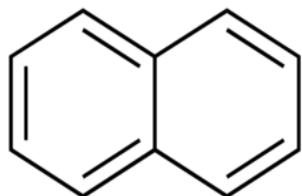


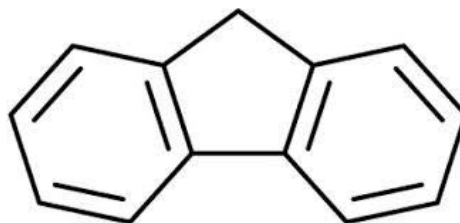
airmoSCAN_{XP}ERT solution

On-Line and In-field autoGC/FID/MS analyzer

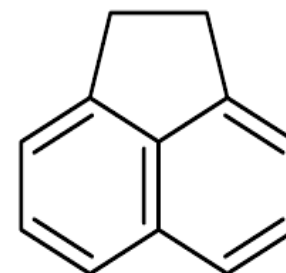
Automatic PAHs Monitoring



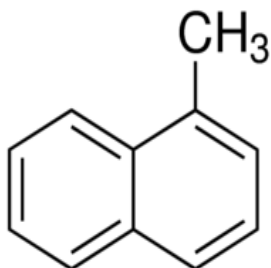
Naphthalene



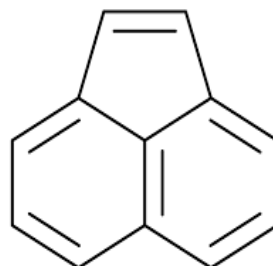
Fluorene



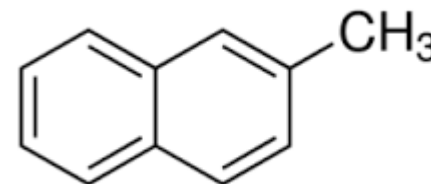
Acenaphthene



1 Methylnaphthalene



Acenaphthylene



2 Methylnaphthalene

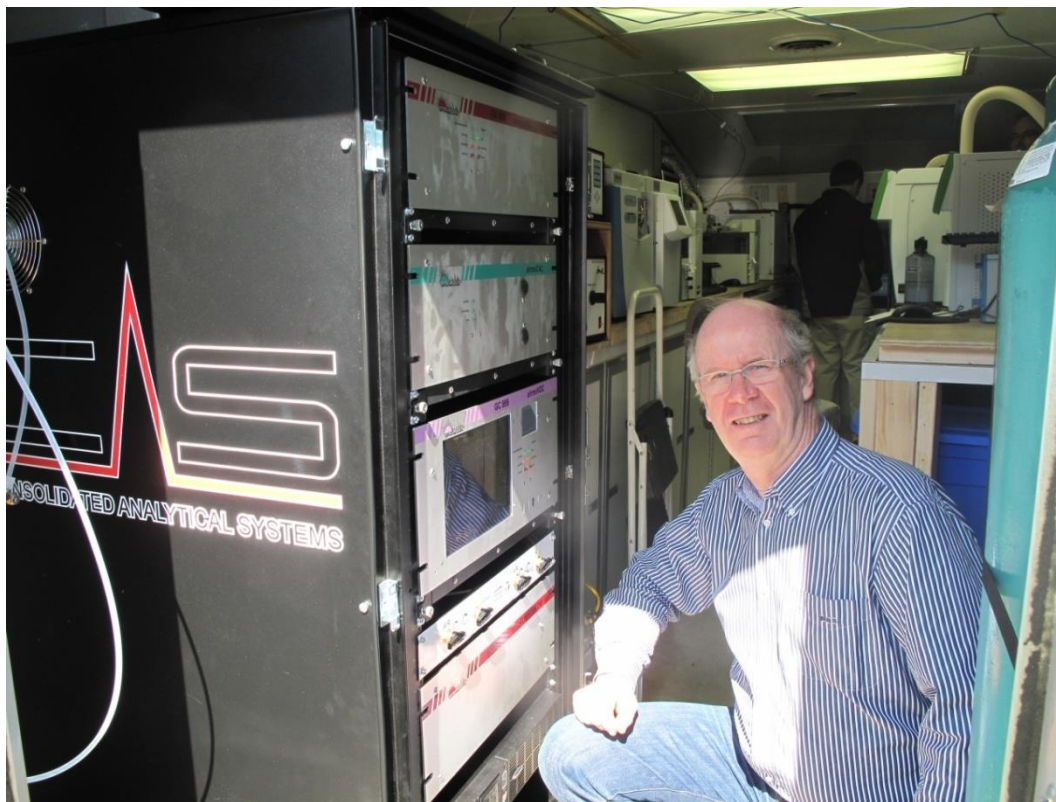
- Continuous air quality and emission gases monitoring



Main challenges :

- Ambient air is polluted by many VOCs coming from petrochemical industry, motor vehicle exhaust, industrial emissions, chemical solvents as well as biogenic emissions .
 - PAMS, Terpenes , Oxygenated, Halogenated, nitrogeneous or sulfur compounds
- Analyze precisely ambient air composition in different locations
- Continuous analysis with automatic validation of results
- More and more compounds (more than 120)
- In total compliance with government regulations

Expert analysis system



airmOzone with auto GC 866 **selected and bought** for final US EPA field tests with **Michel Robert** (European WG 12 for Benzene and VOC measurement)

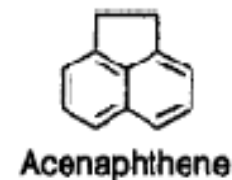
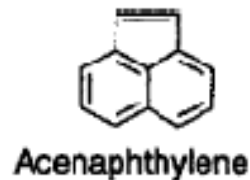
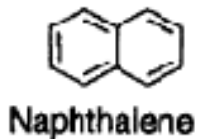
Agenda

- I. Polycyclic aromatic hydrocarbons (PAHs)
- II. Instrument configuration with airmoSCAN XPERT
solution : a trap/GC/FID/MS
- III. Advantages of the solution
- IV. Industrial area study



PAHs

- 100 different chemicals
 - Two or more fused benzene rings



- Incomplete combustion of organic matter at high temperature
 - Anthropogenic
 - Industrial process
 - Vehicle exhausts
 - Domestic heating
 - Natural
 - Forest fires
 - Volcanoes

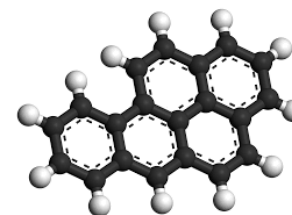


PAHs

- 16 PAHs selected by the US EPA
 - Mutagenicity
 - Carcinogenicity

	PAHs	Abbreviation	Chemical formula	CAS number	Number of fused benzene rings	Molar mass (g/mol)	Boiling point (°C)
1	Naphthalene	NAP	C ₁₀ H ₈	91-20-3	2	128	218
2	Acenaphthylene	ACN	C ₁₂ H ₈	208-96-8	3	152	280
3	Acenaphthene	ACL	C ₁₂ H ₁₀	83-32-9	3	154	279
4	Fluorene	FLR	C ₁₃ H ₁₀	86-73-7	3	166	298
5	Anthracene	ANT	C ₁₄ H ₁₀	120-12-7	3	178	340
6	Phenanthrene	PHN	C ₁₄ H ₁₀	85-01-8	3	178	340
7	Fluoranthene	FLT	C ₁₆ H ₁₀	206-44-0	4	202	384
8	Pyrene	PYR	C ₁₆ H ₁₀	129-00-0	4	202	390
9	Benzo(a)anthracene	BAA	C ₁₈ H ₁₂	56-55-3	4	228	437
10	Chrysene	CHY	C ₁₈ H ₁₂	218-01-9	4	228	448
11	Benzo(a)pyrene	BAP	C ₂₀ H ₁₂	50-32-8	5	252	495
12	Benzo(b)fluoranthene	BBF	C ₂₀ H ₁₂	205-99-2	5	252	481
13	Benzo(k)fluoranthene	BKF	C ₂₀ H ₁₂	207-08-9	5	252	480
14	Benzo(ghi)perylene	BGP	C ₂₂ H ₁₂	191-24-2	6	276	550
15	Indeno[1,2,3-cd]pyrene	ICP	C ₂₂ H ₁₂	193-39-5	6	276	536
16	Dibenz(a,h)anthracene	DBA	C ₂₂ H ₁₄	53-70-3	6	278	524

- In Europe, ambient air legislation targets Benzo(a)pyrene
 - With annual target value of 1 ng/m³



PAHs

- PAHs in the atmosphere are distributed between gas and particle phases
 - Atmospheric conditions
 - Temperature
 - Relative humidity
 - Physical properties
 - Lighter compounds tend to be in gas phase
 - 2-4 rings
 - Heavier ones almost complete association with particles
 - > 4 rings
 - Reactions contribute to the removal of gas-phase PAHs from the atmosphere:
 - ozone
 - $\cdot\text{OH}$
 - $\cdot\text{NO}_3$
 - photolysis at a lesser extent

PAHs

PAH	SINKS	ATMOSPHERIC LIFETIME
Naphthalene	$\cdot\text{OH} \gg \cdot\text{NO}_3, \text{O}_3$	6.8 daylight hours
1-Methylnaphthalene	$\cdot\text{OH} \gg \cdot\text{NO}_3, \text{O}_3$	2.8 daylight hours
2-Methylnaphthalene	$\cdot\text{OH} \gg \cdot\text{NO}_3, \text{O}_3$	2.8 daylight hours
Acenaphthylene	$\cdot\text{NO}_3 > \text{O}_3 > \cdot\text{OH}$	6 nighttime minutes 1 daylight hour
Acenaphthene	$\cdot\text{NO}_3 > \cdot\text{OH} \gg \text{O}_3$	1.2 nighttime hours 1.5 daylight hours
Fluorene	$\cdot\text{OH} > \cdot\text{NO}_3 \gg \text{O}_3$	9.1 daylight hours
Phenanthrene	$\cdot\text{NO}_3 > \cdot\text{OH} \gg \text{O}_3$	4.6 nighttime hours 11.2 daylight hours

- Light compounds are very sensitive to the amount of $\cdot\text{OH}$
- The main source is the photolysis of ozone ($\lambda < 320 \text{ nm}$)
 - $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O} (^1\text{D})$
 - $\text{O} (^1\text{D}) + \text{H}_2\text{O} \rightarrow 2 \cdot\text{OH}$
- Radicals react very rapidly
 - Negligible tropospheric concentration of $\cdot\text{OH}$ can be found during the night

PAHs

- PAH concentrations in ambient air

	PAHs	Abbreviation	Chemical formula	CAS number	Concentration (ng/m3)	% Tot PAH
1	Naphthalene	NAP	C10H8	91-20-3	201.29	91.47
2	Acenaphthylene	ACN	C12H8	208-96-8	5.08	2.31
3	Acenaphthene	ACL	C12H10	83-32-9	7.61	3.46
4	Fluorene	FLR	C13H10	86-73-7	-	-
5	Anthracene	ANT	C14H10	120-12-7	1.19	0.54
6	Phenanthrene	PHN	C14H10	85-01-8	-	-
7	Fluoranthene	FLT	C16H10	206-44-0	2.12	0.96
8	Pyrene	PYR	C16H10	129-00-0	1.67	0.76
9	Benzo(a)anthracene	BAA	C18H12	56-55-3	0.1	0.05
10	Chrysene	CHY	C18H12	218-01-9	0.32	0.15
11	Benzo(a)pyrene	BAP	C20H12	50-32-8	0.12	0.05
12	Benzo(b)fluoranthene	BBF	C20H12	205-99-2	-	-
13	Benzo(k)fluoranthene	BKF	C20H12	207-08-9	-	-
14	Benzo(ghi)perylene	BGP	C22H12	191-24-2	0.35	0.16
15	Indeno[1,2,3-cd]pyrene	ICP	C22H12	193-39-5	0.17	0.08
16	Dibenz(a,h)anthracene	DBA	C22H14	53-70-3	0.03	0.01

PAHs

- Measurements of ambient naphthalene in the South Coast Air Basin

Period of Measurement	Location	[Naphthalene] ng/m ³ (day)	[Naphthalene] ng/m ³ (night)
1986 (late winter, high NOx episode) ¹	Torrance	3315	2875
1986 (summer, smog episode) ²	Glendale	3100	4300
1987 (spring) ³	Reseda	750	1300
1993 (fall, smog episode) ⁴	Los Angeles	6000	
1995 ⁵	Redlands	348 to 715	
2001 to 2002 ⁶	Southern CA	200 to 575	
2002 (summer) ⁷	Los Angeles	~ 350	~ 140
2002 (summer) ⁷	Riverside	~ 225	~ 40
2003 (winter) ⁷	Los Angeles	~ 1400	~ 1000
2003 (winter) ⁷	Riverside	~ 500	~ 150

¹ Arey et al, 1987 ; ² Arey et al, 1989 ; ³ Atkinson et al, 1994 ; ⁴ Fraser, 1998 ; ⁵ Gupta, 1995 ; ⁶ Calvert et al, 2002 ; Eiguren-Fernandez et al, 2004 ; ⁷ Reisen, 2003

PAHs

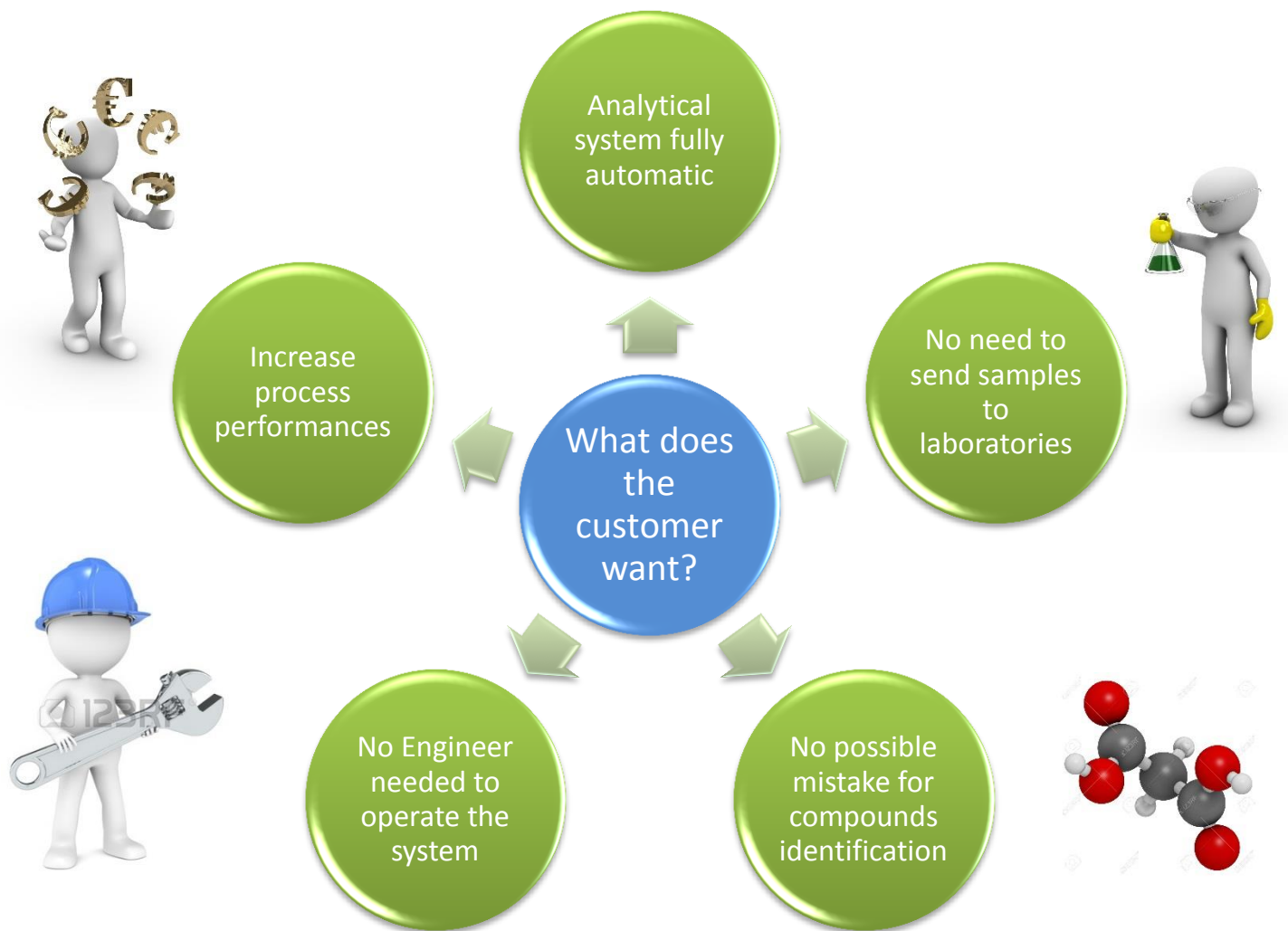
- Very toxic
- Produced naturally and by human activities
- Gaseous or solid
- Lifetimes of light compounds in the gaseous phase is short
- Gaseous phase represent more than 96% of the total PAH amount
- To control their emissions and effects on people's health
 - Need to monitor continuously PAHs
 - Time between measurements < 1 hour
 - Vehicle exhaust
 - Industrial process
 - Naphthalene needs to be monitored
 - Most abundant PAH
 - Mainly gaseous

Agenda

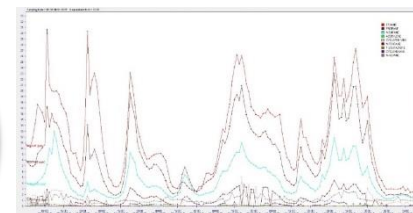
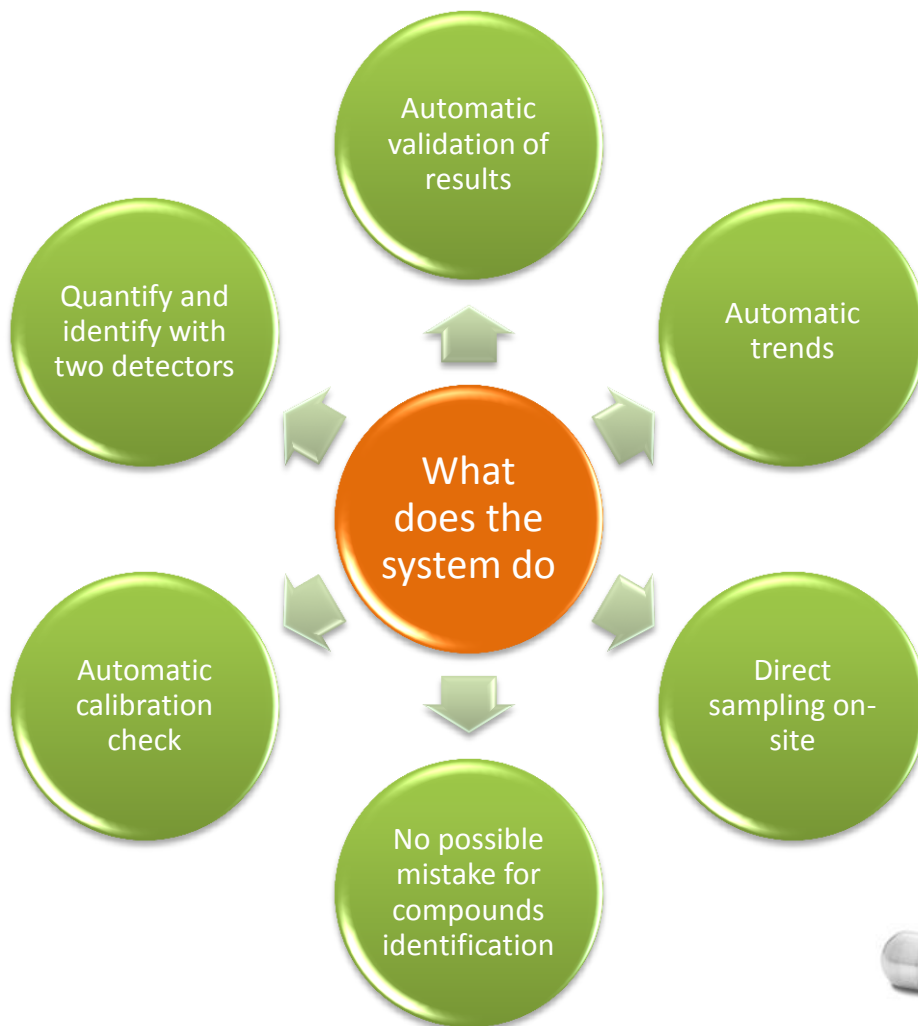
- I. Polycyclic aromatic hydrocarbons (PAHs)
- II. Instrument configuration with airmoSCAN XPERT
solution : a trap/GC/FID/MS
- III. Advantages of the solution
- IV. Industrial area study



Why do we need auto TDGC-FID/MS for PAHs monitoring



Why do we need auto TDGC-FID/MS for PAHs monitoring



airmoSCAN_{XP}ERT PAHs configuration



airmoSCAN XPERT PAH
configuration

airmoC5C15 with Process MS

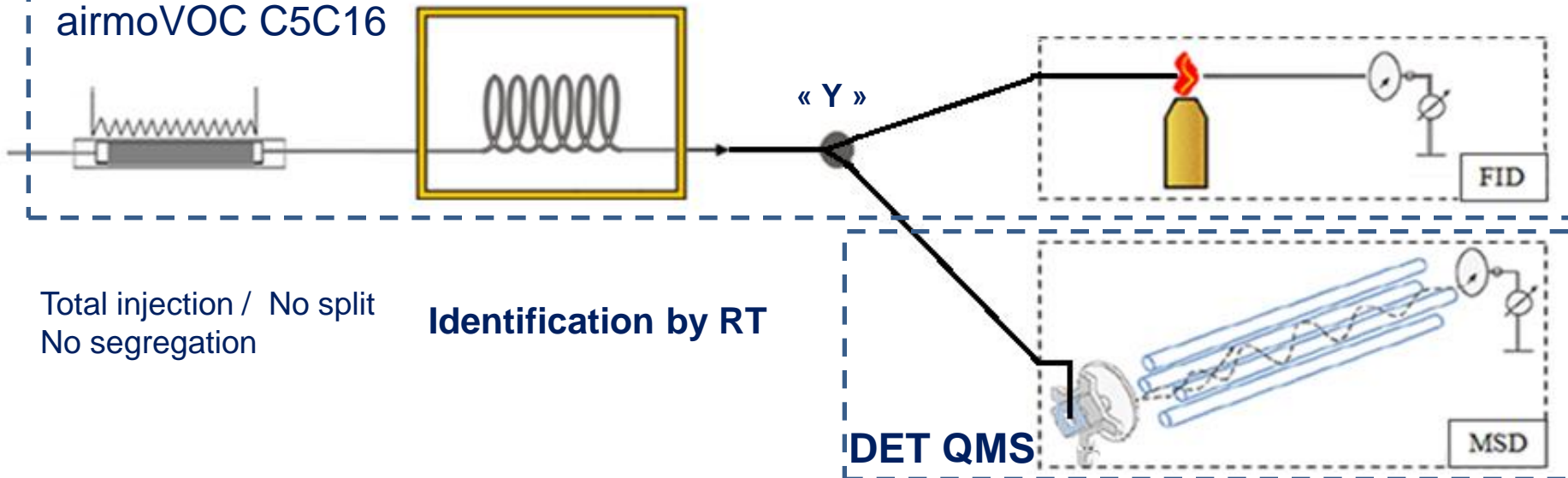
- airmoVOC C5-C16 5U
- Process Mass spectrometer (0-300 amu) 10U
- 1U rack with mouse and key board
- Hydroxychrom (H₂ generator) 4U
- airmoCAL MFC in option
- airmoPURE (zero air generator)
- Sampling pumps included

auto GC FID and MS General operation

MFC for volume
sampling calculation

Chromatographic
metallic column

airmoVOC C5C16



Total injection / No split
No segregation

Identification by RT

TRAP for
pre-concentration

GC for
Speciation

« Y » and MS
multiplexer

Double Detection
MS & FID
by auto GC 866

Agenda

- I. Polycyclic aromatic hydrocarbons (PAHs)
- II. Instrument configuration with airmoSCAN XPERT
solution : a trap/GC/FID/MS
- III. Advantages of the solution
- IV. Industrial area study



Specialty of the solution

➤ Combination of two technologies for Very high sensitivity

1. Auto GC 866 with μ -FID

- Compounds concentration using a **trap** for **Low ppt and ppq**
- **Compounds speciation with** pure hydrogen **First identification** by RT
- Automatic quantification certified by different organisms
 - » mCERTs 2013 ; worldwide expertises recognized by national institutes...
 - » US EPA selected in 2014

Specialty of the solution

➤ Combination of two technologies : Very high sensitivity

2. Auto GC FID 866 with Mass Spectrometer

- Highly sensitive universal detector (ppt – ppb)
- Selective detector
 - Identification by mass analysis : certification of the identification (from ppt level)
 - Automatic quantification in MID mode (ppt or ppb level)
 - Allows deconvolution of chromatographic peaks: automatic quantification of coeluted compounds
 - Identification of unknown compounds by library in SCAN mode

Why two detectors used after speciation ?

- Quantification with GC-MS :
- Response factors = RF are determined experimentally
 - Drift of source conditions require frequent calibration
 - **Calibration must be done on all compounds**
- Quantification with GC-FID :
 - Theoretical response (ECN)¹ factors verified experimentally
 - **Response Factors = RF relative to Benzene or Naphthalene**
 - **Calibration can be done on only one compound**
 - airmoVOC is mCERTs certified and selected by US EPA

¹ Scanlon, J.T., and Willis, D.E., *J. Chromatogr. Sci.* 23, 333-340 (1985)

Why two detectors used after speciation ?

- Quantification with GC-FID is used automatically for all compounds because of bellow reason:
 - long term stability (several years)
 - linearity of FID detectors FID
 - **More precise: GC-FID expert for quantification on peak area**
- Identification is done by GC-FID and confirmed automatically by GC-MSD
 - **GC-MSD expert for identification on mass**
- Quantification with GC-MSD is done automatically on all compounds and is used when: GC-MS:
 - Correlation between RT of FID and MSD is not good
 - Correlation between concentration of FID and MSD is not good
 - Drift of Retention Time
 - Co elution
 - Signal saturation
 - Compounds with bad response factor to FID

Automatic quantification

- Identification and quantification done by FID and MS simultaneously
 - Automatic identification and quantification of all compounds by GC FID:
 - Substance table on airmoVOC C5C16
 - Automatic identification and quantification of all compounds by GC MS in **MID mode**
 - Ion list and window of retention time for C5C16 MS coupling
 - Quantification is done on ion peak height
- Identification and quantification of unknown compounds (not in the list) in **SCAN mode**
 - 1st Comparison with embedded CHROMATOTEC library
 - If not in CHROMATOTEC library the mass spectrum can be sent to CHROMATOTEC for identification by R&D department
 - Comparison with NIST library and confirmation by injection of the pure compounds in airmoSCAN XPERT

Quantification of co-elutions with Vistachrom MS module

- Coeluted compounds
 - GC-MS records all data and inform user of coelutions automatically
 - MS quantify automatically all coeluted compounds
- Retention times recorded by:
 - GC-FID Vistachrom
 - GC-MS software
- GC-MS records all RT even with very important RT modification
 - Easy data reprocess even with large number of molecules

Quantification of co-elutions with Vistachrom MS module

- Automatic Communication
between instruments
 - Complementary
information
 - Alarm systems for co-
elution and modification of
retention times

CHROMATOTEC QC

Cross verification with Permeation tubes & cylinders from different companies

Instruments are tested for 2 weeks with different standards

⇒> **120 different compounds 120**

⇒ More compounds in option

•GC-FID

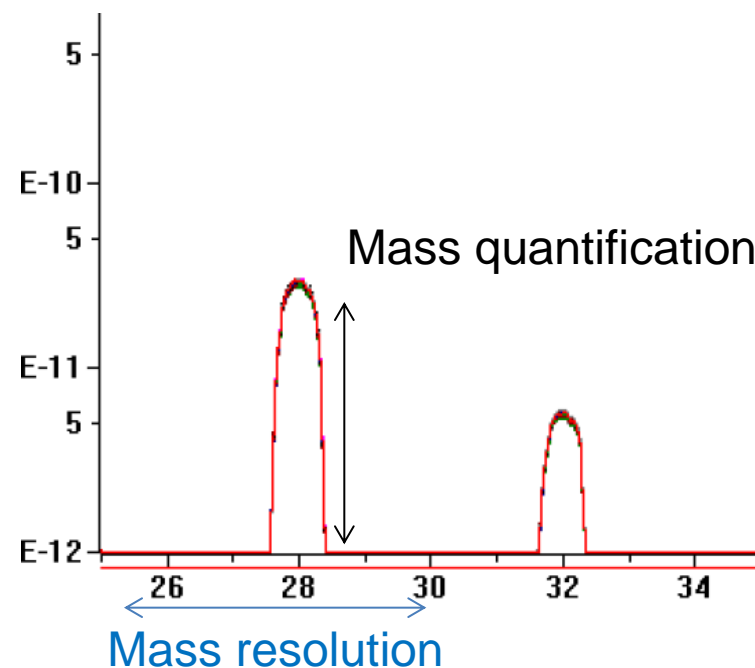
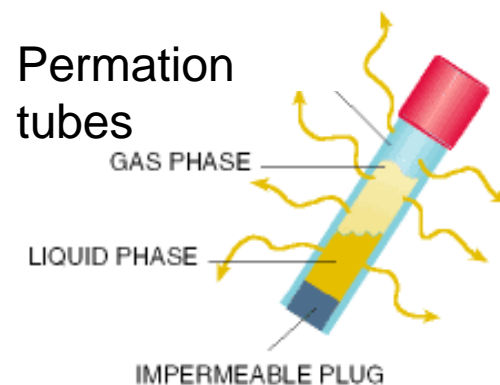
- Relative response factors to Benzene
- Calibration
- Peak speciation

•GC-Mass Spectrometer

- Calibration
- Targeted Ion list for automatic identification and quantification
- Library for fragmentation patterns used to identify unknown compound

Automatic validation/Calibration using permeation tubes

- For quantification
 - GC-FID
 - Automatic **validation** (mCERTS)
 - GC-MS
 - Auto-correction
 - Mass quantification
 - Daily calibration validation
- For mass scale resolution
 - MS
 - Automatic daily validation with CALIB
 - Validation by user
 - Need to be checked once a year

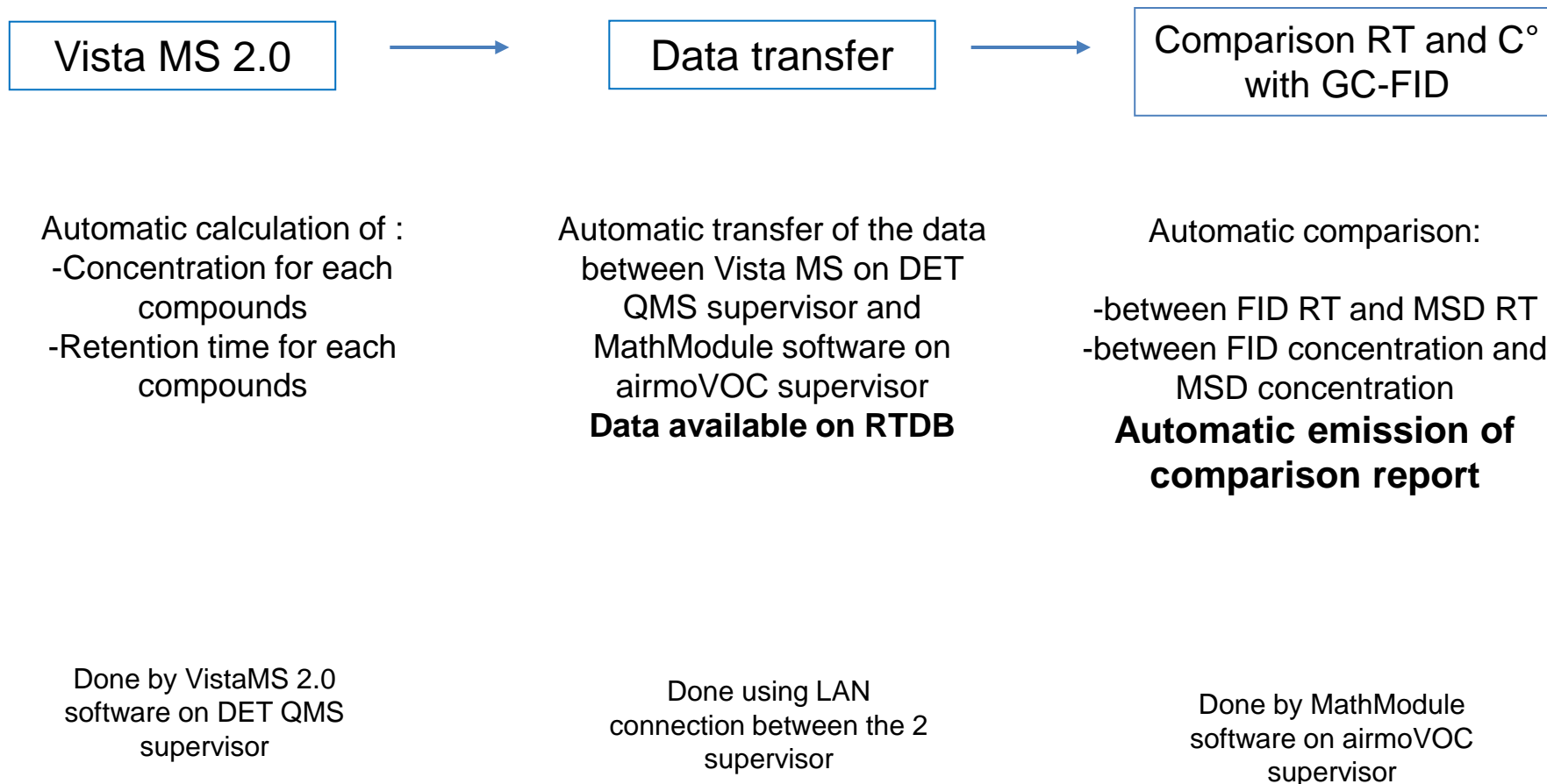


All-in-one solution with embedded supervisor

- Embedded computer including VISTACHROM software used for management of:
 - The analyzers:
 - C5C16
 - Process Mass spectrometer
 - The peripherals
 - Air & Hydrogen generators,
 - Calibrator
 - Streams multiplexer
 - Data acquisition management with Real-Time Data Base (RTDB)
 - Warnings & alerts of all parameters and data stored in RTDB
 - Remote access for easier maintenance



auto GC FID and MS automatic management of the data: analysis



auto GC FID and MS automatic management of the data: analysis

```
140704-MSGC-SynchroAlarm - Bloc-notes
Fichier Edition Format Affichage ?
05:09 MS Result file was not relevant for the substance (0 or 1 was expected instead of INI)
05:09 BENZENE found in MS, not found in GC [MS : 1 / GC : 0]
05:09 TOLUENE found in MS, not found in GC [MS : 1 / GC : 0]
05:09 M_P_XYLENE not found in GC results [Result]
05:09 ##### Synchronization for results : KO####
05:39 ##### Process results for #20730509.Results.AMBMSQU.AMB-30HT ####
05:39 MS Result file was not relevant for the substance (0 or 1 was expected instead of INI)
05:39 M_P_XYLENE not found in GC results [Result]
05:39 ##### Synchronization for results : KO####
06:09 ##### Process results for #20730509.Results.AMBMSQU.AMB-30HT ####
06:09 MS Result file was not relevant for the substance (0 or 1 was expected instead of INI)
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06:39 ##### Process results for #20730509.Results.AMBMSQU.AMB-30HT ####
06:39 MS Result file was not relevant for the substance (0 or 1 was expected instead of INI)
06:39 M_P_XYLENE not found in GC results [Result]
06:39 ##### Synchronization for results : KO####
07:09 ##### Process results for #20730509.Results.AMBMSQU.AMB-30HT ####
07:09 MS Result file was not relevant for the substance (0 or 1 was expected instead of INI)
07:09 BENZENE retention time difference is too high [MS : 270 / GC : 264.86669921875]
07:09 M_P_XYLENE not found in GC results [Result]
07:09 ##### Synchronization for results : KO####
07:36 ##### Process results for #20730509.Results.AMBMSQU.CALIB30M ####
07:36 ##### Synchronization for results : KO####
08:06 ##### Process results for #20730509.Results.AMBMSQU.CALIB30M ####
08:06 ##### Synchronization for results : KO####
08:39 ##### Process results for #20730509.Results.AMBMSQU.AMB-30HT ####
08:39 MS Result file was not relevant for the substance (0 or 1 was expected instead of INI)
08:39 BENZENE found in MS, not found in GC [MS : 1 / GC : 0]
08:39 TOLUENE found in MS, not found in GC [MS : 1 / GC : 0]
08:39 M_P_XYLENE not found in GC results [Result]
08:39 ##### Synchronization for results : KO####
09:09 ##### Process results for #20730509.Results.AMBMSQU.AMB-30HT ####
09:09 MS Result file was not relevant for the substance (0 or 1 was expected instead of INI)
09:09 M_P_XYLENE not found in GC results [Result]
09:09 ##### Synchronization for results : KO####
09:39 ##### Process results for #20730509.Results.AMBMSQU.AMB-30HT ####
09:39 MS Result file was not relevant for the substance (0 or 1 was expected instead of INI)
09:39 M_P_XYLENE not found in GC results [Result]
09:39 ##### Synchronization for results : KO####
```

Outline

- I. Instrument configuration
- II. Advantages of the solution
- III. Industrial area study
 - I. Phase 1: Laboratory tests
 - II. Phase 2: On-site tests

Phase 1

Solution for problems which can happen with instruments in field environment

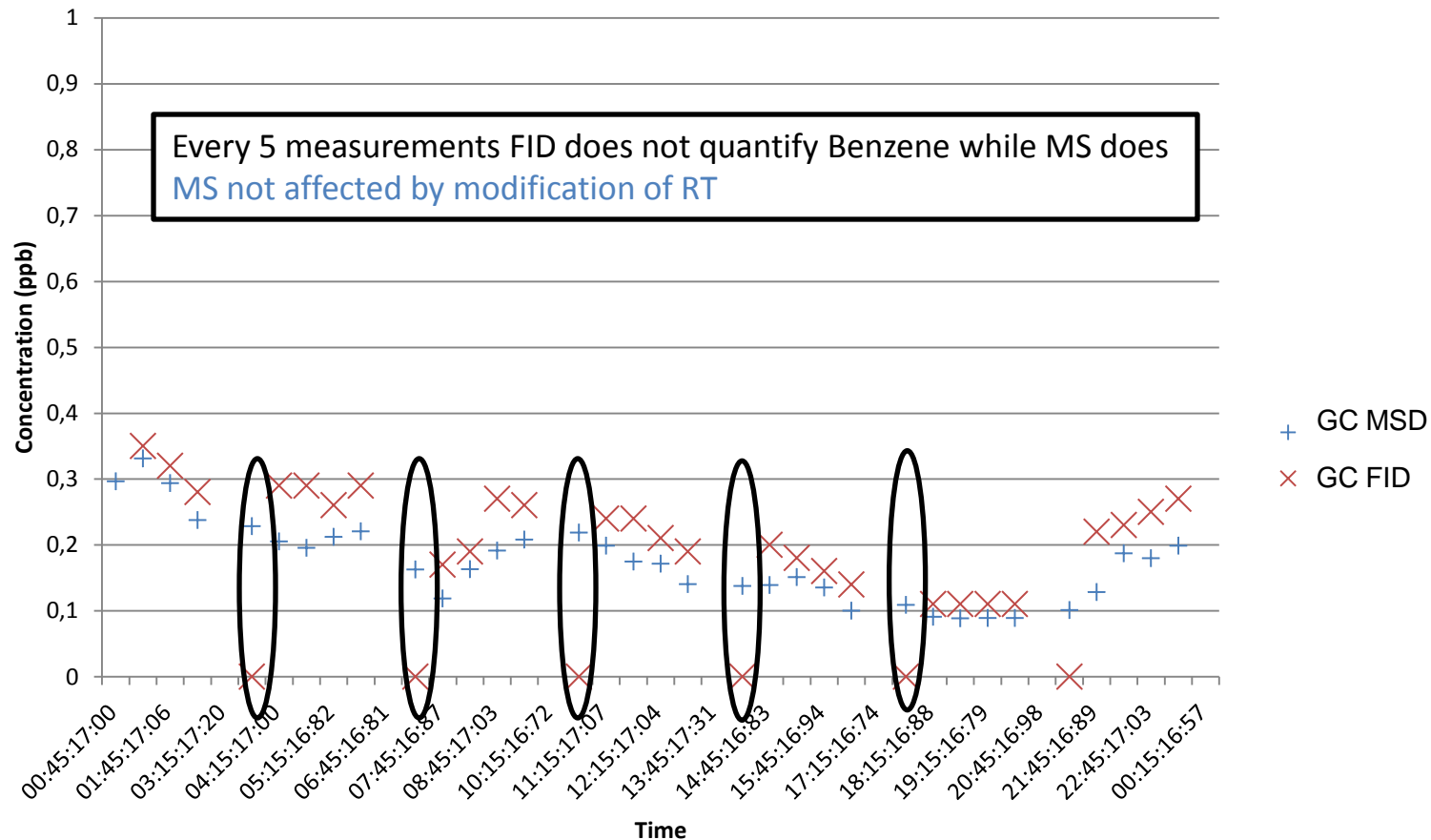
- Important variations of external conditions
 - Temperature
 - Vibration
 - Shelter power off
- Important variation of sample concentration and matrix
 - Humidity
 - High increase of concentration
 - New Unknown compounds and or co-elution

Problems on GCs:

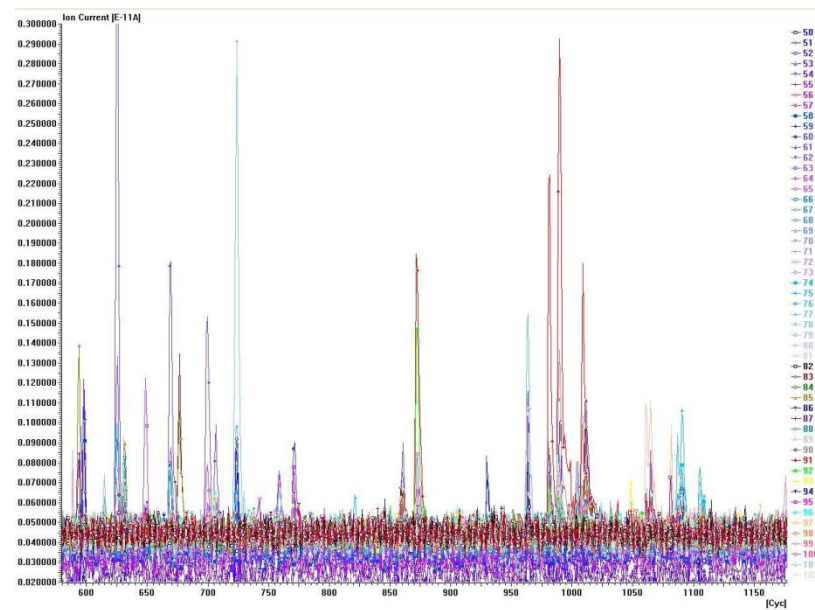
- Modification of retention times
- Signal saturation
- Over-estimation of signal due to co-elution

Phase 1

Important modification of the sample temperature



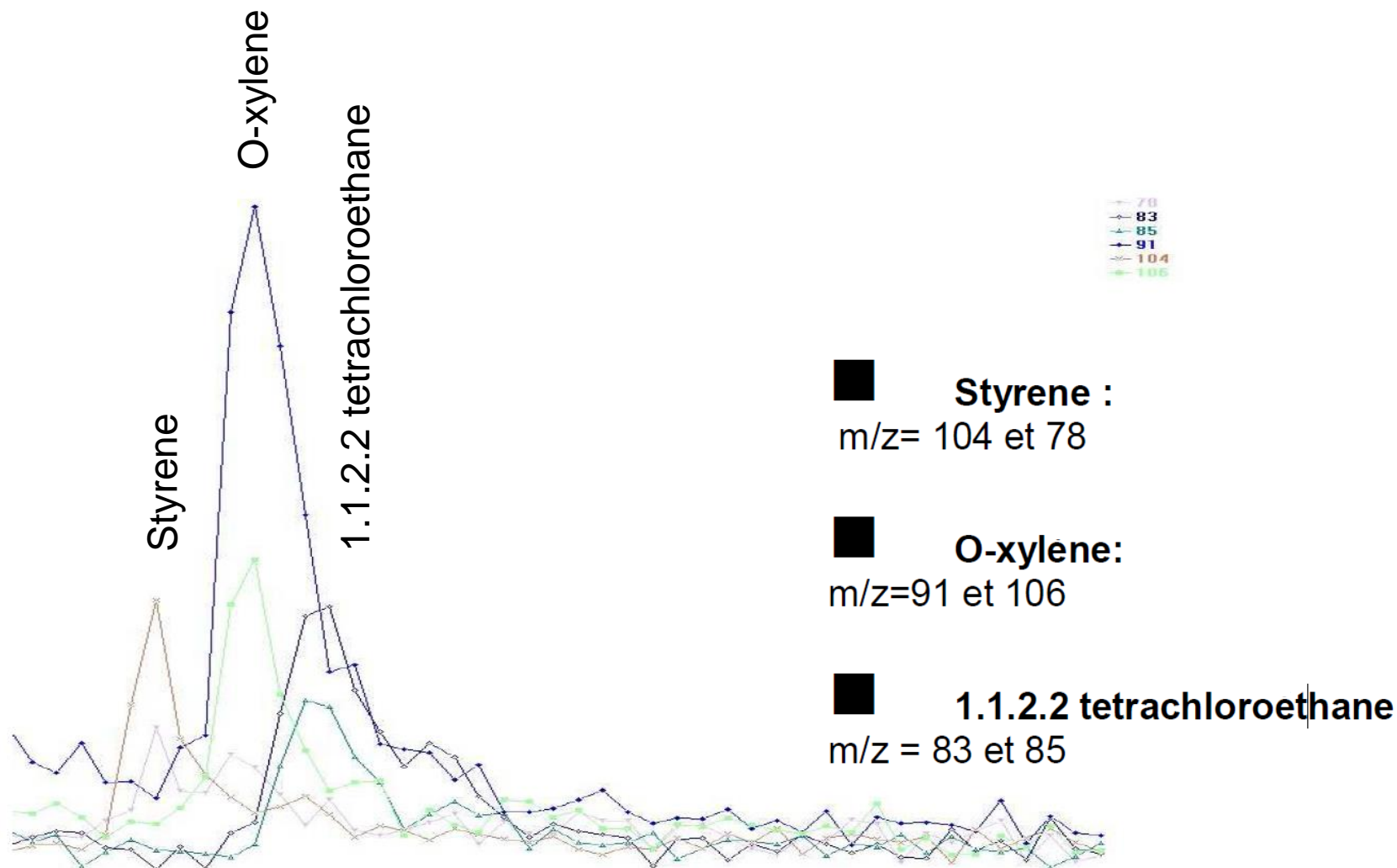
One concentration not measured by the GC-FID



GC-FID

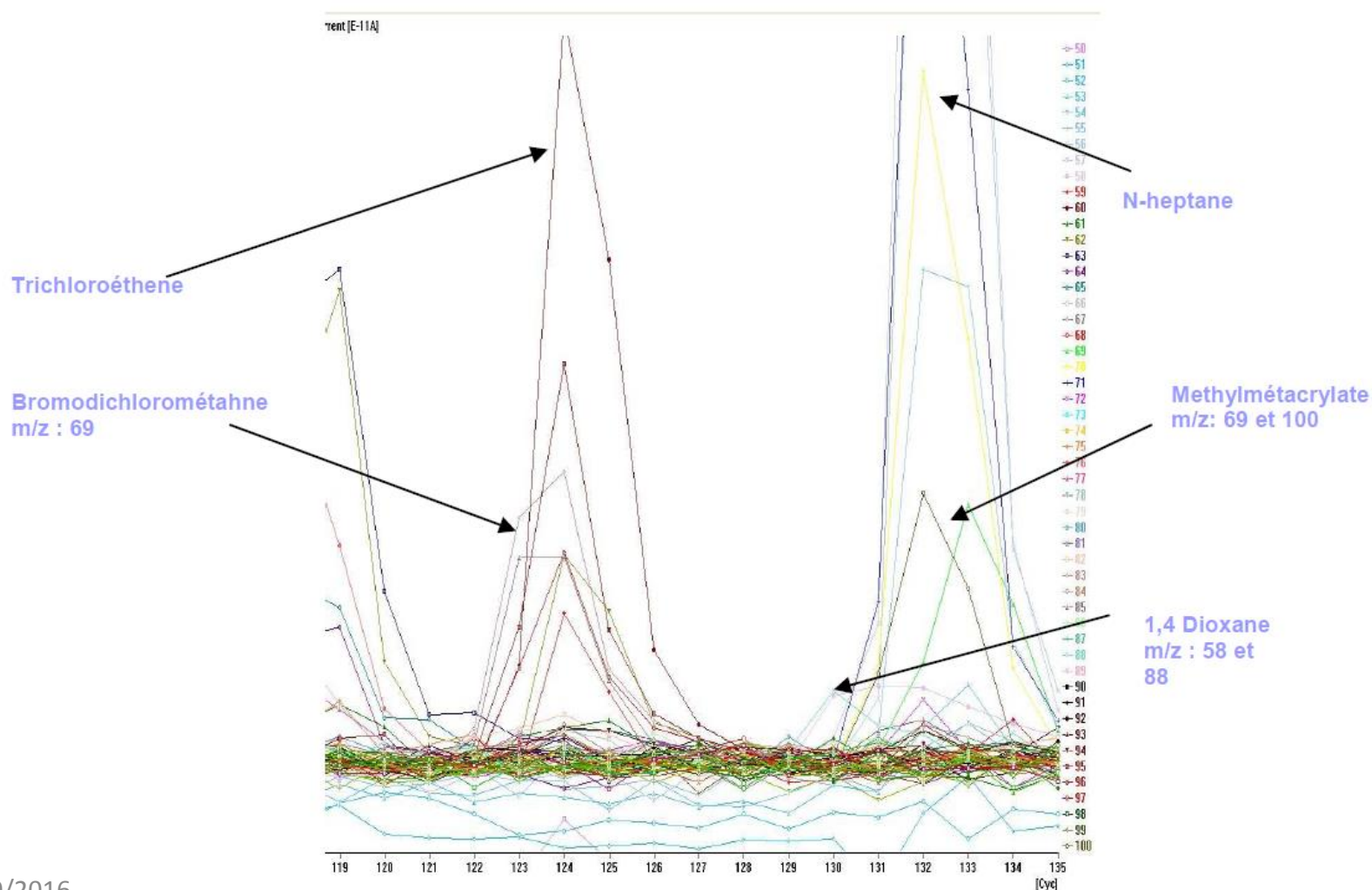
GC-MS

MS Quantification of co-elutions



Quantification of co-elutions

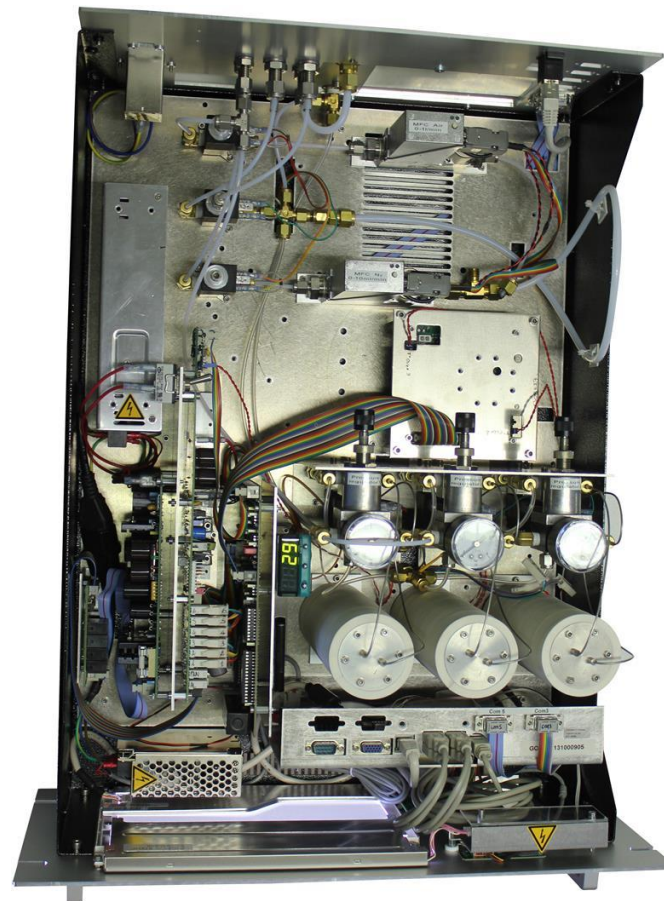
TO15



Laboratory tests

Naphthalene in air

- Permeation tubes
 - 20 ng/min
 - 60 °C
- Analytical conditions
 - Sampling times
 - 300 s – 1200 s
 - At 3 ppb (naphthalene)
 - Concentrations



Laboratory tests

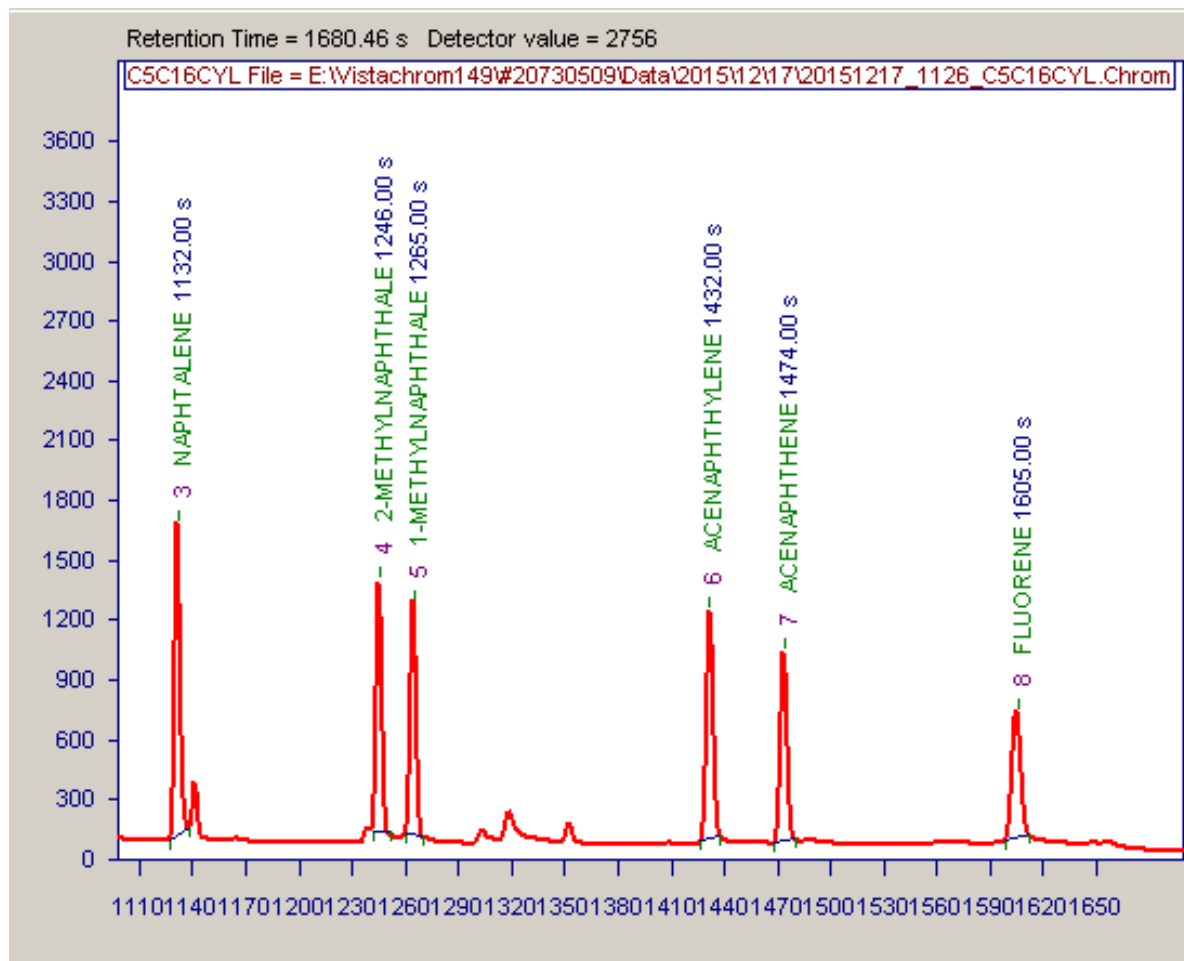
- Sample

- SV Calibration Mix (Restek)

- 18 components
 - 2 mg/ml in methylene chloride

Acenaphthene (83-32-9)
Acenaphthylene (208-96-8)
Anthracene (120-12-7)
Benz(a)anthracene (56-55-3)
Benzo(a)pyrene (50-32-8)
Benzo(b)fluoranthene (205-99-2)
Benzo(ghi)perylene (191-24-2)
Benzo(k)fluoranthene (207-08-9)
Chrysene (218-01-9)
Dibenz(a,h)anthracene (53-70-3)
Fluoranthene (206-44-0)
Fluorene (86-73-7)
Indeno(1,2,3-cd)pyrene (193-39-5)
1-Methylnaphthalene (90-12-0)
2-Methylnaphthalene (91-57-6)
Naphthalene (91-20-3)
Phenanthrene (85-01-8)
Pyrene (129-00-0)

Laboratory tests

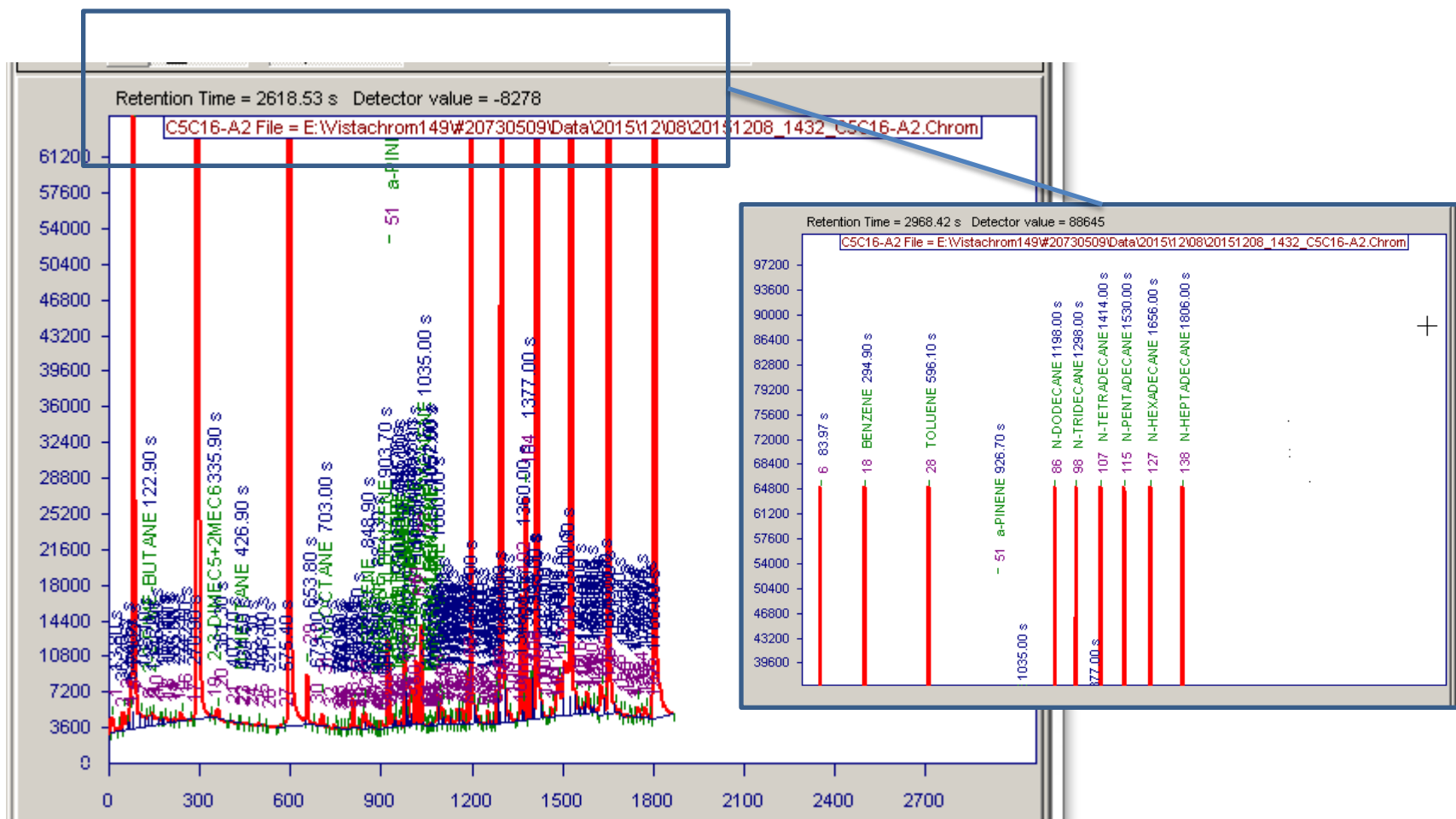


6 first PAHs are analyzed

Laboratory tests

- Mass spectrometer can identify and quantify
 - Automatic identification and quantification without reprocess
 - Index of toxicity can be automatically calculated at each analysis
- Analysis by GCMS of 6 PAHs
 - Naphthalene
 - 1 MethylNaphthalene
 - 2 MethylNaphthalene
 - Acenaphtylene
 - Acenapthene
 - Flurorene
 - Straight Alkane can be measured also up to C17

Straight alkane analysis



Outline

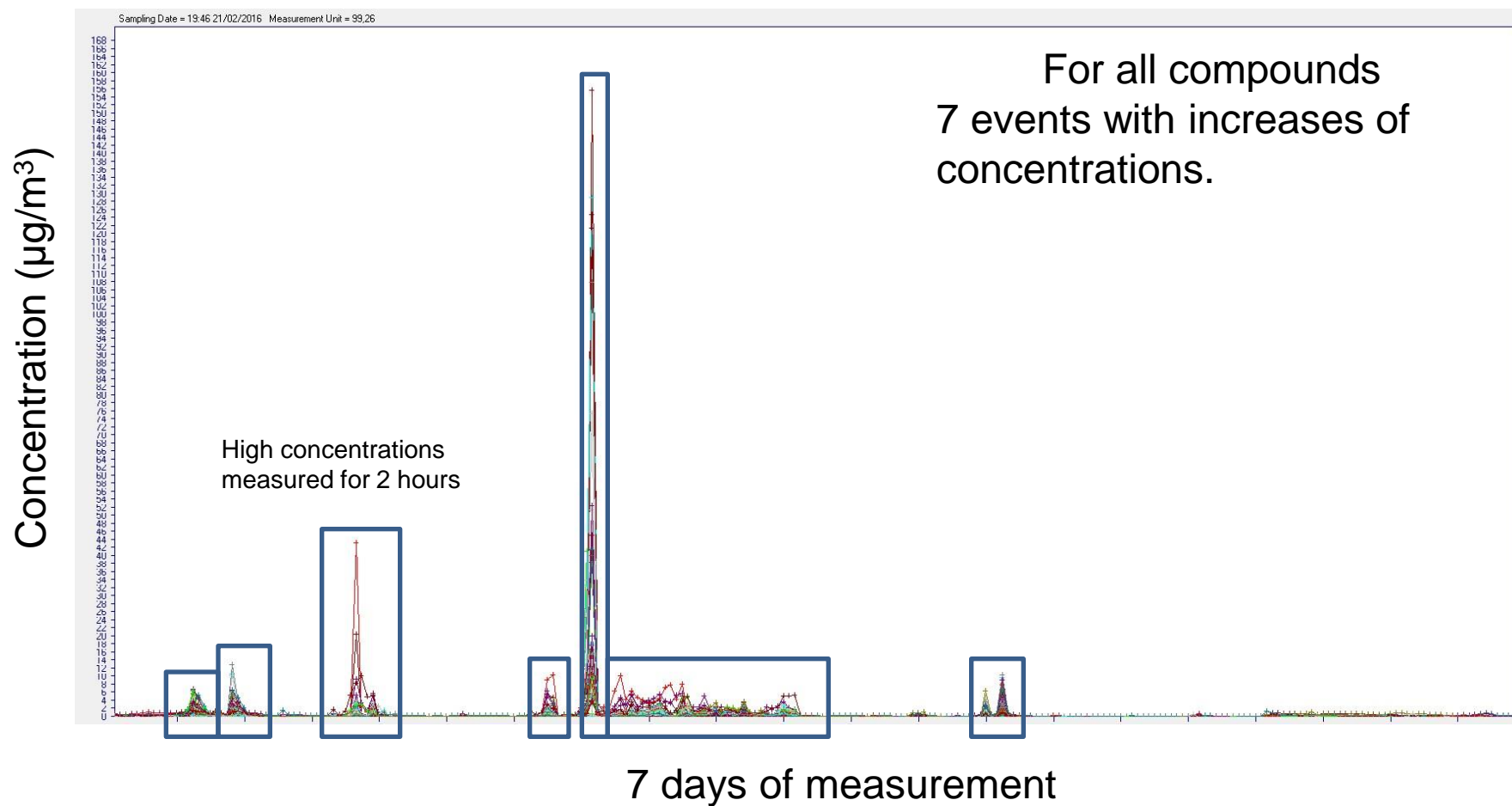
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 - II. Phase 2: On-site tests

Field tests

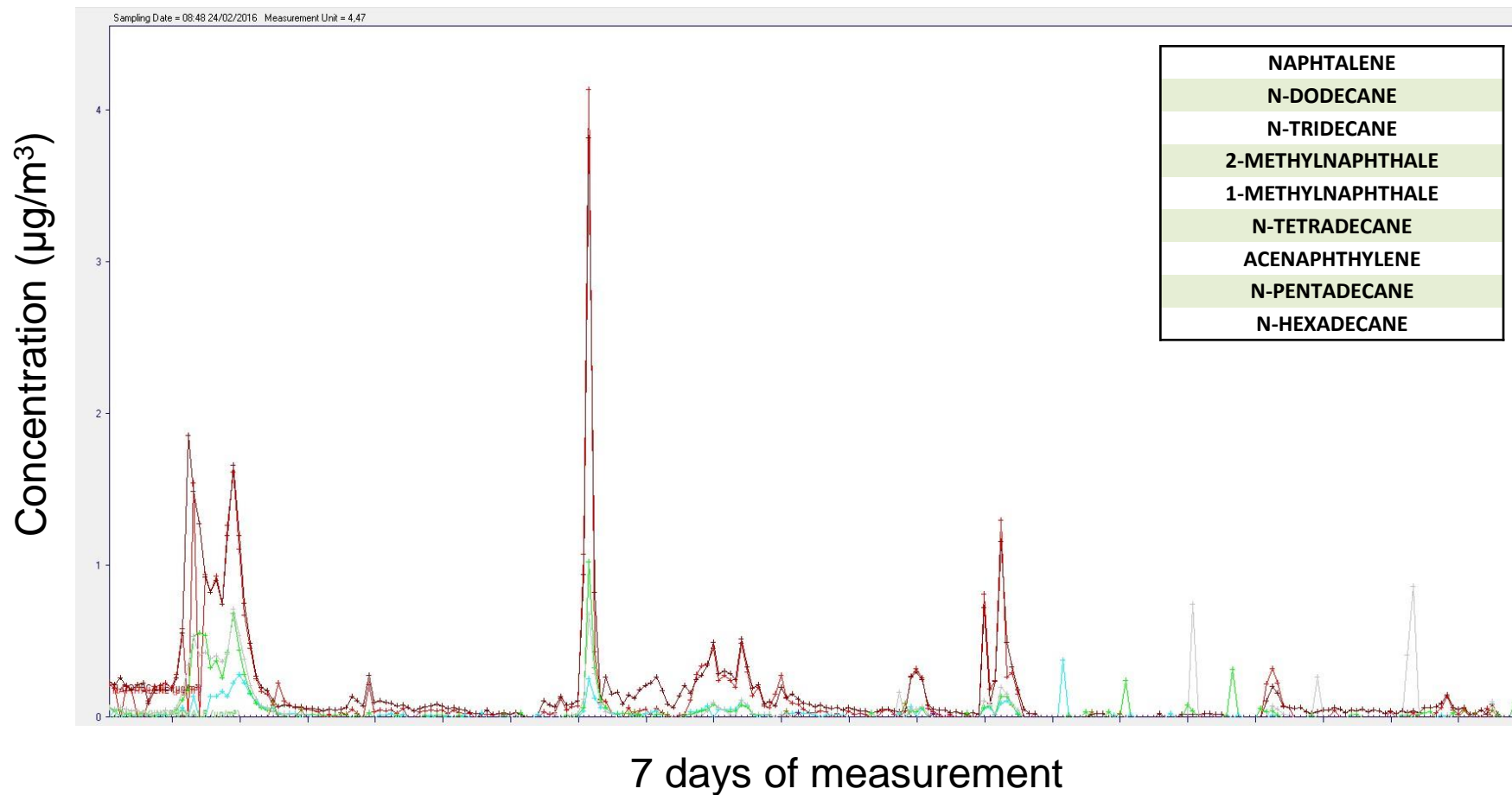
- Continuous monitoring of C5-C16 and 6 first PAHs
- Location
 - South of France
- Industrial site
- Collaboration with South France Air Quality Management district
 - air languedoc roussillon

Monitored compounds	
1-PENTENE	I-PROPYLBENZENE
N-PENTANE	A-PINENE
2-2-DIME-BUTANE	N-PROPYLBENZENE
2-ME-PENTANE	M-ETHYLTOLUENE
3-ME-PENTANE	P-ETHYLTOLUENE
2-ME-1-PENTENE	135-TMB
1-HEXENE	O-ETHYLTOLUENE
N-HEXANE	B-PINENE
ME-CYCLOPENTANE	124-TMB
2-4-DIME-PENTANE	1-3-DICL-BENZENE
BENZENE	N-DECANE
CYCLOHEXANE	1-4-DICL-BENZENE
2-3-DIMEC5+2MEC6	123-TMB
3-ME-HEXANE	LIMONENE
224-TME-PENTANE	M-DIETHYLBENZENE
N-HEPTANE	P-DIETHYLBENZENE
ME-CYCLOHEXANE	N-UNDECANE
234-TME-PENTANE	NAPHTALENE
TOLUENE	N-DODECANE
2-ME-HEPTANE	N-TRIDECANE
3-ME-HEPTANE	2-METHYLNAPHTHALE
N-OCTANE	1-METHYLNAPHTHALE
ETHYLBENZENE	N-TETRADECANE
M&P-XYLENES	ACENAPHTHYLENE
STYRENE	N-PENTADECANE
O-XYLENE	N-HEXADECANE
N-NONANE	

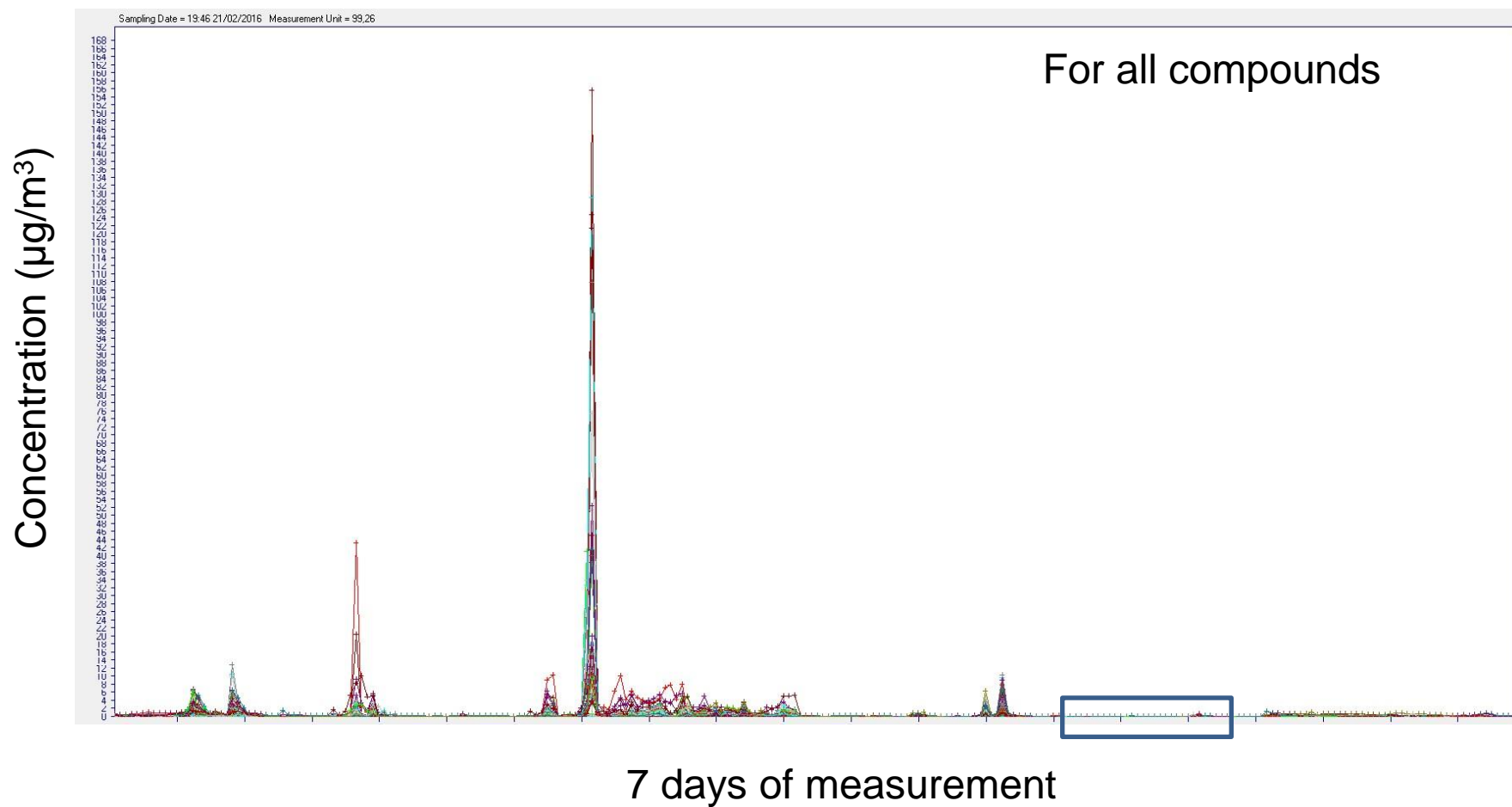
Field tests



Field tests



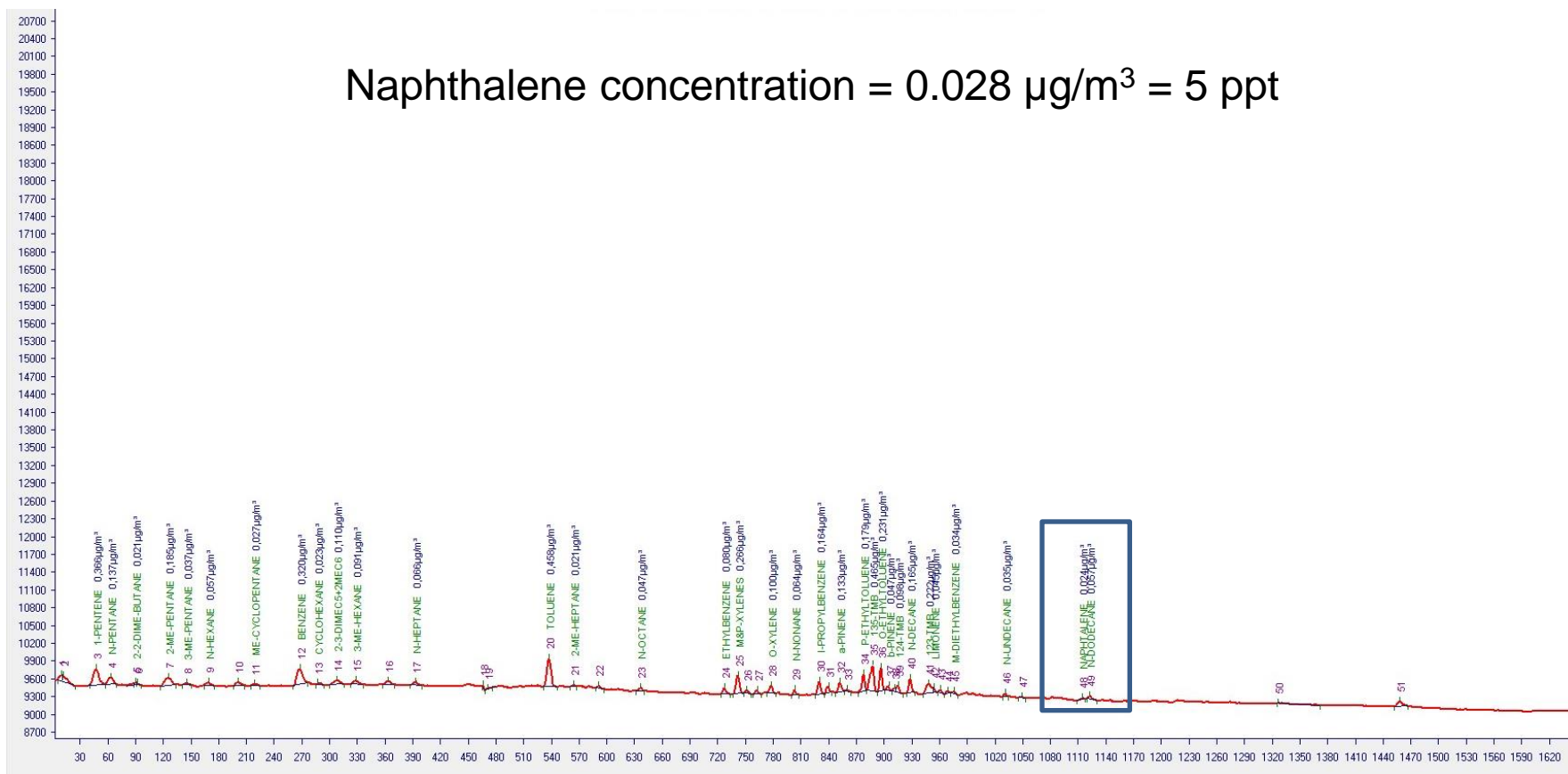
Field tests



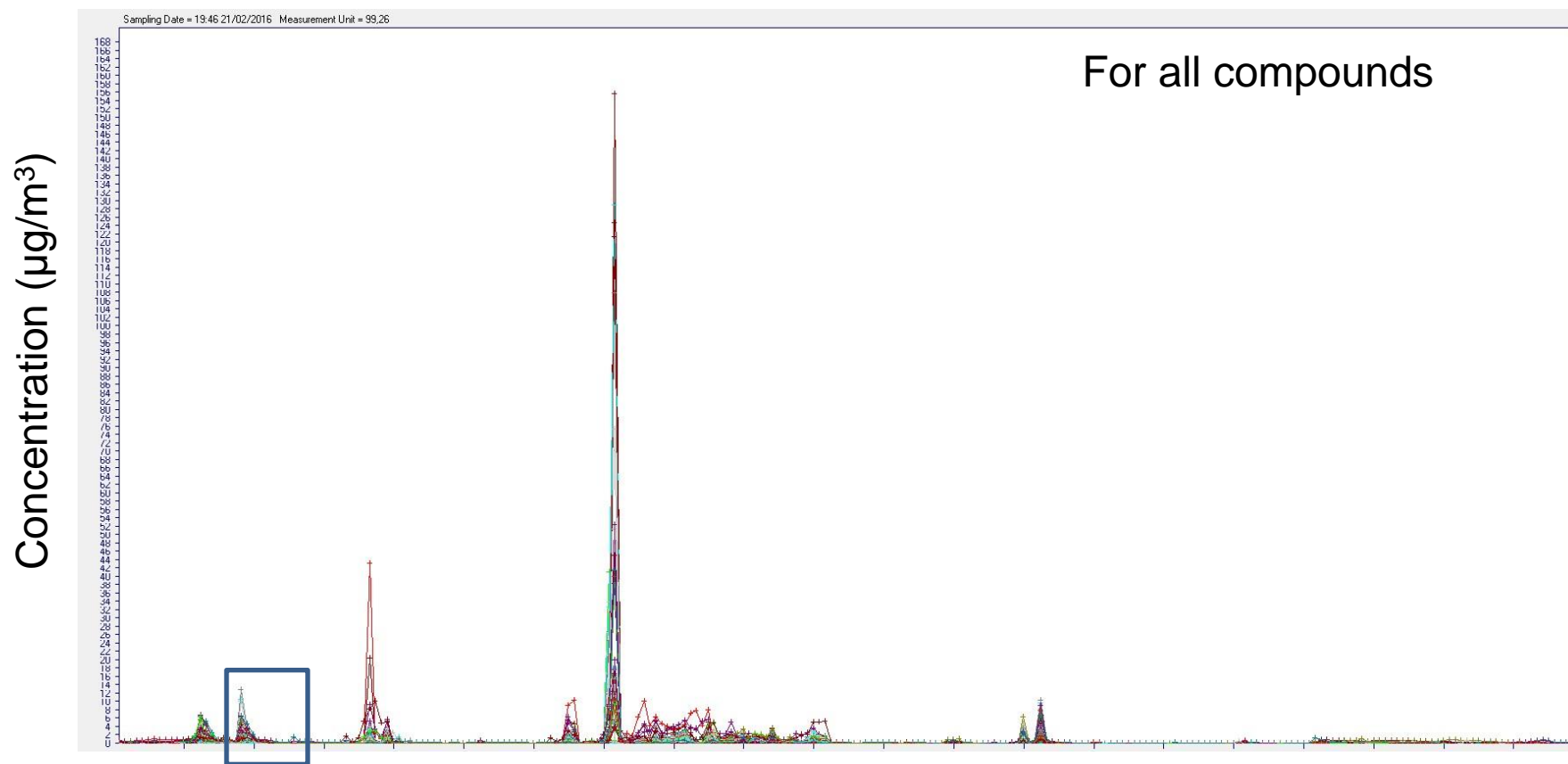
Field tests

Low concentration profile

Naphthalene concentration = $0.028 \mu\text{g}/\text{m}^3 = 5 \text{ ppt}$

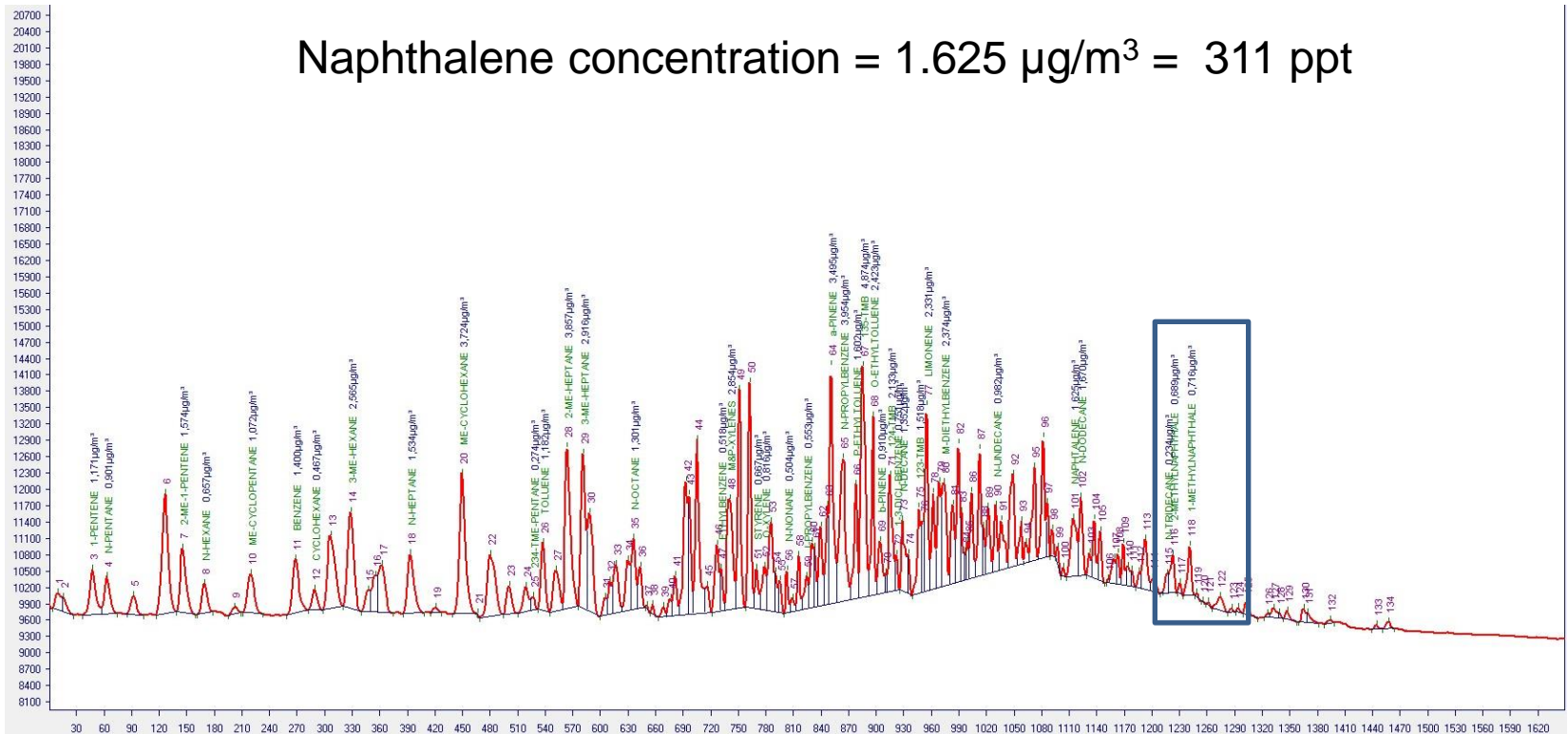


Field tests



Field tests

Naphthalene concentration = $1.625 \mu\text{g}/\text{m}^3 = 311 \text{ ppt}$



Field tests

- Analysis of VOCs and PAHs
 - From C5 – C16 for straight alkanes / alkenes and aromatic hydrocarbons
 - From Naphthalene to Fluorene for PAHs
- Continuous monitoring allows the measurement of short increases of concentrations

Conclusion



- AirmoSCAN XPERT PAH Composed by airmoC5C16 and Process MS
 - Continuous system
 - 1 hour cycle
 - Automatic validation by process MS
 - Analyze 6 first PAHs
 - System restart in one hour

Conclusion



- Double identification & quantification of all chemicals compounds from C5 to C16 thanks to the autoGC/FID/MS
 - Concentrations from **ppt**, ppb, ppm to %
 - Embedded supervisor with RTDB
- Automatic data validation using embedded permeation tubes
- Flexible & evolutive system
 - airmVOC C5C16 upgrade with MS
 - Easy to use for non-chemists
 - **mCERTs certified for working 24h/24, 7d per week**
 - **> 3 month without operator intervention**

Current status & Perspectives

- Other compounds
 - Aldehydes ; Sulfur (HCHO ; Mercaptans)
 - **CH₄ / NMTHC / THC and VOC up to Naphthalene**
 - Odors
- MS coupled with auto GC FID 866
 - VOC ; OVOC ; halogenated compounds
 - VOC, OVOC
 - **PAH's in particulate phase from C17 to c22 & PAC's, PCB's / DIOXINES**





Sales Contact



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Thank you for your attention !