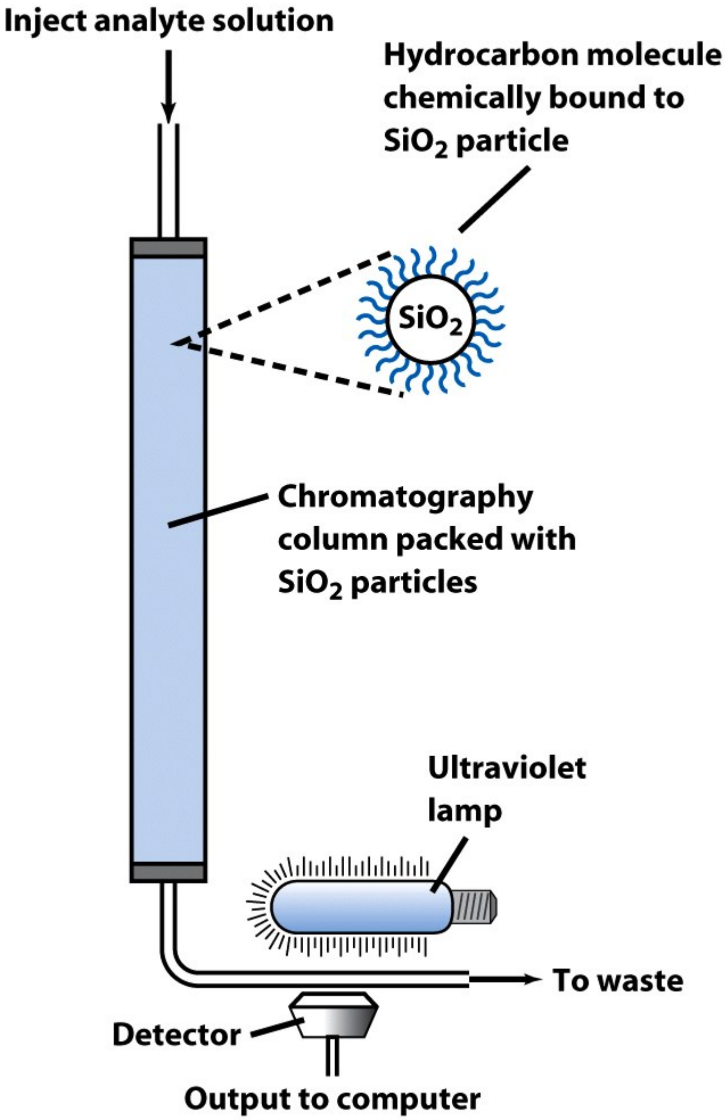


Figure 0-4a
Quantitative Chemical Analysis, Seventh Edition

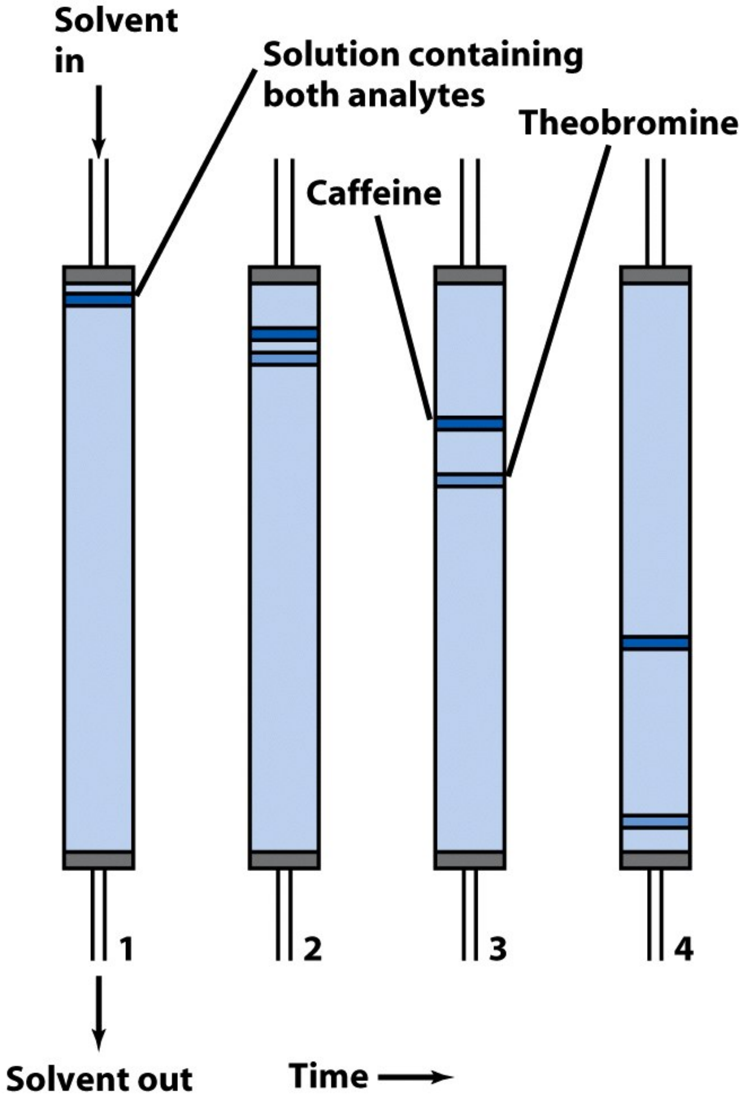
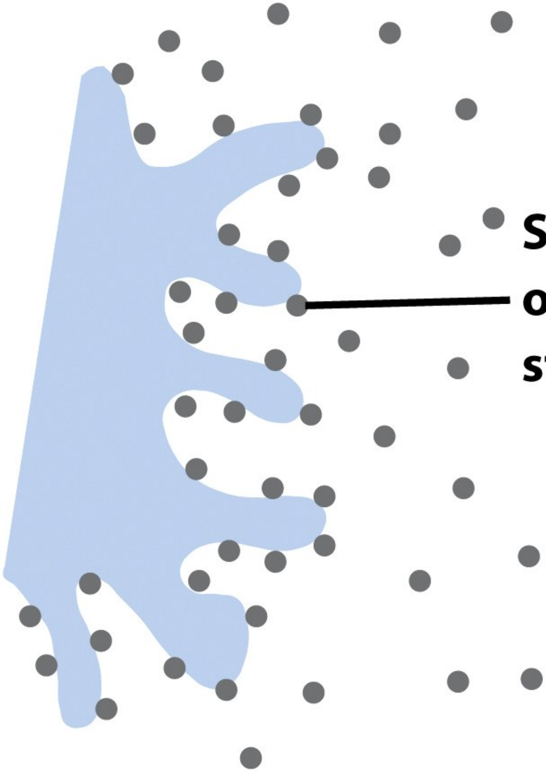


Figure 0-4b
Quantitative Chemical Analysis, Seventh Edition

Inside an HPLC column

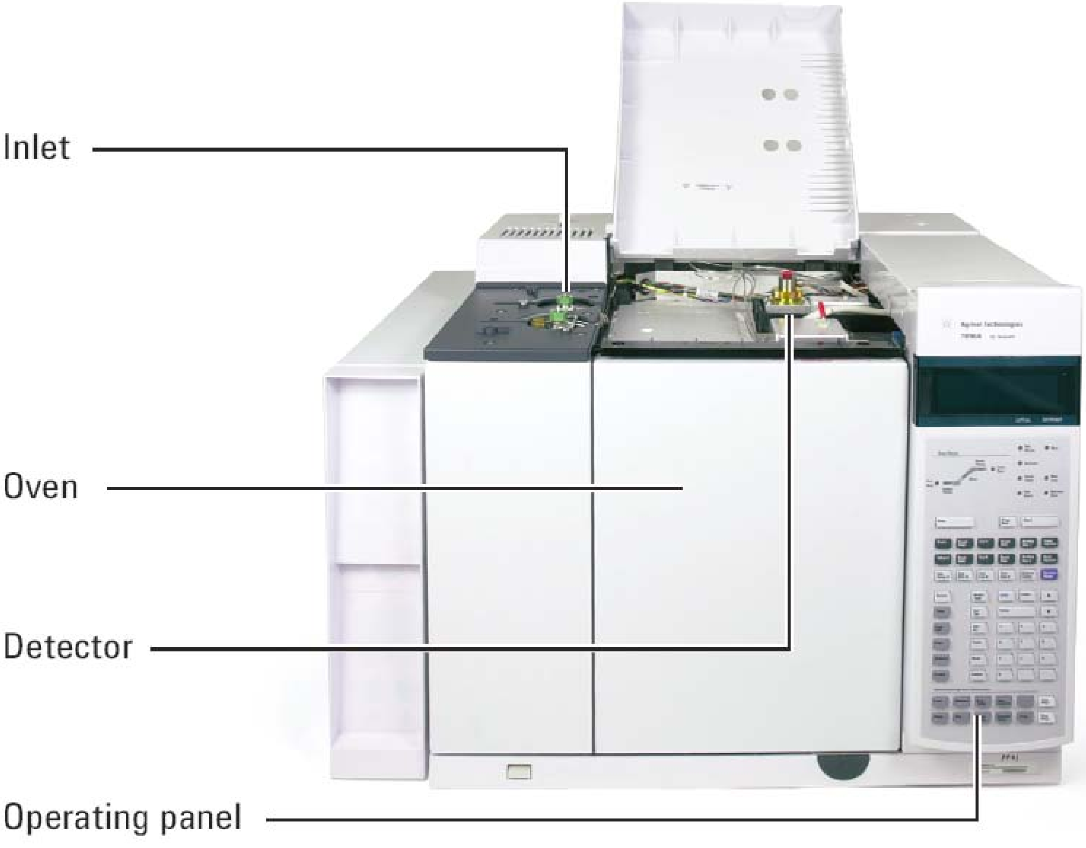


Solute adsorbed on surface of stationary phase

Adsorption chromatography

Figure 23-6 part 1
Quantitative Chemical Analysis, Seventh Edition

Gas chromatography



Components in a GC-FID system

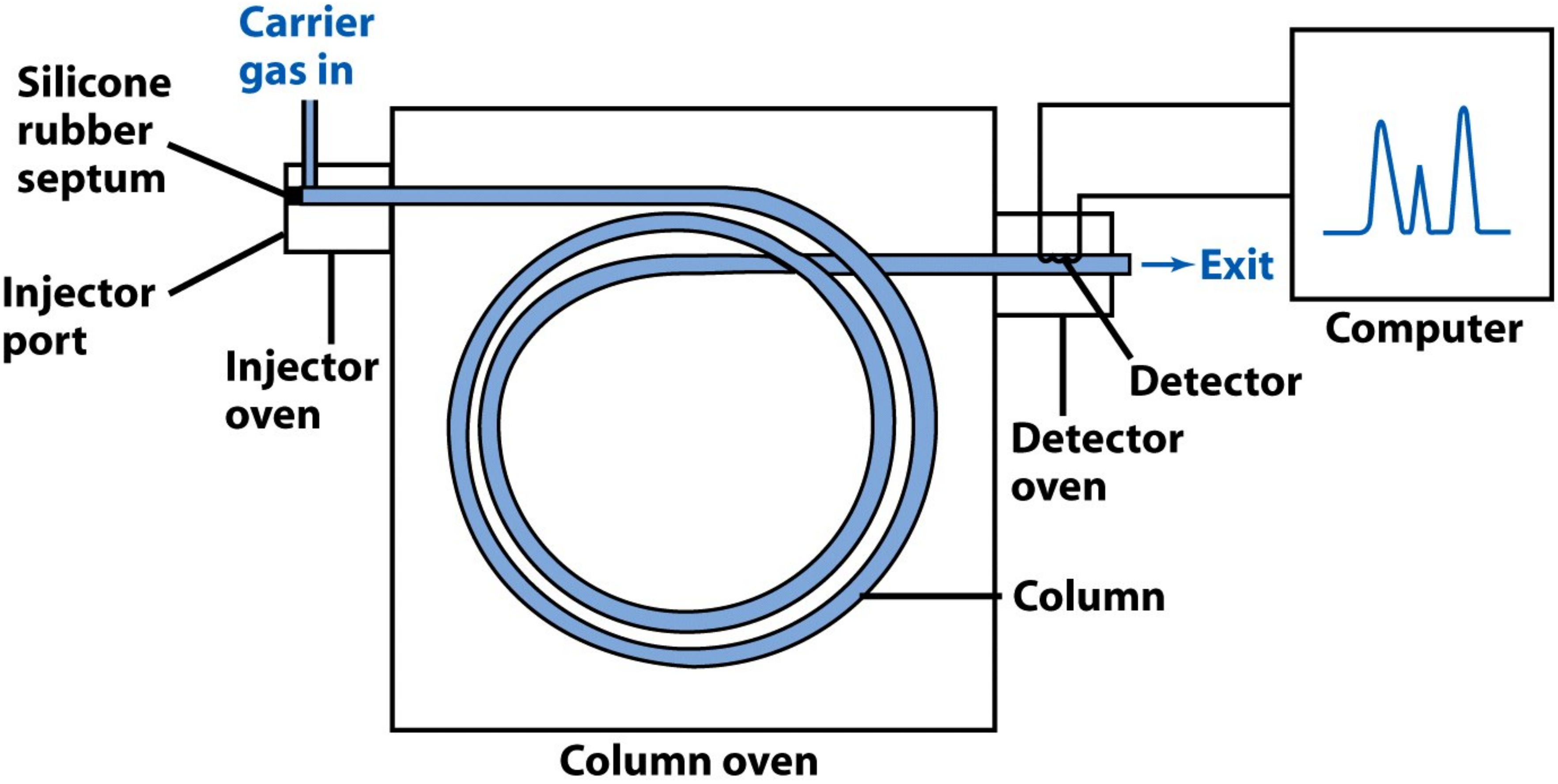


Figure 24-1
Quantitative Chemical Analysis, Seventh Edition

Cross-section of a GC-column

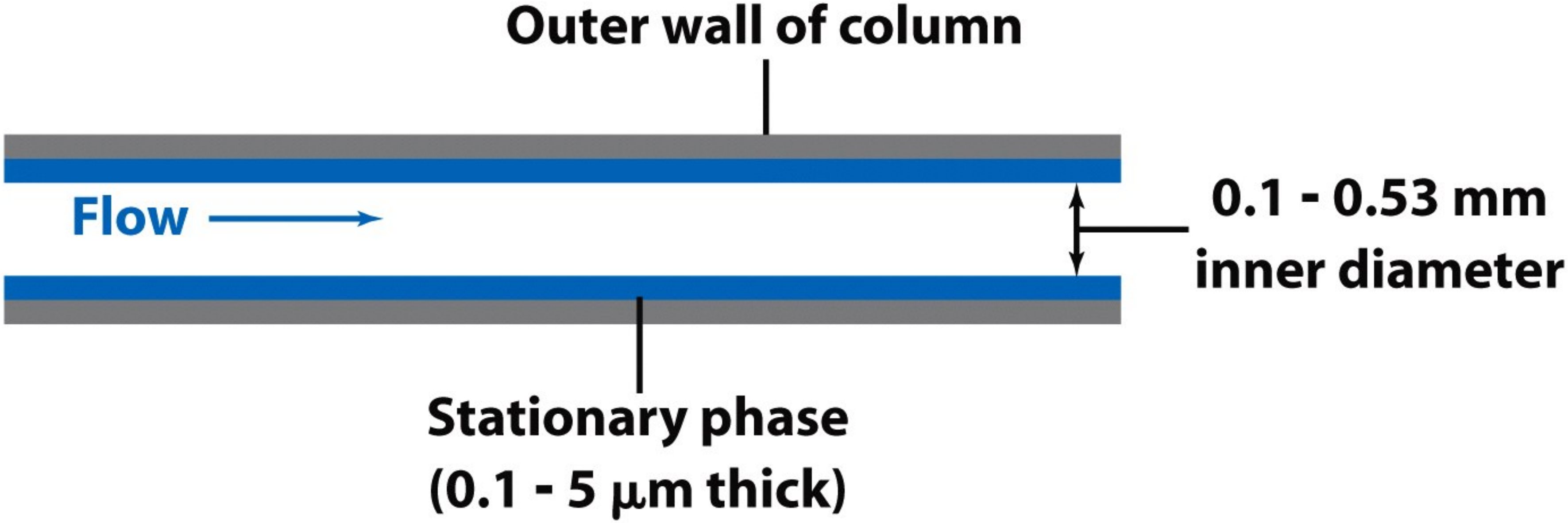


Figure 24-2a
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Length typically 30 m (15-100)

Inside a GC-column

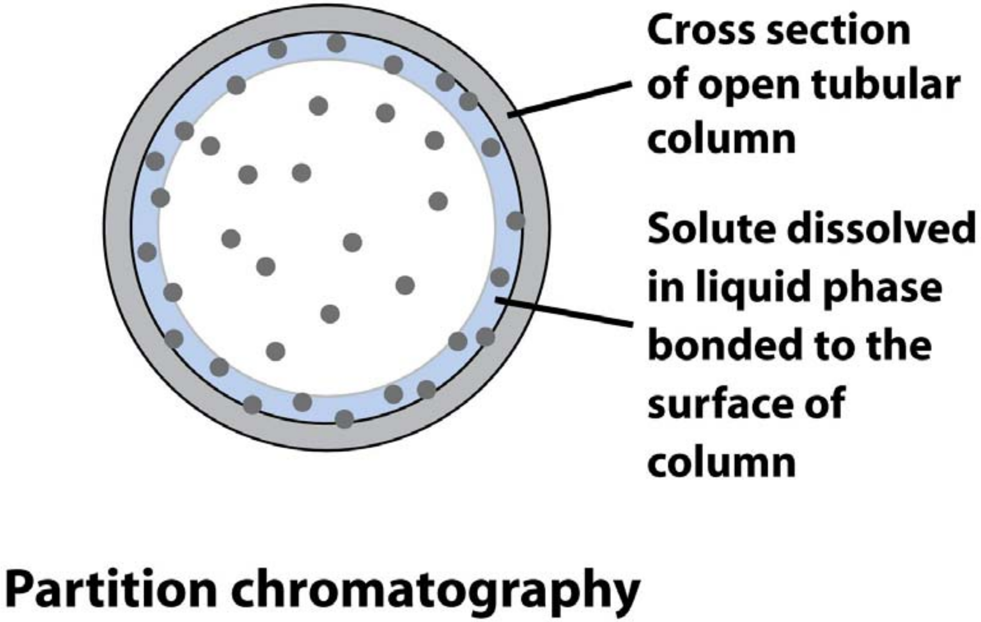

Figure 23-6 part 2
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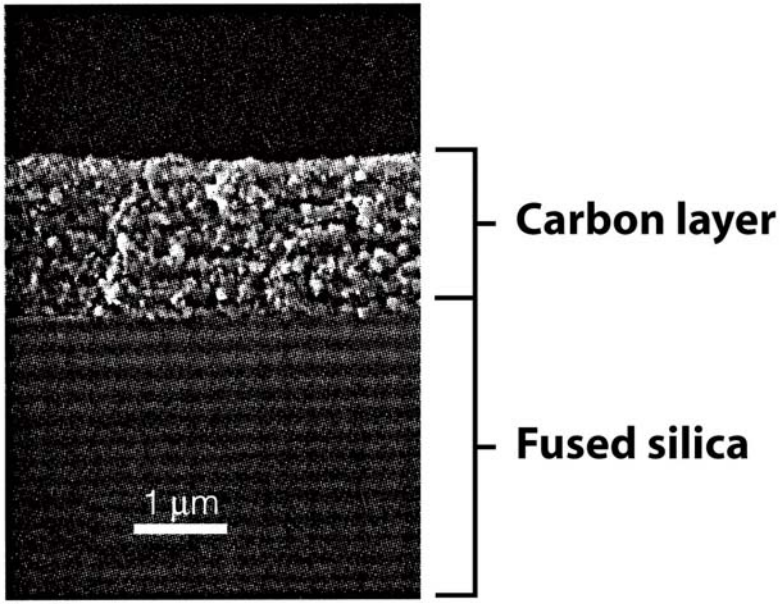

Figure 24-3a
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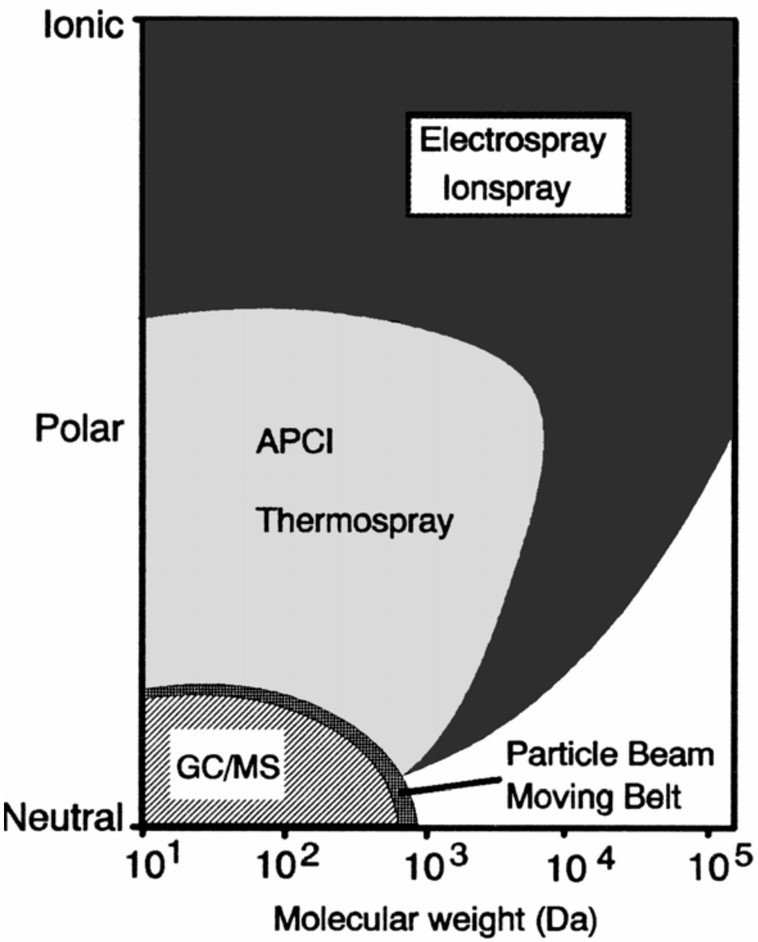
Which type of analysis for which molecule?



De Hoffmann, Charette and Stroobant: Mass spectrometry, prnciples and applications,Wiley, 1996.

Electrospray ionization

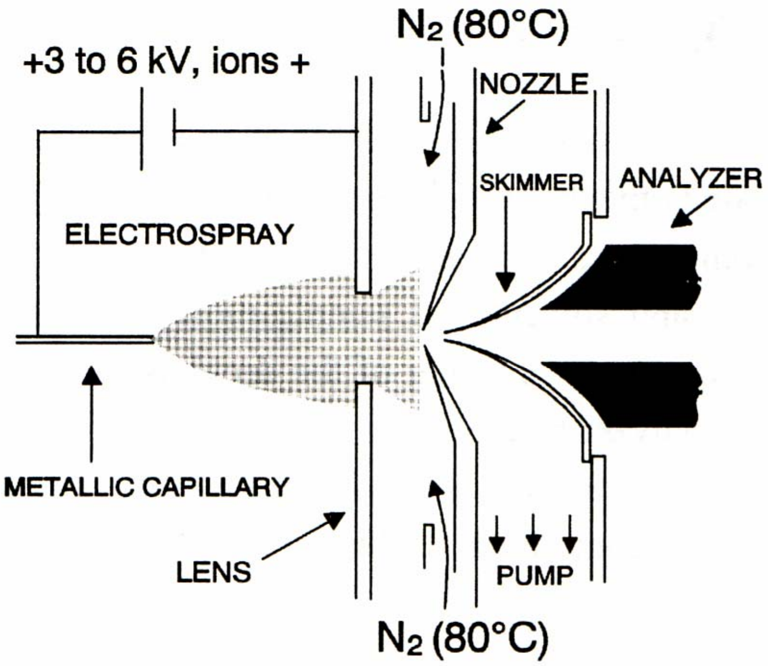
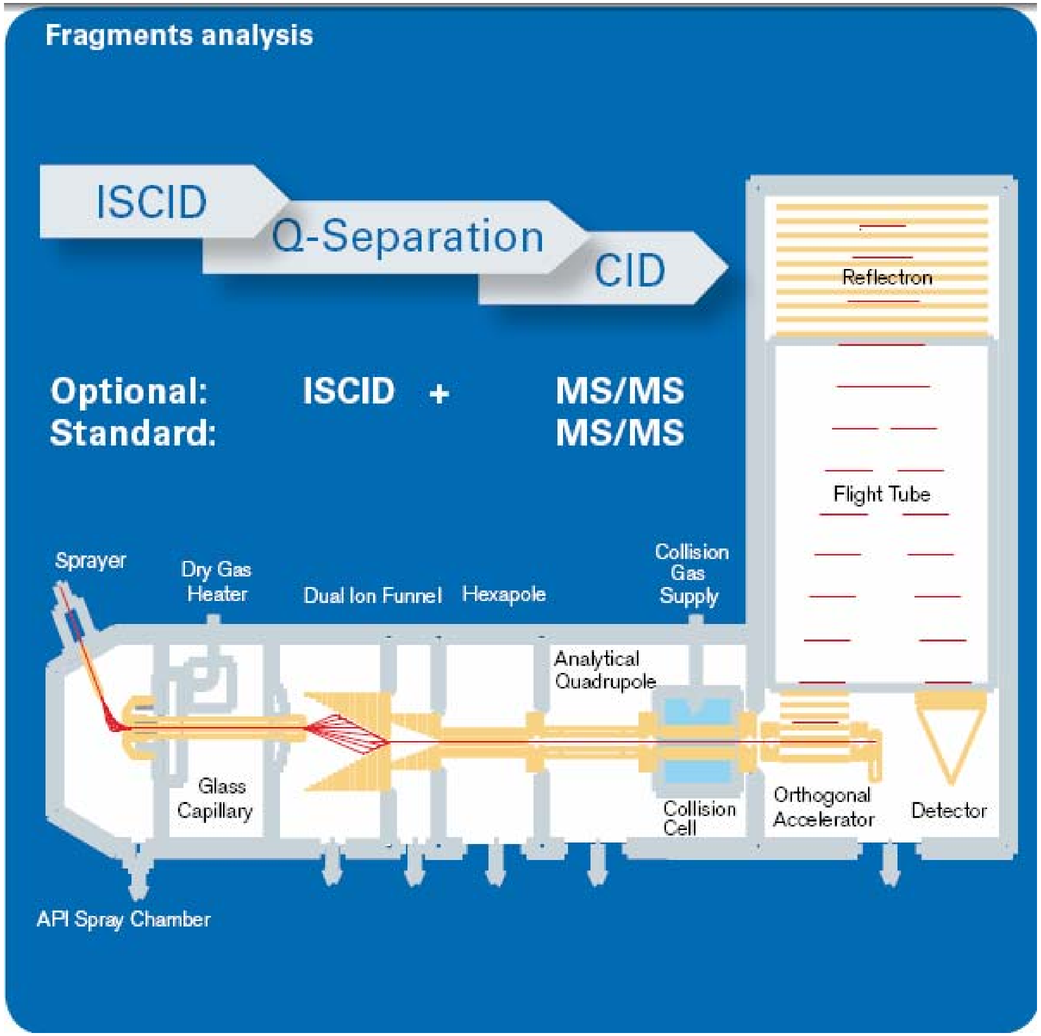


Figure 1.14: Diagram of an electrospray source [24] .

De Hoffmann, Charette and Stroobant: Mass spectrometry, prnciples and applications,Wiley, 1996.

Q-TOF-MS


Fragments analysis
ISCID
Q-Separation
CID
Optional: ISCID + MS/MS
Standard: MS/MS
Reflectron
Flight Tube
Sprayer
Dry Gas Heater
Dual Ion Funnel
Hexapole
Collision Gas Supply
Analytical Quadrupole
Glass Capillary
Collision Cell
Orthogonal Accelerator
Detector
API Spray Chamber

GC-MS Selected Ion Monitoring

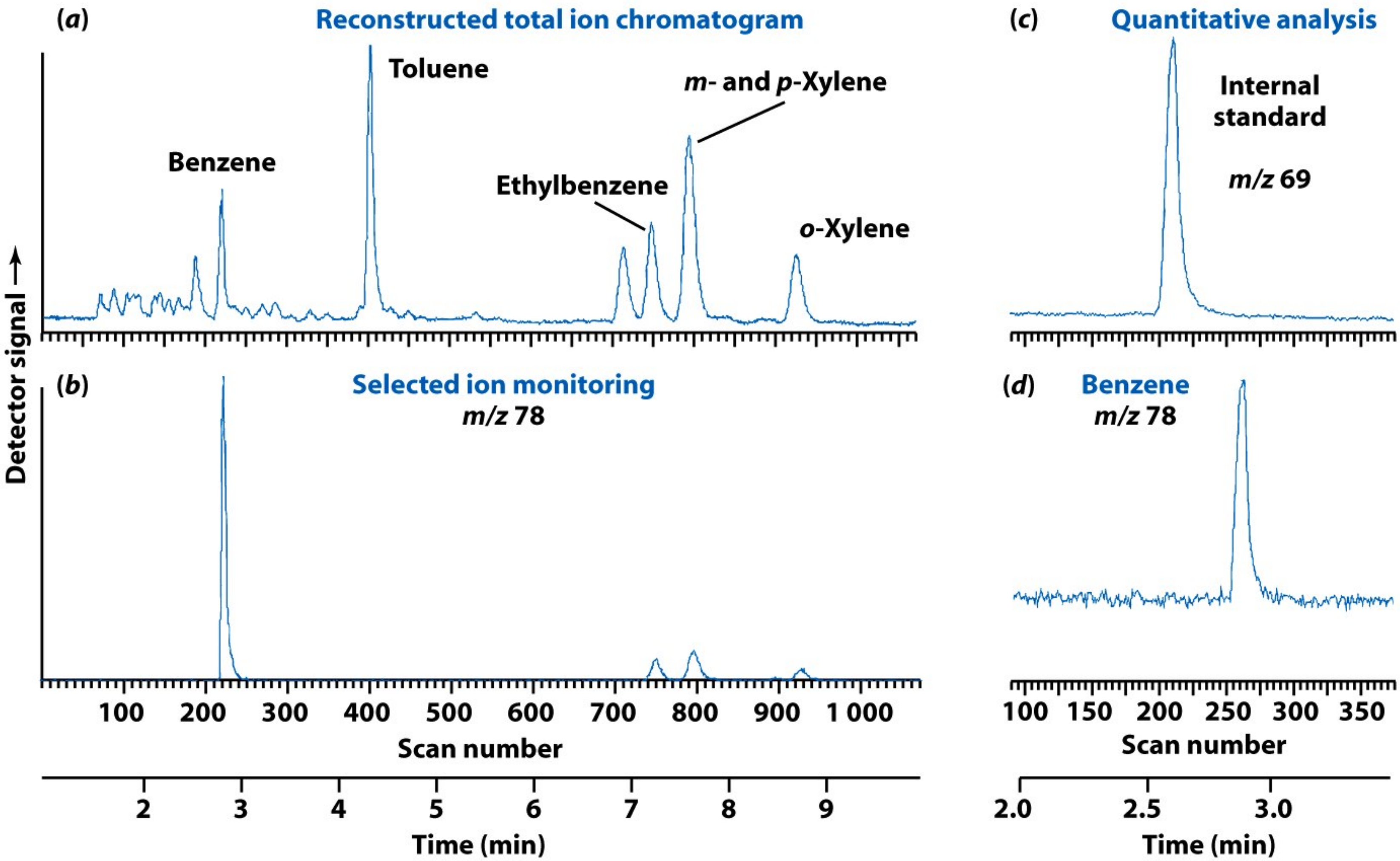


Figure 24-21
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HPLC-MS

- **Analysis of organic acids in particles from oxidation of α-pinene**

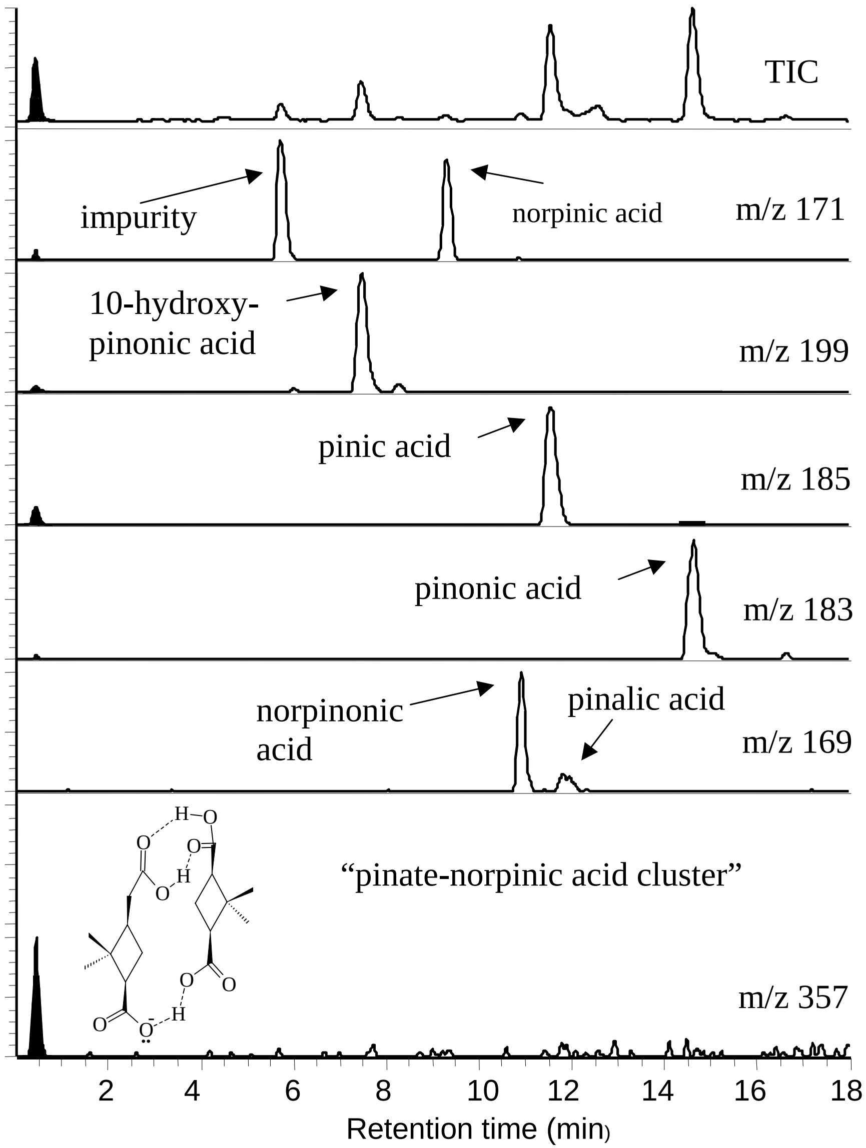

Figure 4. HPLC-ESI-MS chromatograms (TIC and extracted ions) of carboxylic acids in SOA from gas phase oxidation of α-pinene with ozone. Black peaks at 30 s derive from post column flow injection.

Glasius et al., EST, 2000

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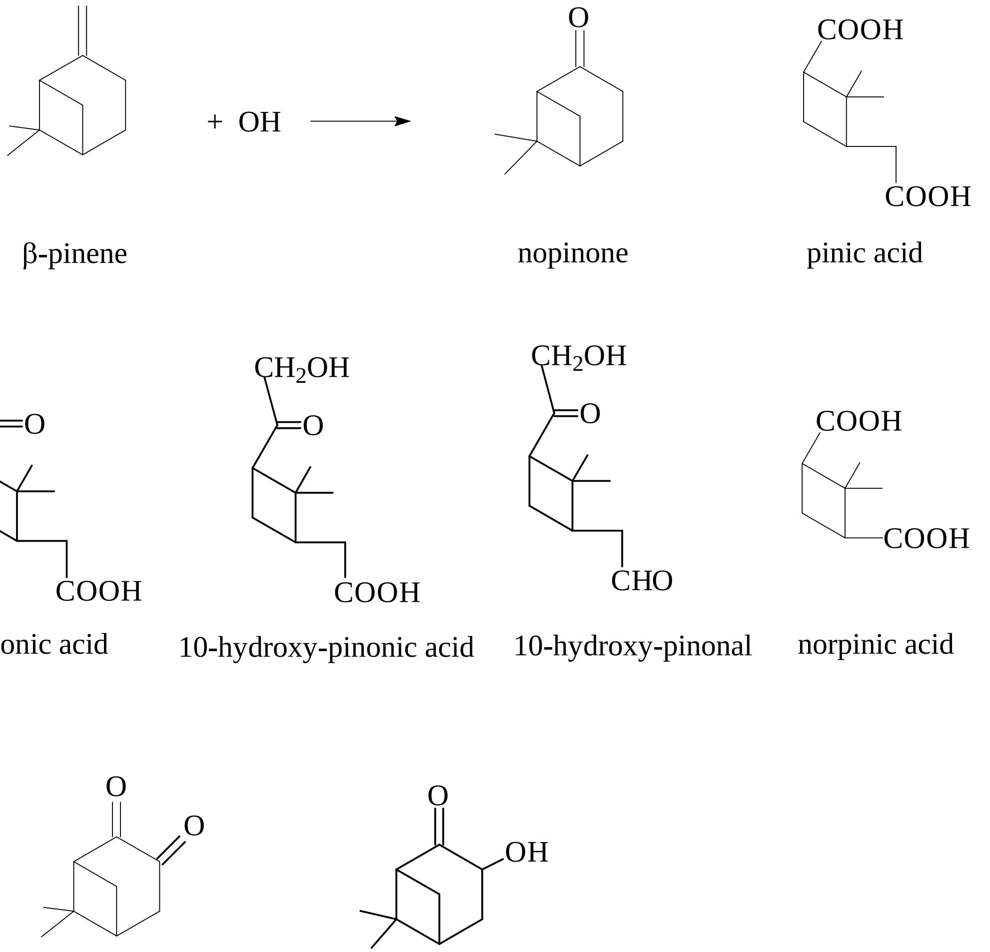
Identification of oxidation products



β-pinene

nopinone

pinic acid

pinonic acid

10-hydroxy-pinonic acid

10-hydroxy-pinonal

norpinic acid

3-oxo-nopinone

2-hydroxy-nopinone

Glasius et al., EST, 2000

Hyphenated LCxLC-MS

- Simultaneous separation on two HPLC columns with different properties
- Here ion-exclusion and C18

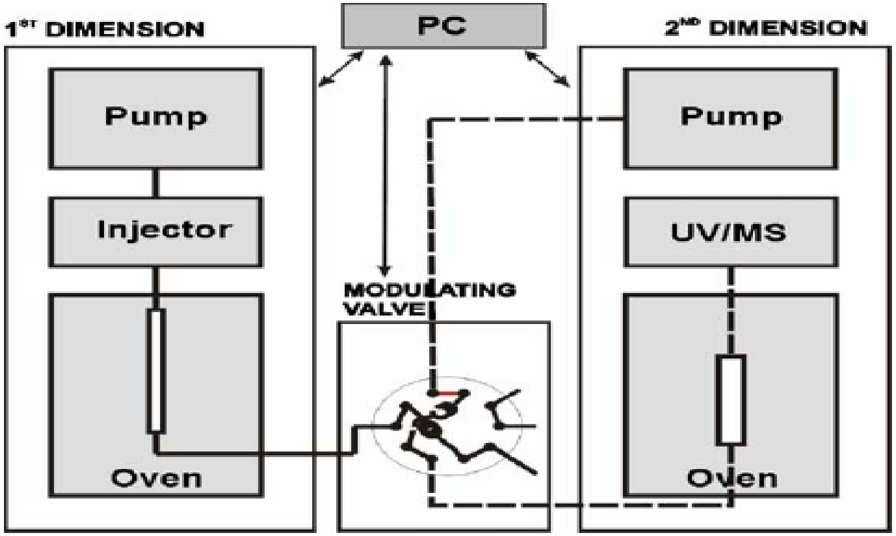


Fig. 1. LC × LC consisted of two LC modules, modulating valve with two sampling loops attached, and additional TOF-MS detector.

J. Pól et al. / J. Chromatogr. A 1130 (2006) 64–71

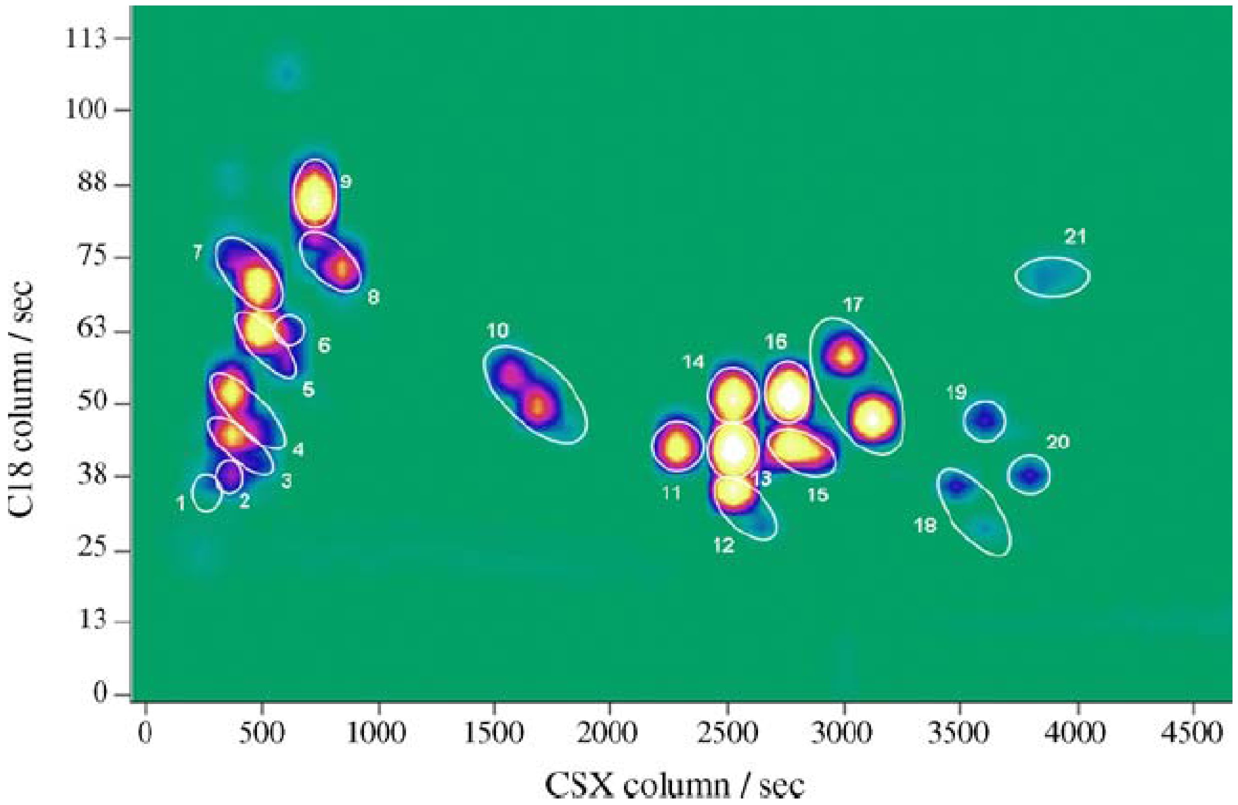
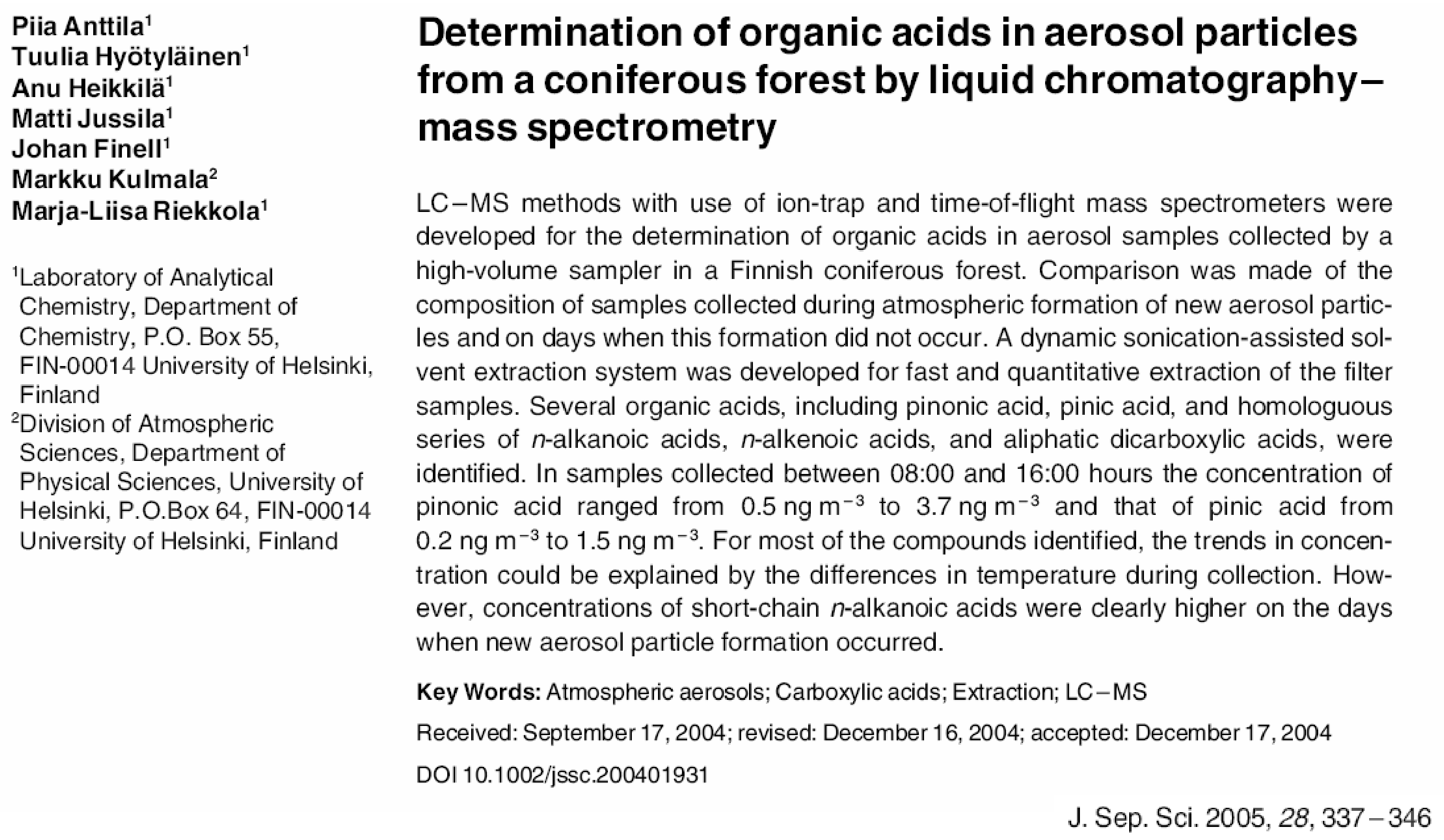


Fig. 3. Contour plot of two-dimensional LC separation of standard mixture of carboxylic acids. (1) Tartaric acid, (2) pimelic acid, (3) pinic acid, (4) suberic acid, (5) pinonic acid, (6) azelaic acid, (7) 4-ketopimelic acid, (8) sebacic acid, (9) azelaic acid, (10) impurity (*m*/*z* = 201.1), (11) impurity (*m*/*z* = 215.1), (12) 2-phenoxybenzoic acid, (13) tetradecanedioic acid, (14) citronellic acid, (15) hexadecanedioic acid, (16) capric acid, (17) lauric acid, (18) impurity (*m*/*z* = 339.2), (19) impurity (*m*/*z* = 225.2), (20) palmitic acid, (21) stearic acid.

J. Pól et al. / J. Chromatogr. A 1130 (2006) 64–71



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Determination of organic acids in aerosol particles from a coniferous forest by liquid chromatography–mass spectrometry

LC–MS methods with use of ion-trap and time-of-flight mass spectrometers were developed for the determination of organic acids in aerosol samples collected by a high-volume sampler in a Finnish coniferous forest. Comparison was made of the composition of samples collected during atmospheric formation of new aerosol particles and on days when this formation did not occur. A dynamic sonication-assisted solvent extraction system was developed for fast and quantitative extraction of the filter samples. Several organic acids, including pinonic acid, pinic acid, and homologuous series of *n*-alkanoic acids, *n*-alkenoic acids, and aliphatic dicarboxylic acids, were identified. In samples collected between 08:00 and 16:00 hours the concentration of pinonic acid ranged from 0.5 ng m^{-3} to 3.7 ng m^{-3} and that of pinic acid from 0.2 ng m^{-3} to 1.5 ng m^{-3}. For most of the compounds identified, the trends in concentration could be explained by the differences in temperature during collection. However, concentrations of short-chain *n*-alkanoic acids were clearly higher on the days when new aerosol particle formation occurred.

Key Words: Atmospheric aerosols; Carboxylic acids; Extraction; LC–MS

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DOI 10.1002/jssc.200401931

J. Sep. Sci. 2005, *28*, 337–346

Table 1. Compounds identified by LC-TOFMS in aerosol samples.

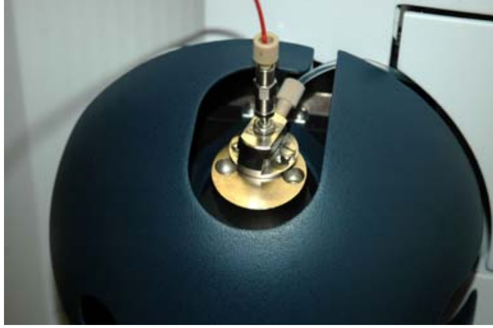
M nominal	RT [min]	[M–H] measured	[M–H] calculated	Δ [mDa]	Δ [ppm]	Molecular formula	Compound
186	24.3	185.08320	185.08084	–2.36	–12.75	$C_9H_{14}O_4$	Pinic acid[a),b)]
184	27.6	183.10480	183.10157	–3.23	–17.64	$C_{10}H_{16}O_3$	Pinonic acid[a),b)]
188	31.1	187.09906	187.09649	–2.57	–13.74	$C_9H_{16}O_4$	*n*-Nonanedioic acid[a)]
202	34.4	201.11446	201.11214	–2.32	–11.54	$C_{10}H_{18}O_4$	*n*-Decanedioic acid[a)]
130	36.4	129.09040	129.09101	0.61	4.73	$C_7H_{14}O_2$	*n*-Heptanoic acid[c)]
216	38.5	215.12934	215.12779	–1.55	–7.21	$C_{11}H_{20}O_4$	*n*-Undecanedioic acid[c)]
144	40.6	143.10696	143.10666	–0.30	–2.10	$C_8H_{16}O_2$	*n*-Octanoic acid[b)]
230	40.8	229.14491	229.14477	–0.14	–0.61	$C_{12}H_{22}O_4$	*n*-Dodecanedioic acid[c)]
244	43.7	243.15976	243.15909	–0.67	–2.76	$C_{13}H_{24}O_4$	*n*-Tridecanedioic acid[c)]
158	44.4	157.12237	157.12231	–0.06	–0.38	$C_9H_{18}O_2$	*n*-Nonanoic acid[b)]
170	46.1	169.12083	169.12231	1.48	8.75	$C_{10}H_{18}O_2$	*n*-Decenoic acid[c)]
258	47.4	257.17652	257.17474	–1.78	–6.92	$C_{14}H_{26}O_4$	*n*-Tetradecanedioic acid[c)]
172	47.8	171.13892	171.13796	–0.96	–5.61	$C_{10}H_{20}O_2$	*n*-Decanoic acid[b)]
184	47.8	183.13570	183.13796	2.26	12.34	$C_{11}H_{20}O_2$	*n*-Undecenoic acid[c)]
198	49.1	197.15367	197.15361	–0.06	–0.30	$C_{12}H_{22}O_2$	*n*-Dodecenoic acid[c)]
186	49.4	185.15550	185.15361	–1.89	–10.21	$C_{11}H_{22}O_2$	*n*-Undecanoic acid[b)]
212	50.1	211.16910	211.16926	0.16	0.76	$C_{13}H_{24}O_2$	*n*-Tridecenoic acid[c)]
200	51.4	199.16995	199.16926	–0.69	–3.46	$C_{12}H_{24}O_2$	*n*-Dodecanoic acid[b)]
226	52.2	225.18511	225.18491	–0.20	–0.89	$C_{14}H_{26}O_2$	*n*-Tetradecenoic acid[c)]
214	52.4	213.18642	213.18491	–1.51	–7.08	$C_{13}H_{26}O_2$	*n*-Tridecanoic acid[b)]
240	53.3	239.20138	239.20056	–0.82	–3.43	$C_{15}H_{28}O_2$	*n*-Pentadecenoic acid[c)]
228	53.5	227.20081	227.20056	–0.25	–1.10	$C_{14}H_{28}O_2$	*n*-Tetradecanoic acid[b)]
254	54.2	253.21679	253.21621	–0.58	–2.29	$C_{16}H_{30}O_2$	*n*-Hexadecenoic acid[c)]
242	54.5	241.21700	241.21621	–0.79	–3.28	$C_{15}H_{30}O_2$	*n*-Pentadecanoic acid[b)]
280	53.9	279.23193	279.23186	–0.07	–0.25	$C_{18}H_{32}O_2$	*n*-Octadecadienoic acid
256	55.3	255.23145	255.23186	0.41	1.61	$C_{16}H_{32}O_2$	*n*-Hexadecanoic acid[b)]
282	55.6	281.24735	281.24751	0.16	0.57	$C_{18}H_{34}O_2$	*n*-Octadecenoic acid[c)]

Chemical analysis of particle samples at AU

- The organic composition is analysed by advanced analytical methods
  - HPLC-Q-TOF-MS and MALDI-TOF-MS
  - Sources to carbon in particles
    - manmade/natural
    - biomass/fossil fuel combustion
    - sea/land sources

- To improve understanding of the interaction between sources, particles and climate

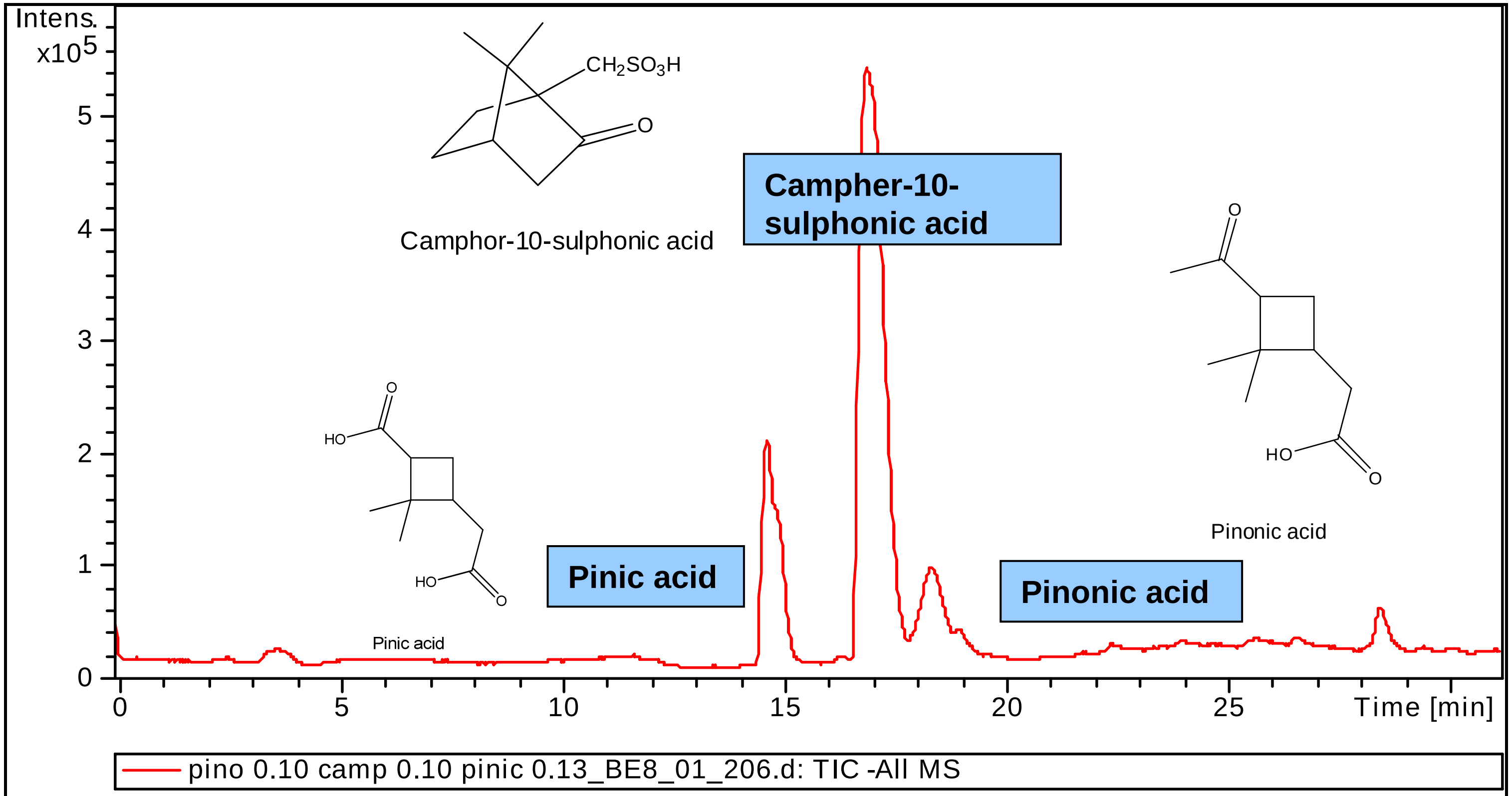
High-performance liquid chromatography quadrupol time-of-flight mass spectrometry (HPLC-Q-TOF MS)



1. Particle collection on filter
2. Extraction in methanol (ultrasound)
3. Evaporation of solvent and redissolve in methanol/water
4. Analysis with HPLC-Q-TOF with ESI inlet

   Mass range: 50-40,000 m/z

   Accuracy: <3 ppm deviation (internal cal.)


Intens.
x10^5
5
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10
15
20
25
Time [min]
CH2SO3H
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Camphor-10-sulphonic acid
Campher-10-sulphonic acid
O
HO
HO
O
Pinic acid
Pinic acid
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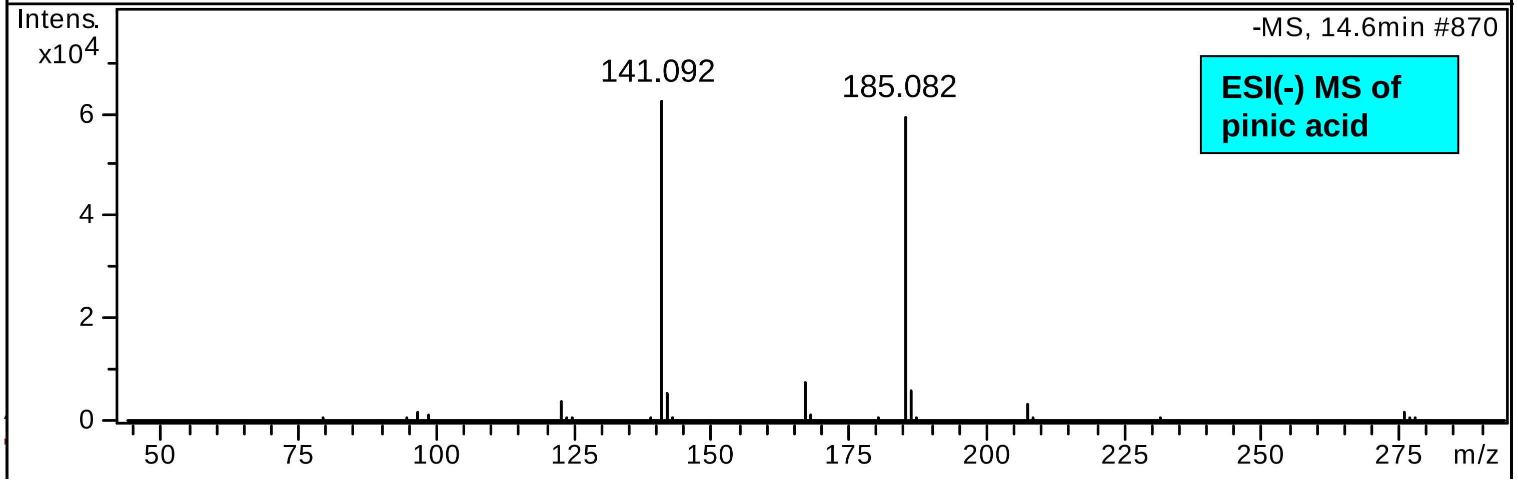
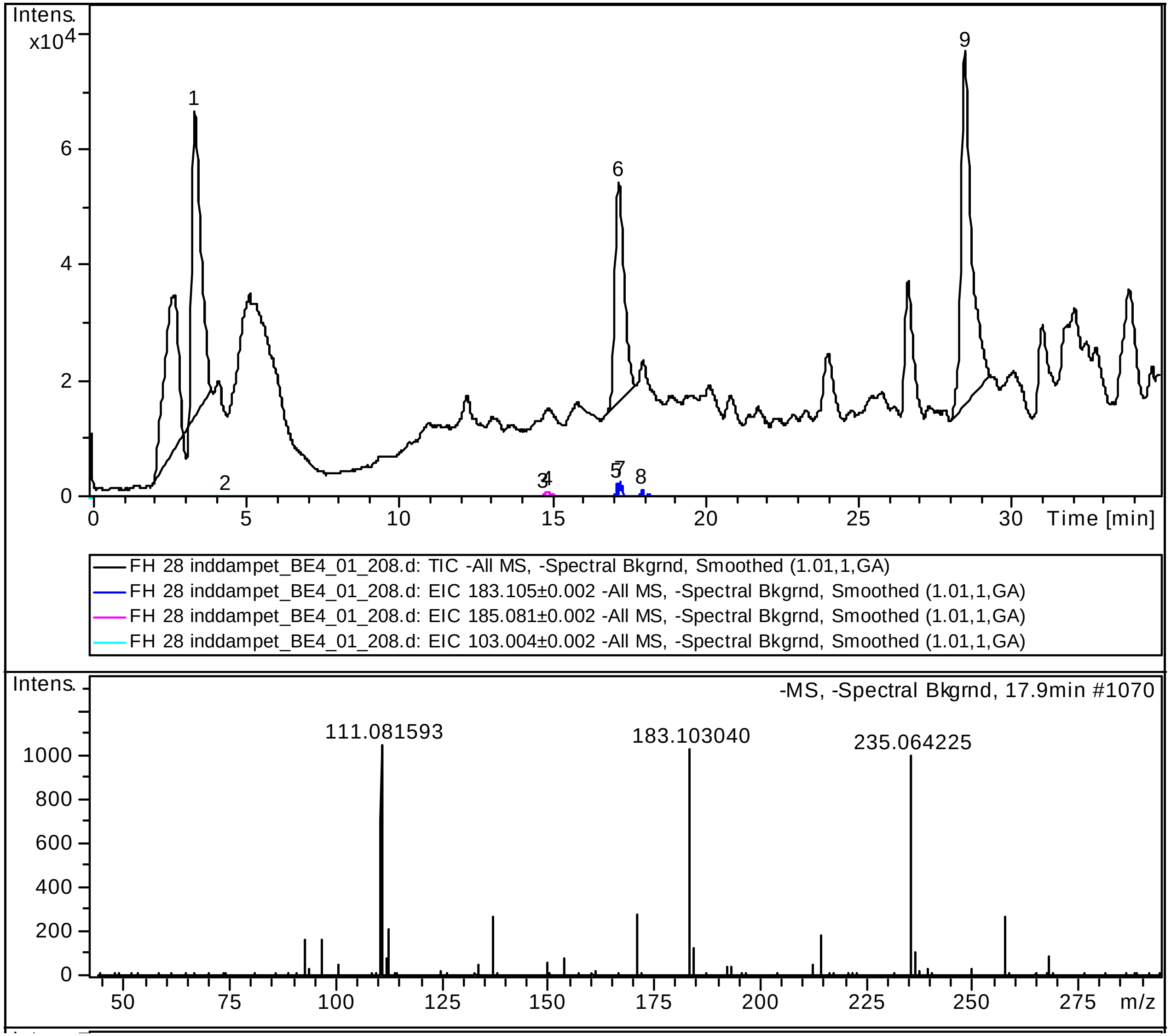
Pinonic acid
Pinonic acid
pino 0.10 camp 0.10 pinic 0.13_BE8_01_206.d: TIC -All MS


Intens.
x10^4
6
4
2
0
-MS, 14.6min #870
141.092
185.082
ESI(-) MS of pinic acid
50
75
100
125
150
175
200
225
250
275
m/z

Analysis of aerosol from a forest



Sources to fine particles in air

- **Globally**
  - **Natural fires, volcanoes**
  - **Ocean**
  - **Combustion of biomass and fossil fuels**
  - **Secondary formation from gases**

- **Danish direct emissions**
  1. **Wood combustion for heating**
  2. **Traffic**

Danish PM$_{2.5}$ emissions

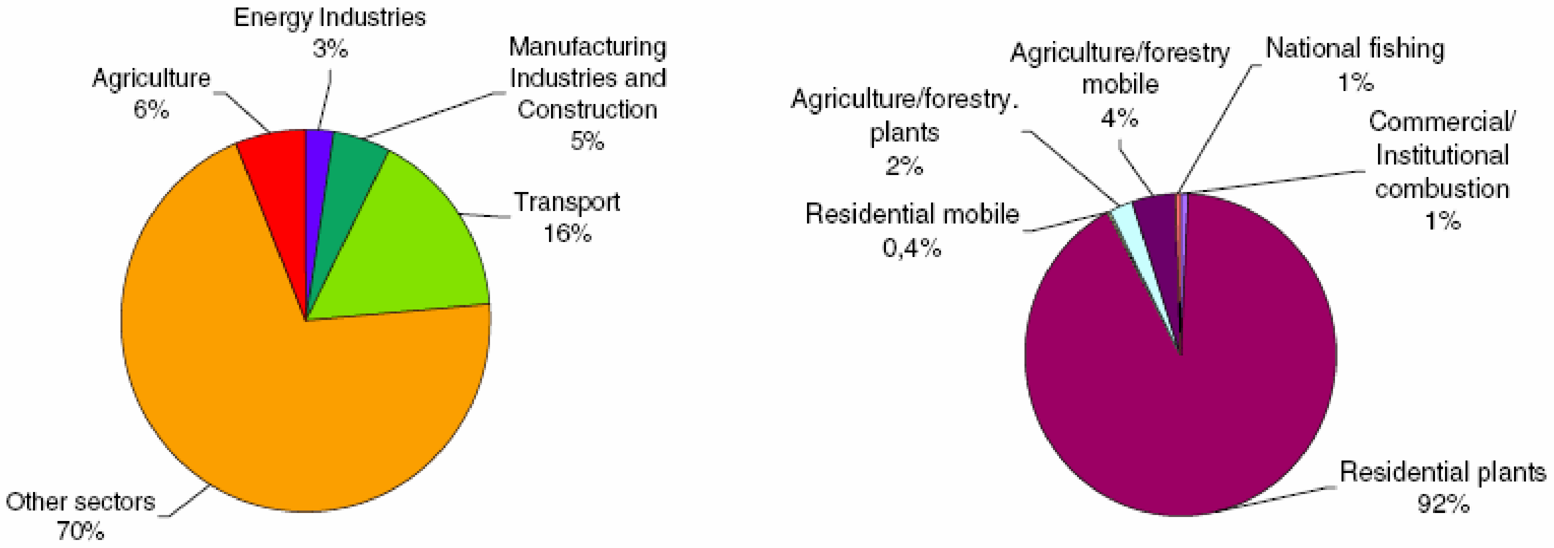
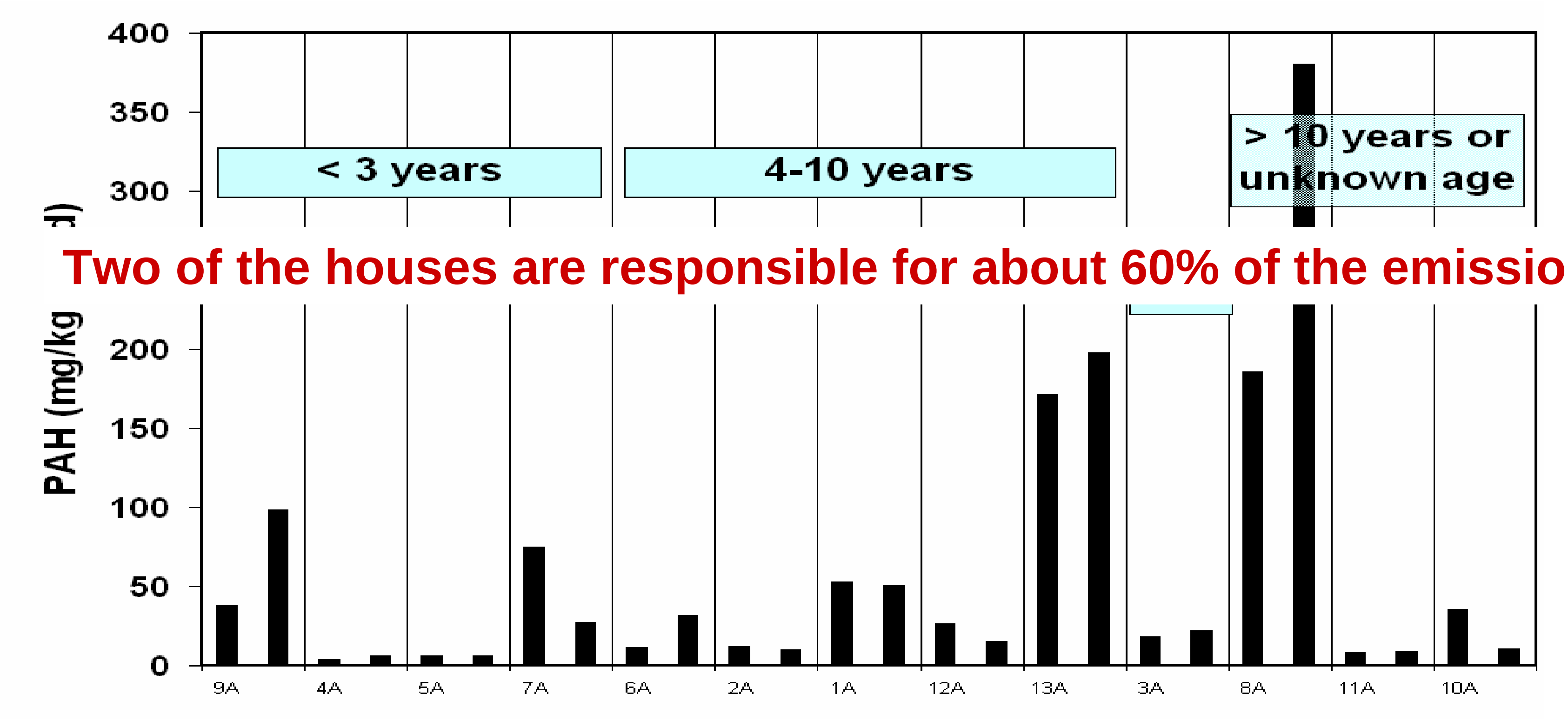


Figure 2.9 PM$_{2.5}$ emissions. Distribution by main sector and on sub-sectors for other fuels combustion for 2006.

Emissions of PAH - 2005



Two of the houses are responsible for about 60% of the emissions!

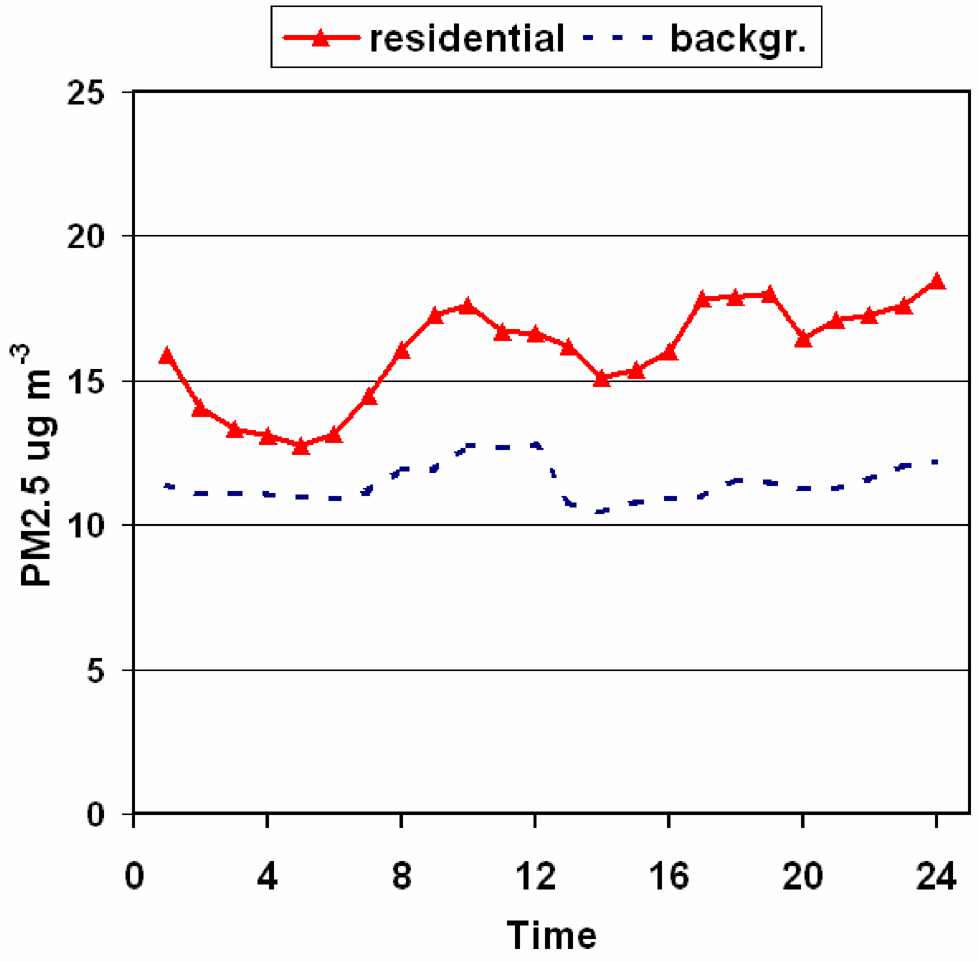
Composition of wood smoke

- Combustion of wood results in:
- **Ash** - mainly inorganic salts
- **Gases** - mainly volatile organic compounds
  - CO and a variety of hydrocarbons
- **Particles/soot** - elemental carbon and organic compounds
  - such as polycyclic aromatic compounds (PAH) and levoglucosan (tracer of wood combustion)

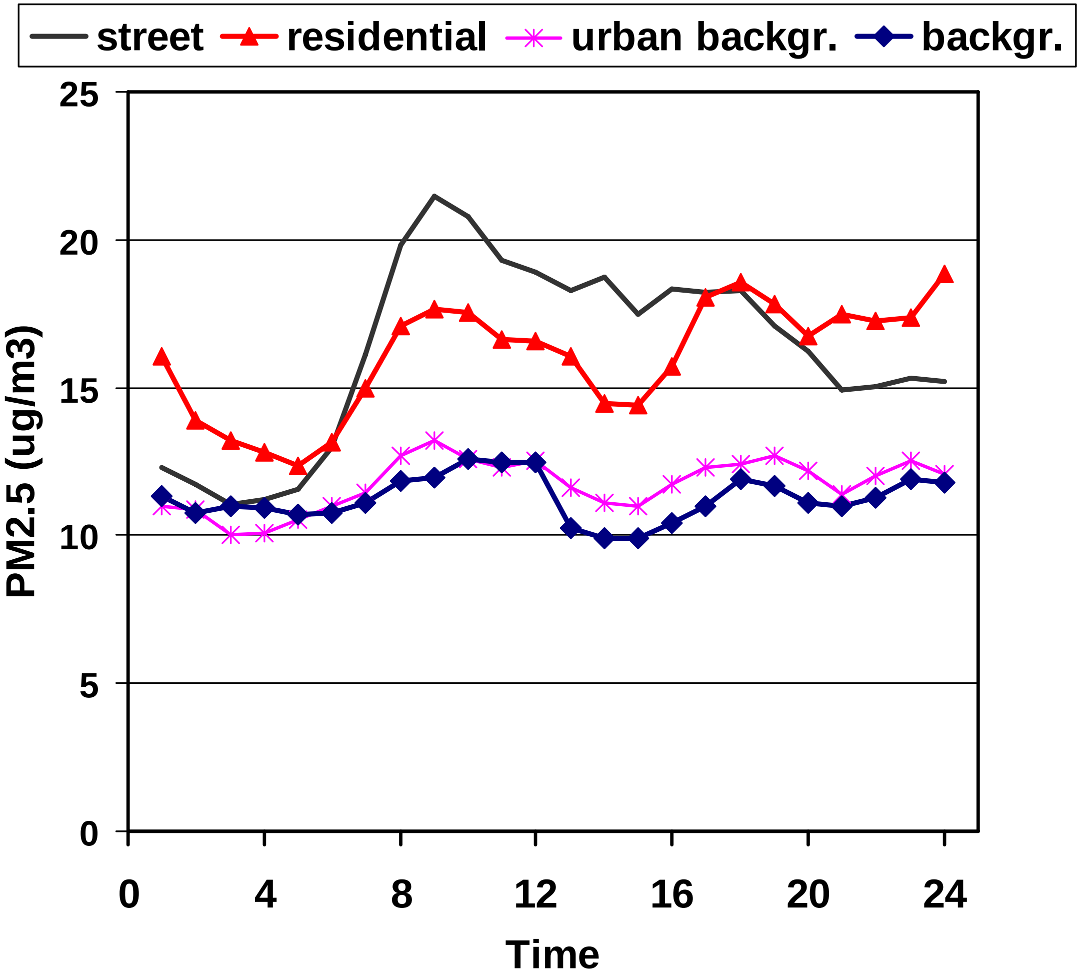
Ambient measurement campaigns 1.

- Small town with about 2500 inhabitants app. 30 km west of Copenhagen.
- Measurements in area with adjoined rows of houses.
- No district heating or natural gas in immediate area.

Winter diurnal $PM_{2.5}$ averages



Winter diurnal $PM_{2.5}$ averages

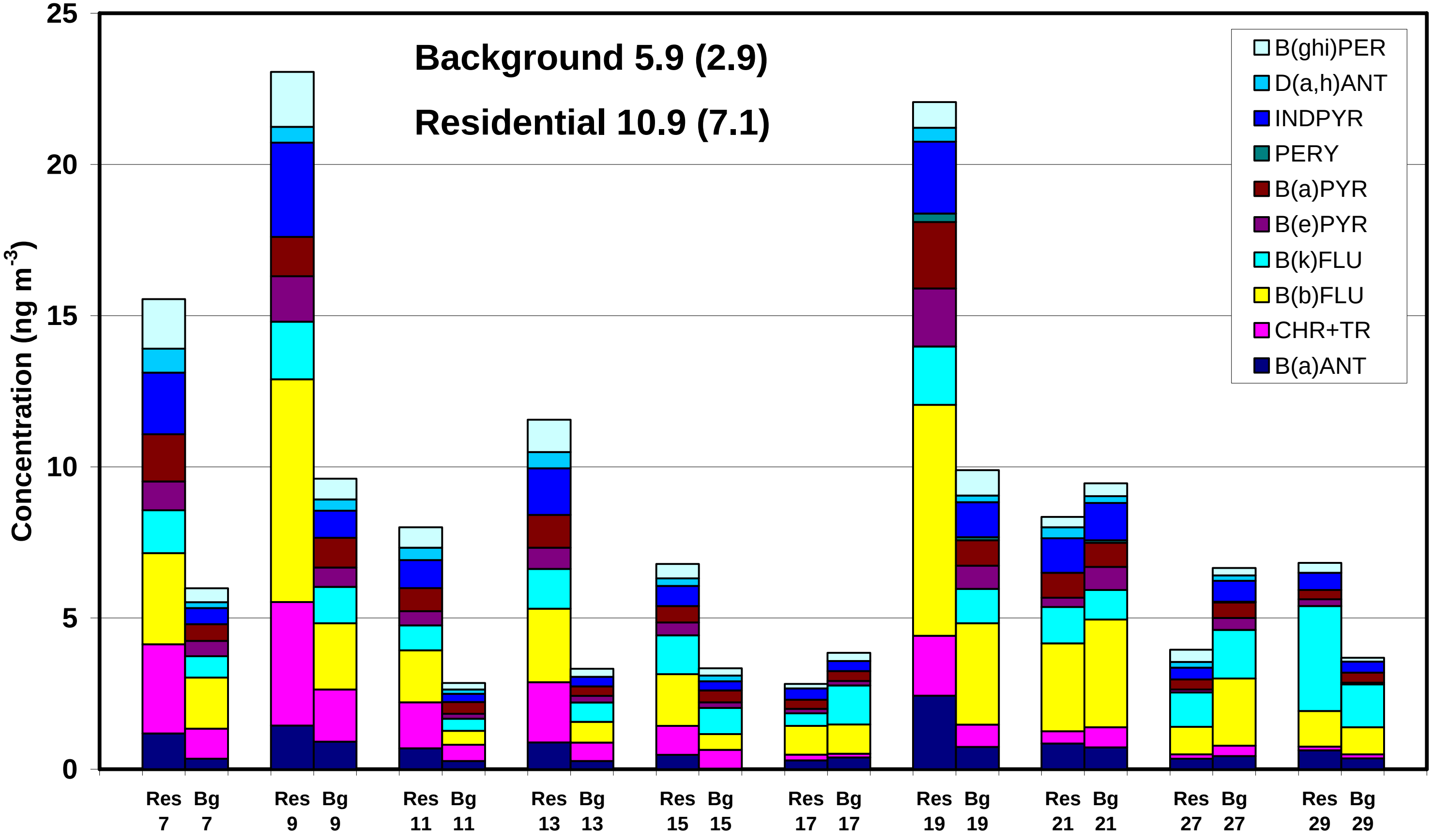


Glasius et al., Atmos. Environ. 2006

Ambient measurements area 2

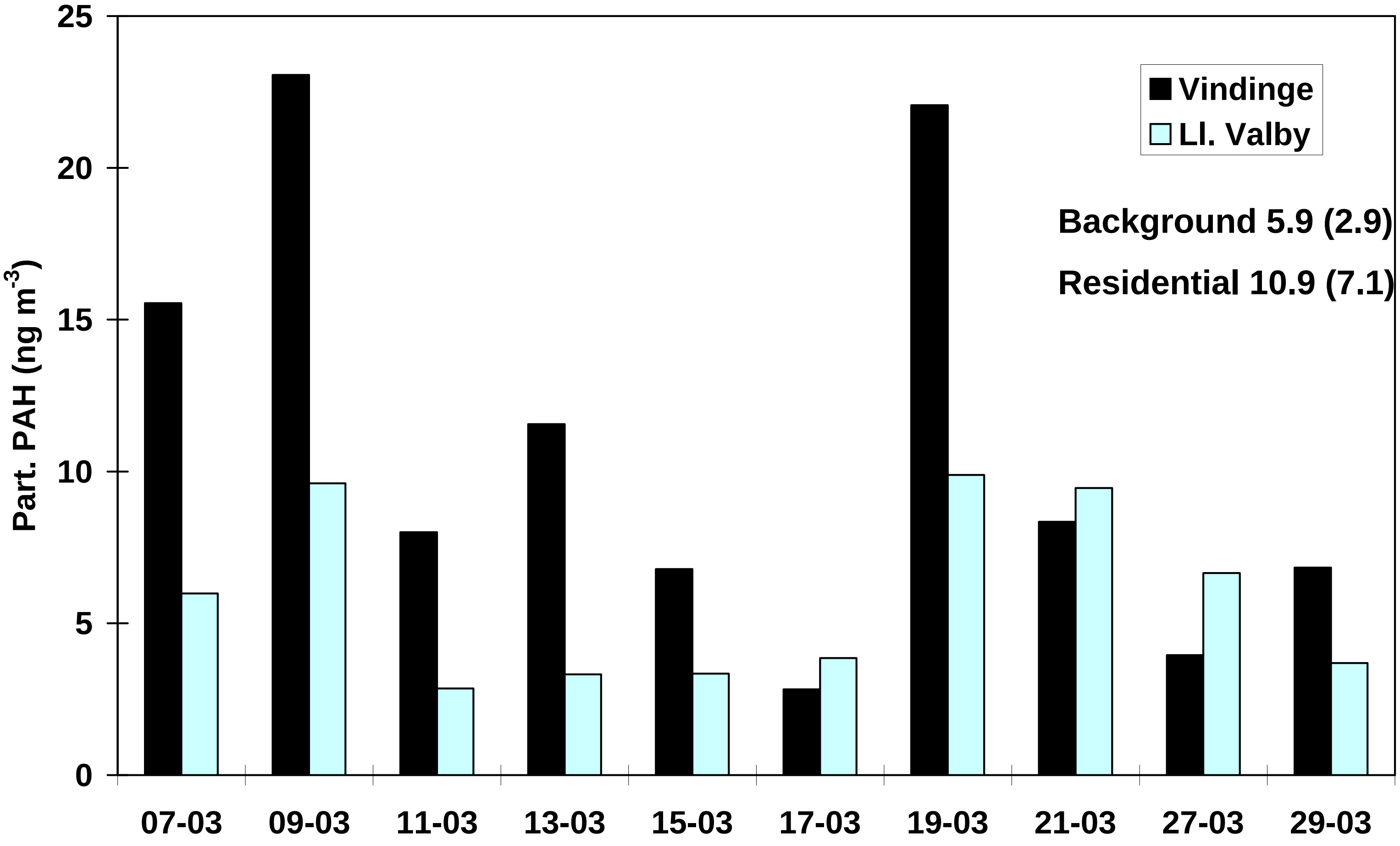
- Another small town (Vindinge)
- Area with detached houses.
- Primarily heating by combustion of natural gas (60-80 %).
- Active woodstoves in about on fourth of the houses.

PAH in evening samples from residential and background areas



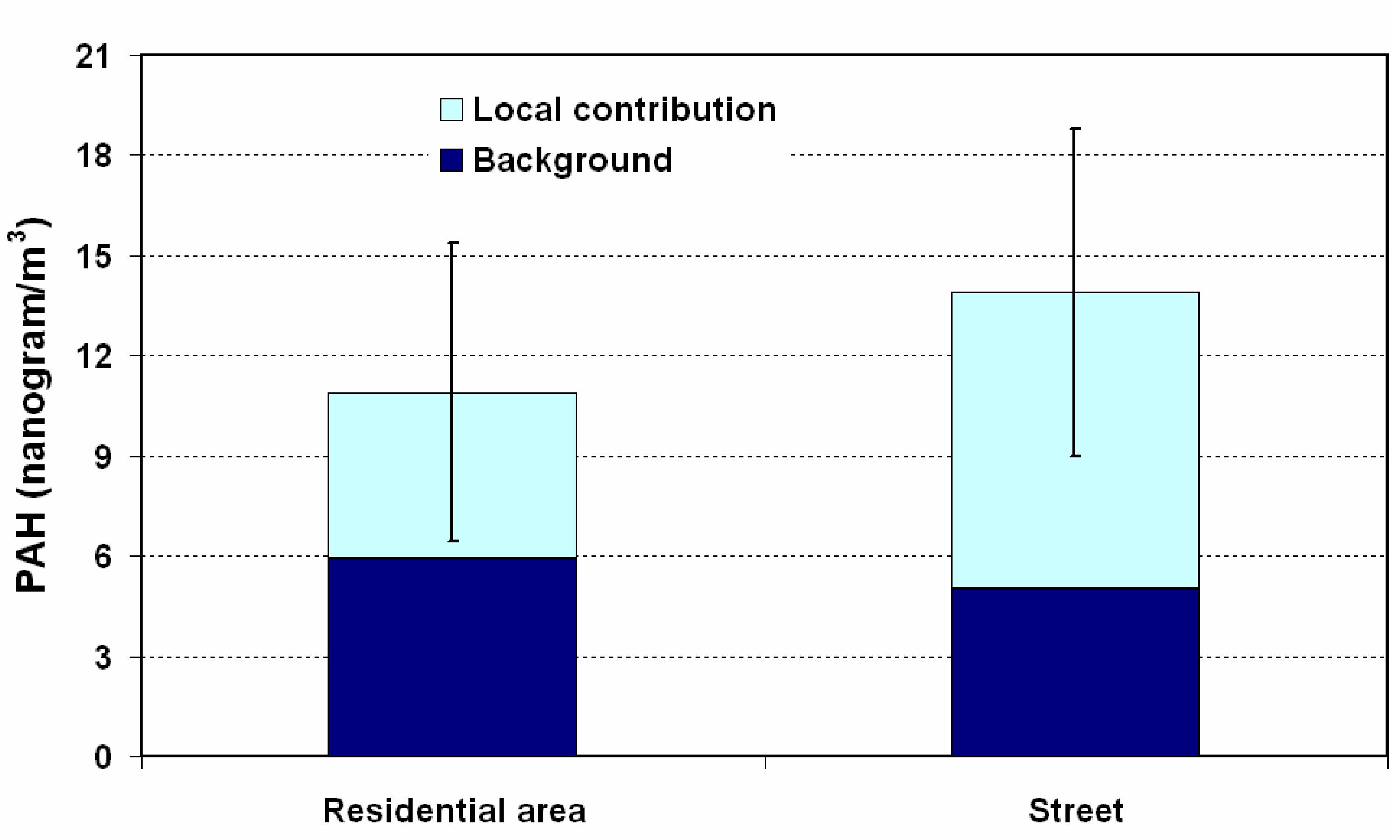
Glasius et al., Atmos. Environ. 2008, accepted

PAH in evening samples from residential and background areas



Glasius et al., Atmos. Environ. 2008, accepted

Particulate PAH - comparison of area 2 and street level



Levoglucosan - tracer of cellulose

- Levoglucosan (and mannosan) are monosaccharide anhydrides
  - formed during combustion of cellulose and hemicellulose.
- specific organic tracers of combustion of wood and paper.
- Stable (?), particulate compounds
- Average contribution to $PM_{2.5}$ (evening and night)
  - 1.6 % in background area
  - 3.7 % in residential area

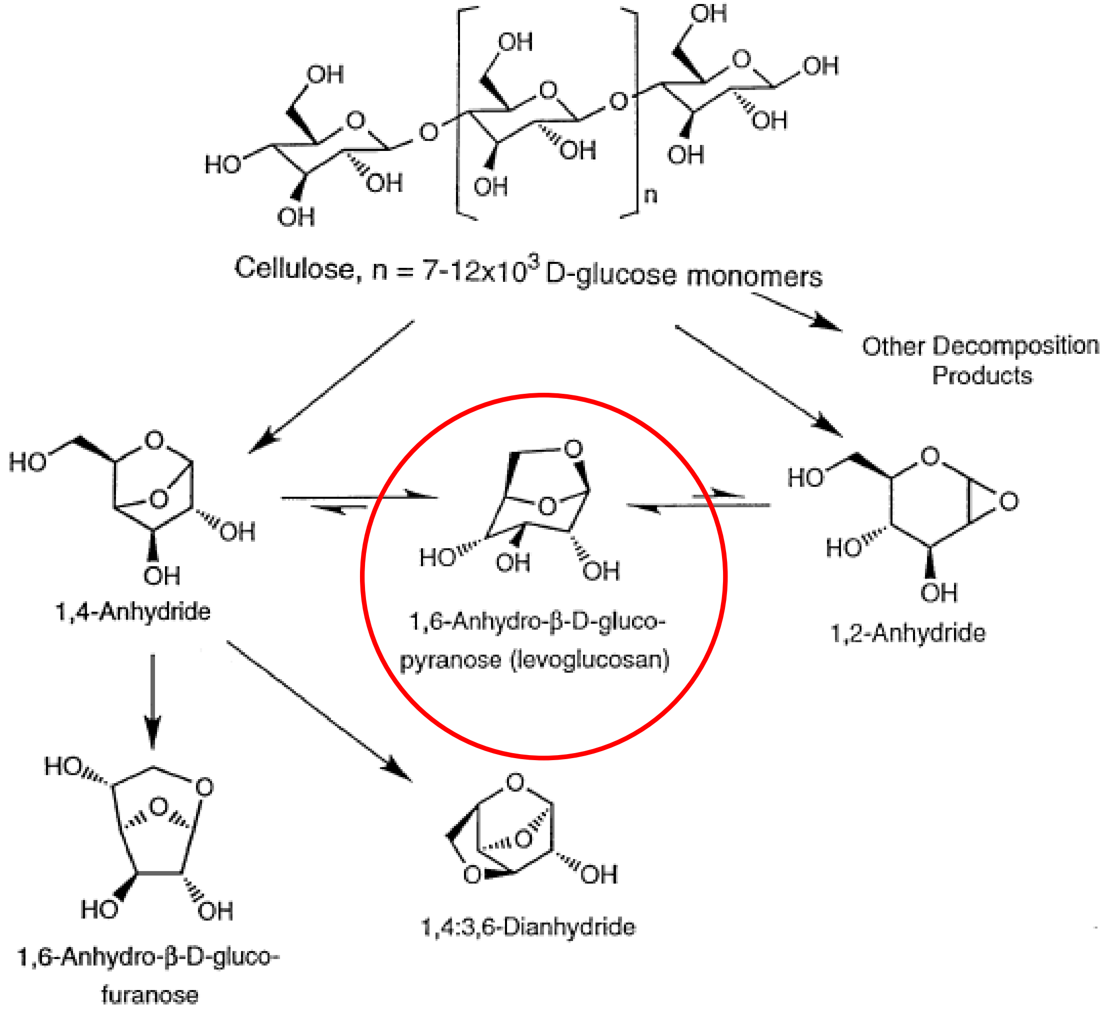
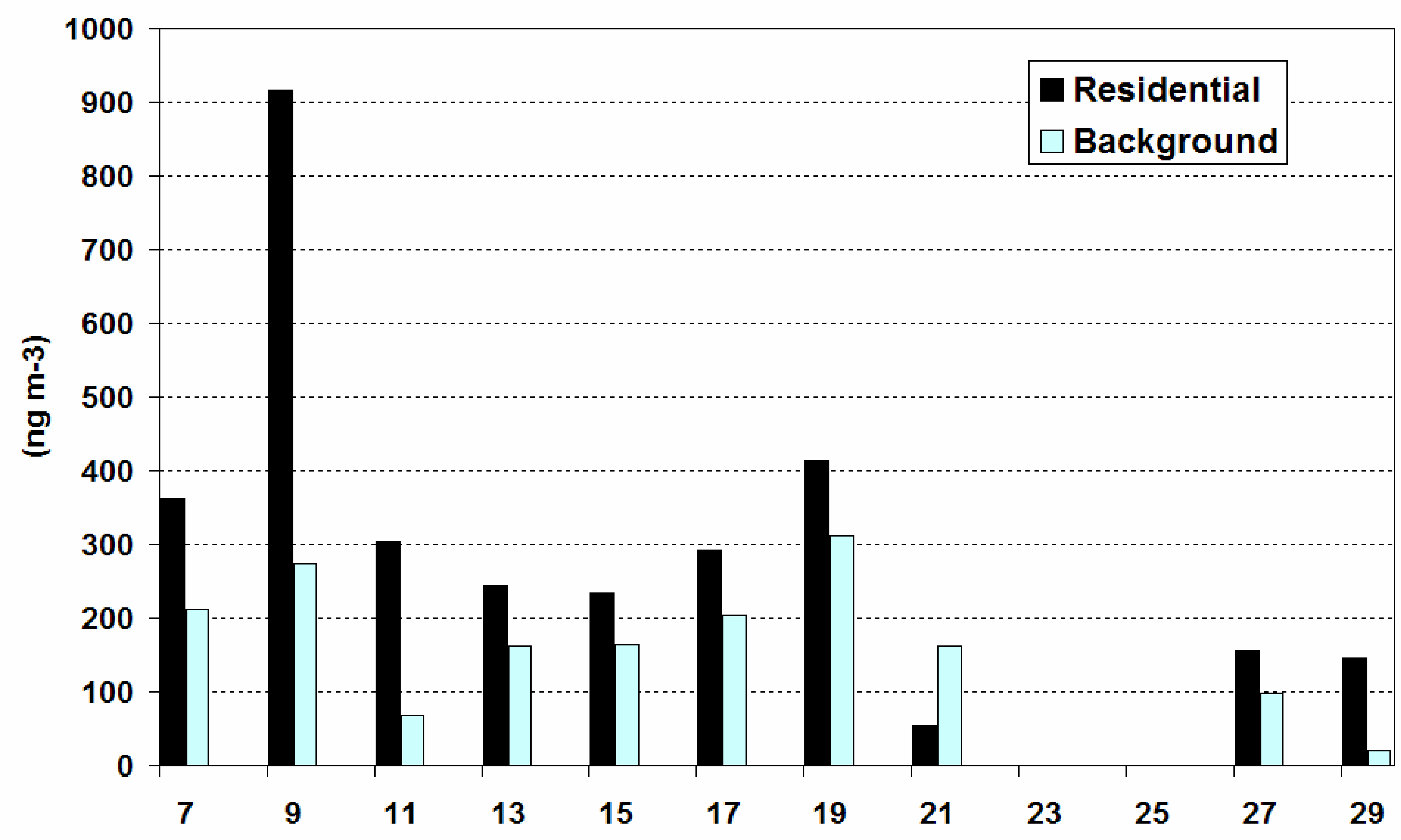


Fig. 1. Schematic showing the major structures of the products from pyrolysis ($T > 300°C$) of cellulose (from review by Shafizadeh, 1984).

Levoglucosan + mannosan in evening samples



Glasius et al., Atmos. Environ. 2008, accepted

Woodsmoke in developed countries

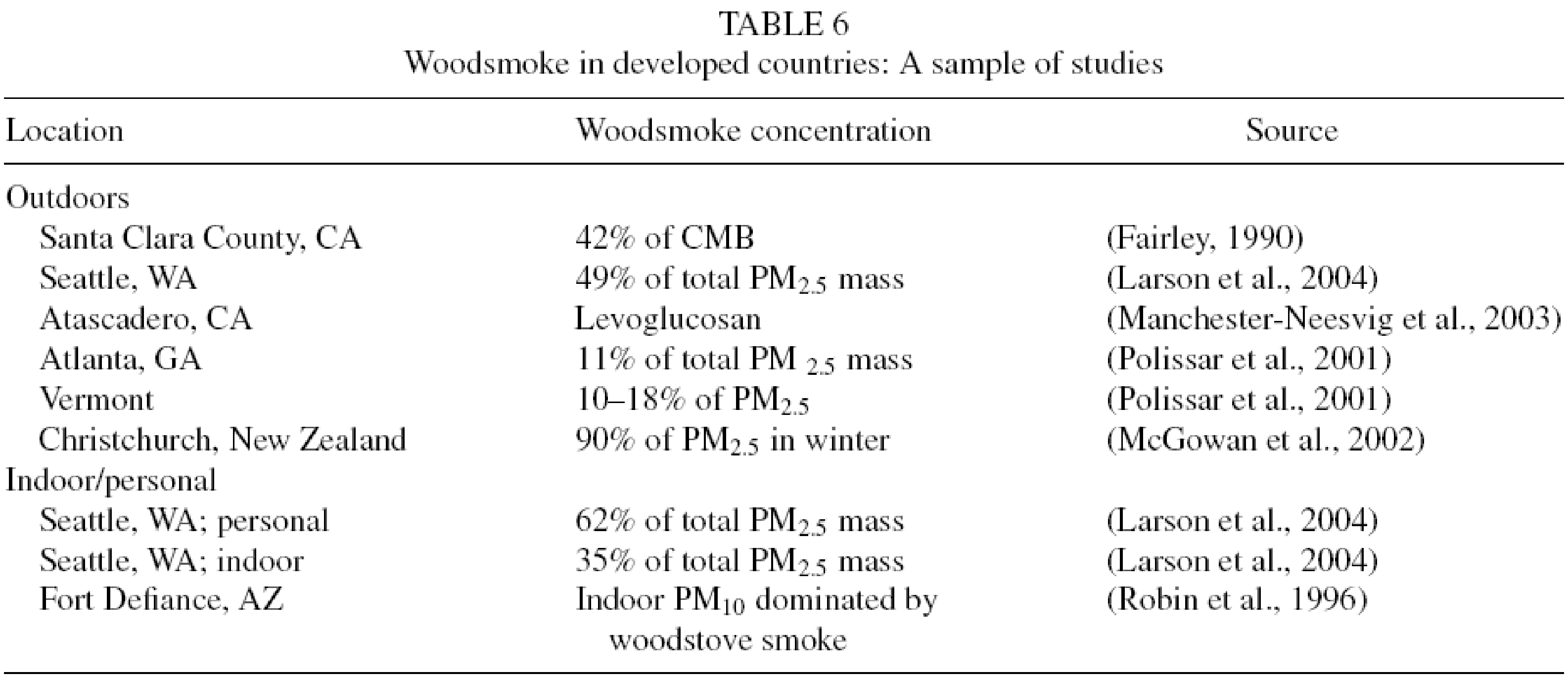


TABLE 6
Woodsmoke in developed countries: A sample of studies

Location	Woodsmoke concentration	Source
Outdoors		
Santa Clara County, CA	42% of CMB	(Fairley, 1990)
Seattle, WA	49% of total $PM_{2.5}$ mass	(Larson et al., 2004)
Atascadero, CA	Levoglucosan	(Manchester-Neesvig et al., 2003)
Atlanta, GA	11% of total $PM_{2.5}$ mass	(Polissar et al., 2001)
Vermont	10–18% of $PM_{2.5}$	(Polissar et al., 2001)
Christchurch, New Zealand	90% of $PM_{2.5}$ in winter	(McGowan et al., 2002)
Indoor/personal		
Seattle, WA; personal	62% of total $PM_{2.5}$ mass	(Larson et al., 2004)
Seattle, WA; indoor	35% of total $PM_{2.5}$ mass	(Larson et al., 2004)
Fort Defiance, AZ	Indoor PM_{10} dominated by woodstove smoke	(Robin et al., 1996)

Naeher et al., J. Inhalation Toxicology, 2006

So what should we measure?

- Depends on purpose
  - climate studies
  - health effect studies
  - characterisation / reaction studies
- Concept of tracers of sources and properties

- Important to have long time series!

Important issues in aerosol sampling and analysis

- All steps must be quantitative for all investigated compounds
  - Sampling
    - volatility/reactivity
  - Extraction and clean-up
  - Analysis procedure
- Quality control samples are essential
- Always be critical!

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Thank you for your attention!