CHROMATOTEC® GROUP

ONLINE GAS ANALYZER EXPERTS

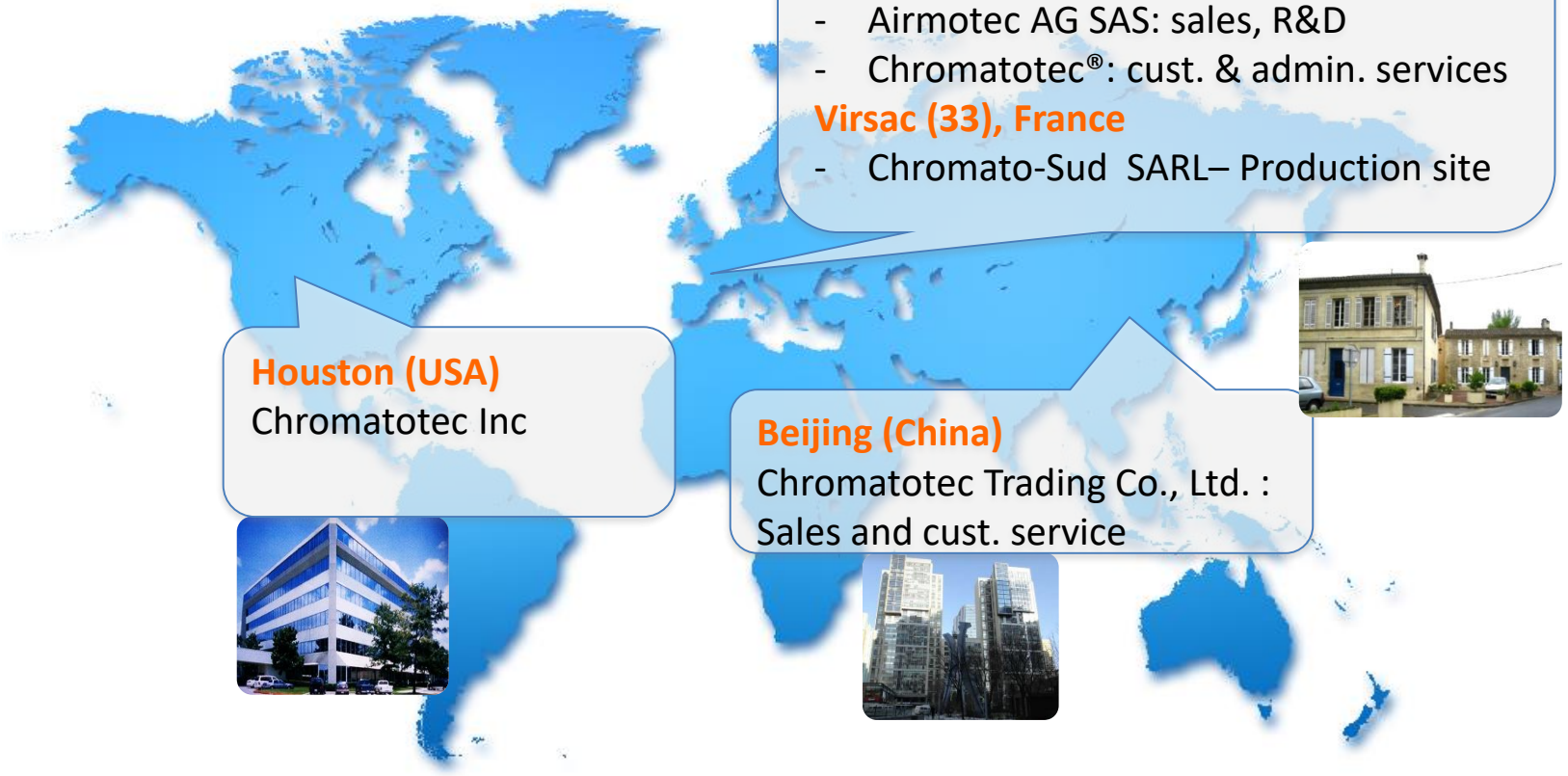
# Development of an on-line and field dual TD-GC-FID/MS for automatic and continuous ambient air & odor monitoring

Contact : mickael.gezat@chromatotec.com

# Who Chromatotec is?

- ISO 9001 French manufacturer  (family company) specialized in analytical solutions
- Up to 30 years on design and sales of automatic gas chromatograph
- 50 peoples
- Worldwide presence through local partners
- Most of the solutions are deployed outside France

# Chromatotec presence



**Saint-Antoine (33), France**
- Chromatotec Group Holding
- Airmotec AG SAS: sales, R&D
- Chromatotec®: cust. & admin. services

**Virsac (33), France**
- Chromato-Sud SARL– Production site



**Houston (USA)**
Chromatotec Inc



**Beijing (China)**
Chromatotec Trading Co., Ltd. :
Sales and cust. service

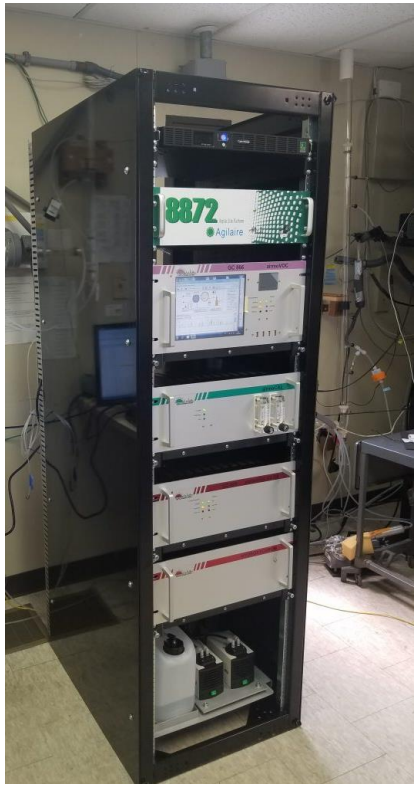
# Our specificity

- Turnkey solutions provider with
  - autoGC
  - multiplexing system
  - calibration system
  - gas generators
- Parternship to provide all-in-one solution

- Amount of certifications per country and on top 3 of providers selected by US EPA on autoGC evaluation

# Our specificity

- On-line and on field monitoring (not only lab)
- Speciation of VOCs & Sulfurs compounds at µg/m3 (ppb)
- Results correlated with dynamic olfactometry
- Automatic data validation
- Standalone solutions without gas cylinders or specific standards during routine use
- Design of solutions (GC PID, GC FID, GC TCD, GC MS, GC FPD or GC SSWCD and more)
- Tracking ppt concentration levels in air and/or process
- As sensitive as human nose on odorants



# Certificates

- ✓ Worldwide recognition with certifications relating to the relevant standards, performed by :


1996 2006 2009 2009 2010 2012 2013 2014

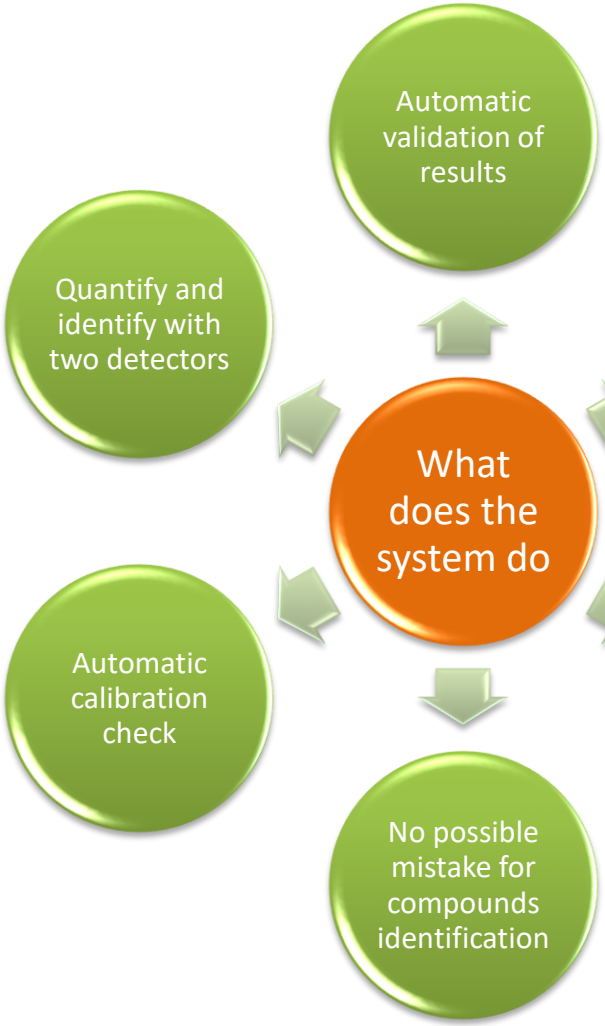
- ✓ **US EPA use Chromatotec solutions (2009) and have selected the company as one of the top 3 of 88 companies working on Ambient market for PAMS 56 monitoring**

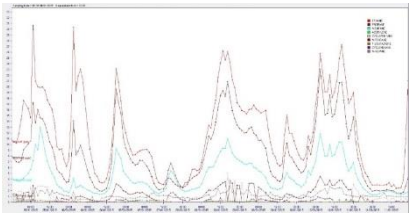
- ✓ EN 14662-3 (2013): Method to establish the performance criteria for the measurement of Benzene concentration using an automated sampling pump with in-situ gas chromatography.
  - Laboratory and on-site tests have been passed successfully by the NPL
  - Benzene and 12 other VOCs have been tested

- ✓ **airmotec/Chromatotec® : manufacturer with EN 14662-3**
  - En 14662-3: compulsory for ambient air monitoring in Europe
- ✓ Atex certification

# auto TDGC-FID/MS for what?

# auto TDGC-FID/MS for what?



# airmoSCAN XPERT

- GC FID 1 : airmoVOC C6-C12 5U **mCERTS certified with embedded PC and remote access**

- Mass spectrometer (0-300 amu) with MS **using hyperbolic quadrupole**

airmoS in option for sulfur compounds (if Sulfur compounds quantification needed)
(14 compounds: including H2S, Mercaptans, Sulfides, etc)

- 1U rack with mouse and key board

- **GC FID 2 :** airmoVOC C2-C6

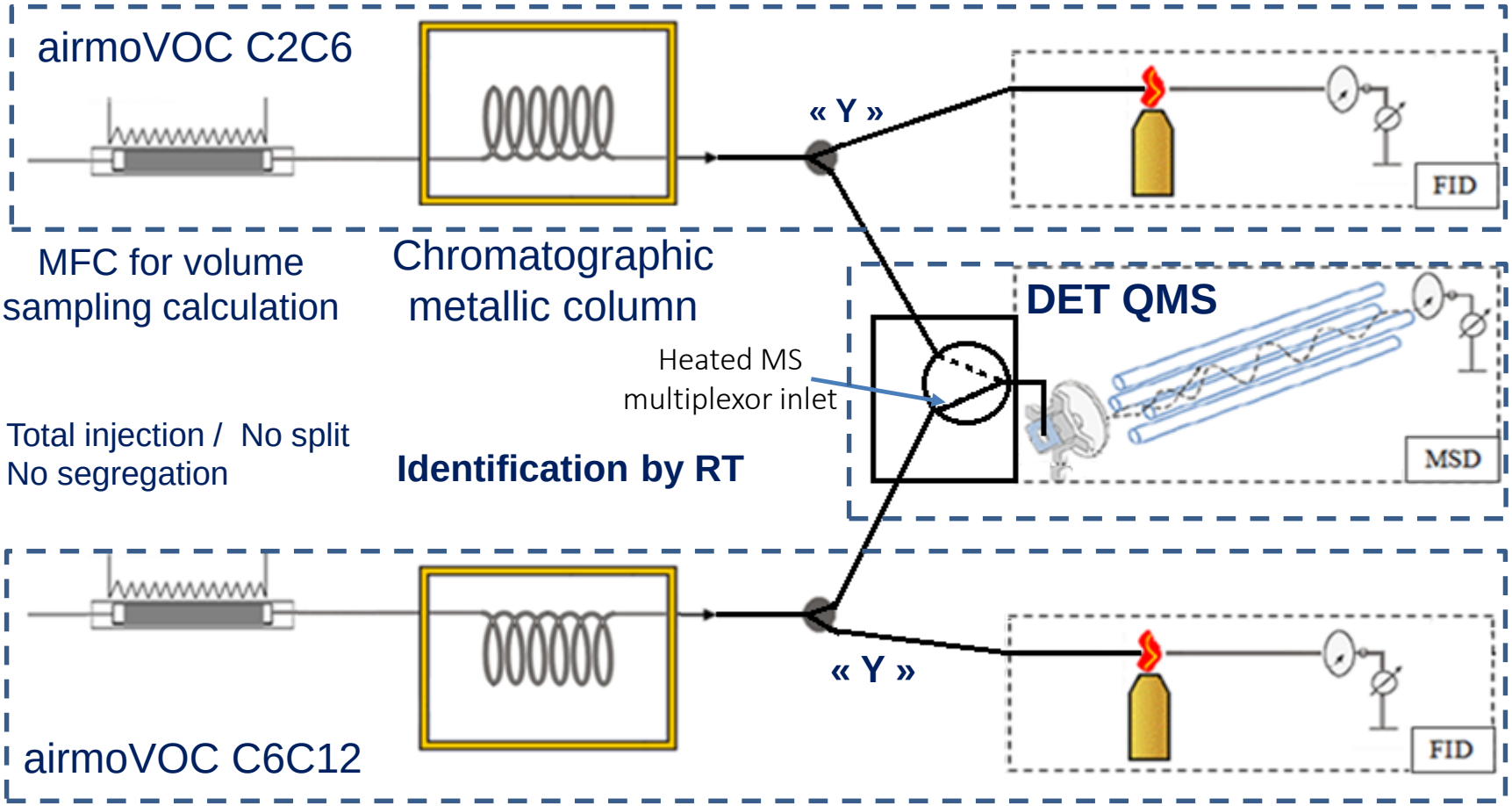
- Hydrogen generator : Hydroxychrom 4U

- Automatic calibration with permeation tube : airmoCAL

- airmoPURE (zero air generator) & Sampling pumps included


**airmOzone MS configuration**

# auto GC FID and MS General operation



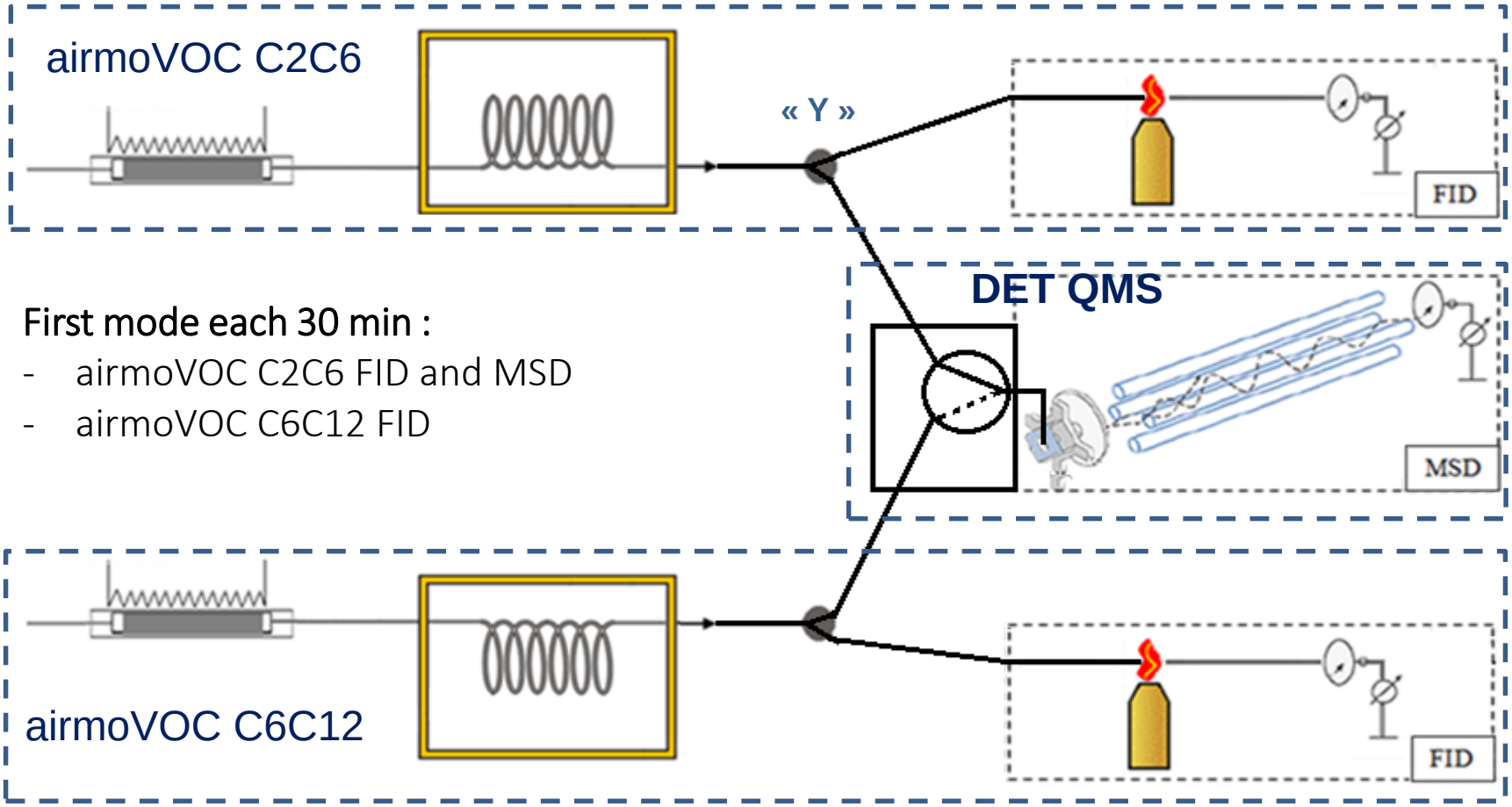

**TRAP for pre-concentration**

**GC for Speciation**

**« Y » and MS multiplexer**

**Double Detection MS & FID by auto GC 866**

# auto GC FID and MS
# Cycle operation

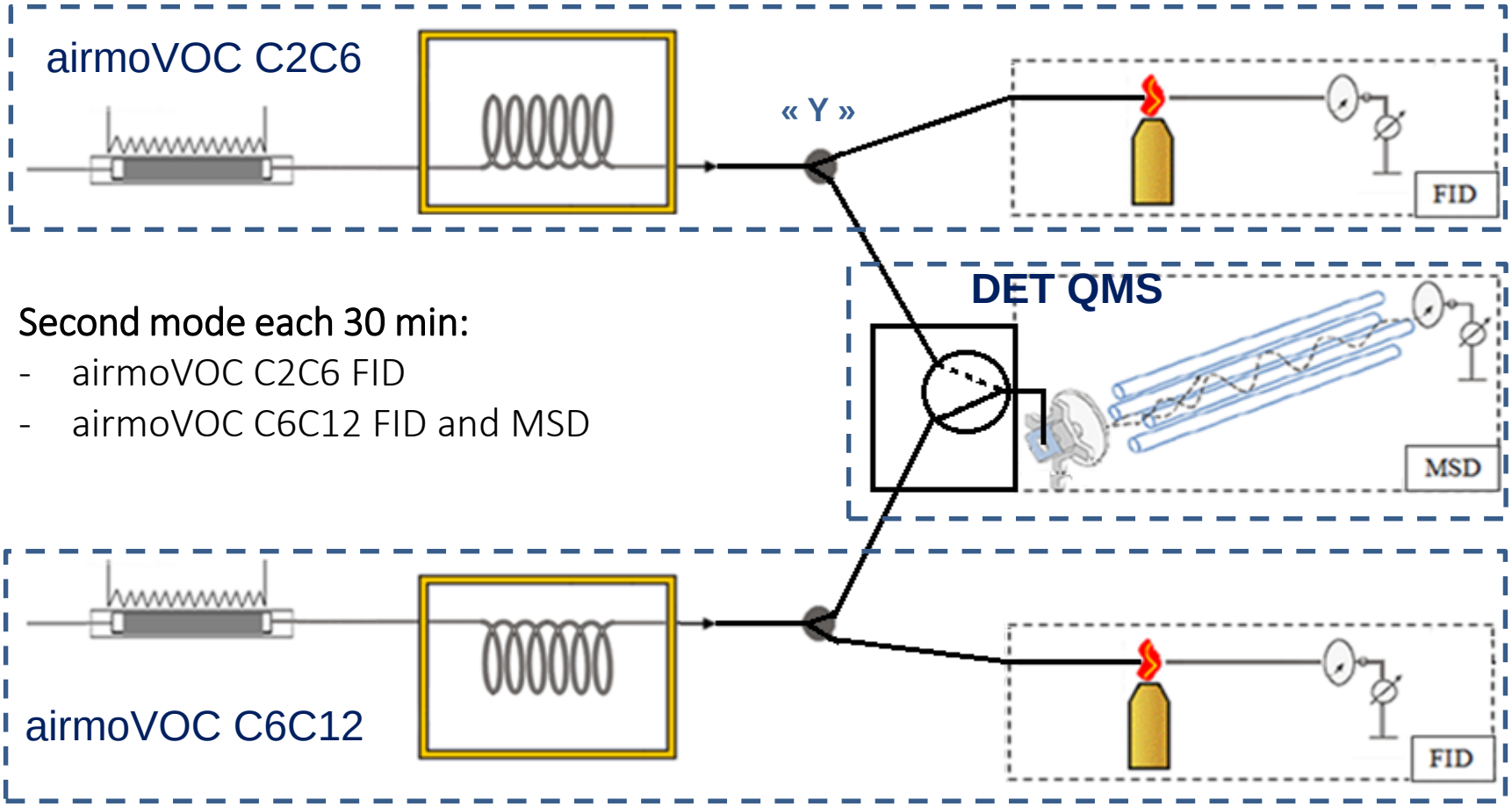



First mode each 30 min :

- airmoVOC C2C6 FID and MSD
- airmoVOC C6C12 FID

Automatic quantification by FID on all VOCs and validation of identification of C2C6 VOCs

# auto GC FID and MS
# Cycle operation




Second mode each 30 min:

- airmoVOC C2C6 FID
- airmoVOC C6C12 FID and MSD

Automatic quantification by FID on all VOCs and validation of identification of C6C12 VOCs

# Specificity 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 analysis**
   - Compounds speciation with pure hydrogen First identification by RT
   - Automatic quantification certified by different organisms
     - » mCERTs 2013 ; worlwide expertises recognized by national institutes...
     - » US EPA selected in 2014

# Specificity 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-FID is used automatically for all compounds because of below reasons:
  - long term stability
  - linearity of FID detectors on known range of concentration
    - **To be 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 spectrometer**
- Quantification with GC-MSD is done automatically on all compounds and is used when:
  - 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 of 123 VOCs

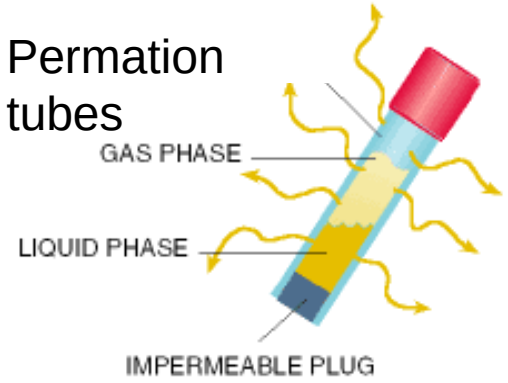
- **Identification and quantification done by FID and MS simultaneously**
  - Automatic identification and quantification of 123 VOCs by GC FID:
    - Substance table on airmoVOC C2C6 and C6C12

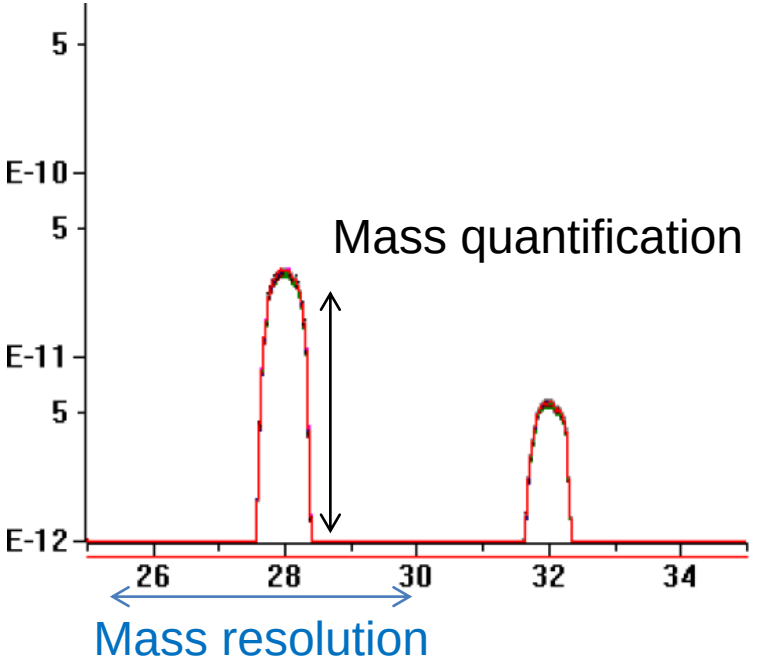
- Identification and quantification of unknown compounds (not in the list) in **SCAN mode**
  - 1st Comparison with embedded CHROMATOTEC library
  - If not in CHROMATOTEC library the mass spectrum can be sent to CHROMATOTEC for identification by R&D department

# 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



# VOC PAMS 56 with auto GCs- FID : airmOzone or with auto GCs C2C6/C6C12-FID-MS : airmoScan Xpert

## PAMS 56 (*)

### C2 to C6

C2

Ethane = C2
Ethene / ethylene

C3

Propane = C3
Propene
isobutane (2-méthyl propane )

C4

n-butane = C4
Acetylene
trans-2-butène
1-butene
cis-2-butène
Cyclopentane
Iso-pentane (2-methyl butane )

C5

n-pentane =C5
trans-2-pentene
1-pentene
cis-2-pentène
2,2-dimethylbutane
methylcyplopentane
2,3-dimethylbutane
2-methylpentane
3-methylpentane

C6

n-hexane =C6
isoprene
2-methyl-1-pentene

### C6 to C12

C6

2,4-dimethylpentane
Benzene
Cychohexane
2-methylhexane
2,3-dimethylpentane
3-methylhexane
2,2,4-trimethylpentane

C7

n-heptane =C7
Methylcyclohexane
2,3,4-trimethylpentane
Toluene
2-methylheptane
3-methylheptane

C8

n-octane =C8
Ethylbenzene
m-xylene
p-xylene
Styrene
o-xylene

C9

n-nonane =C9
iso propylbenzene
n-propylbenzene
m-ethyltoluene
p-ethyltoluene
1,3,5 trimethylbenzene
o-ethyltoluene
1,2,4 trimethylbenzene

C10

n-Decane =C10
1,2,3 trimethylbenzene
m-diethylbenzene
p-diethylbenzene

C11

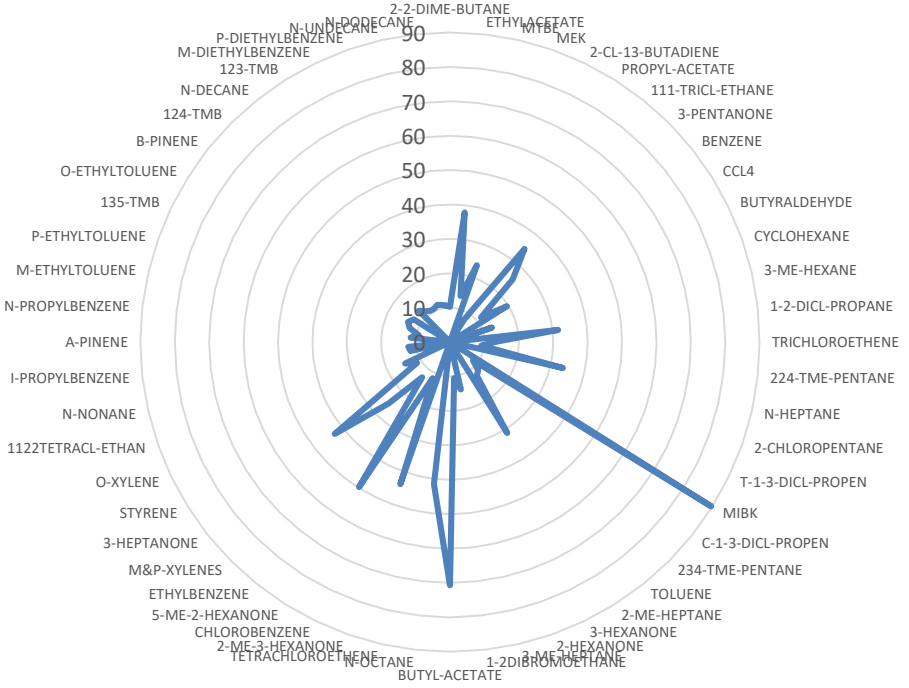
56) n-Undecane

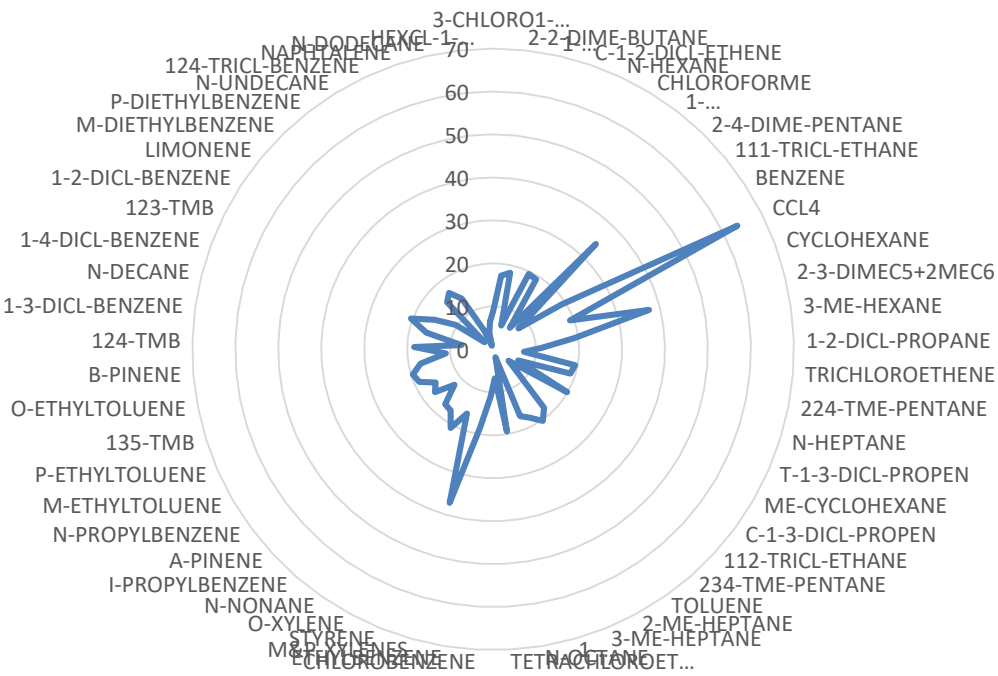
## Ozones precursors



(*)PAMS : Photochemical Assessment Monitoring Stations (PAMS)

# Differences of ambient air around sites in USA & China around industrial areas




Chemical fingerprints are different with easy plant differentiation

# VOC PAMS 56 & TO 14 with auto GCs- FID : airmOzone or with auto GCs C2C6/C6C12-FID-MS : airmoScan Xpert

## TO 14 (*)

(*) TOXICS

1) Di chloro di fluoro Methane * = 1
2) Chloro Methane * = 2
**3) 1,2-di chloro tetra fluoro Ethane ***
4) Vinyl chloride = chloro Ethylene= 3
5) 1.3-butadiene = 5
6) Bromomethane
**7) Ethyl chloride = chloro Ethane ***
8) tri chloro fluoro Methane * = 4
9) Acrylonitrile *
10) 1.1-di chloro Ethylene = 6
11) Di chloro Methane * = 7
12) 3-chloro-1-propene = allyl chloride
13) Tri chloro tri fluoro Ethane * = 8
14) 1.1-dichloro Ethane *
15) c-1.2-dichloro Ethylene
16) Chloroform = Tri Chloro Methane *
17) 1.2-dichloroethane *
18) 1.1.1-trichloroethane *
**19) Benzene**
20) Carbon tetrachloride *
21) 1.2-dichloropropane *
22) Trichloroethylene
23) t-1.3-dichloropropene
24) c-1.3-dichloropropene
25) 1.1.2-trichloroethane *
**26) Toluene = methylbenzene**
27) 1.2-dibromoethane
28) Tetrachloroethylene
29) Chlorobenzene
**30) Ethylbenzene**
**31) m+p-xylene =dimethylbenzene**
**32) Styrene**
**33) o-xylene+1,1,2,2tetrachloroEthane***
**34) 4-ethyltoluene (P)**
**35) 1.3.5-TMB**
**36) 1.2.4-TMB**
37) 1.3-dichlorobenzene**+benzylchloride**
38) 1.4-dichlorobenzene
39) 1.2-dichlorobenzene
40) 1.2.4 -trichlorobenzene
41) hexachloro-1,3-butadiene

## Ozones precursors & Toxics : 88 compounds including PAMS 56 + T014

# VOC **123** with auto GCs C2C6/C6C12-FID-MS : airmoScan Xpert

+ PAMS 56
+ Haloalkanes
+ O,N VOC
+ 1,3 butadiene
+ Method 502-2
+ Terpenes / TO15

## Haloalkanes

| | |
|---|---|
| 1 | Freon12 |
| 2 | Chloromethane |
| 3 | Vinylchloride |
| 4 | Bromomethane |
| 5 | Chloroethane |
| 6 | Freon11 |
| 7 | Dichloroethylene |
| 8 | Freon113 |
| 9 | Dichloromethane |
| 10 | 1,1-Dichloroethane |
| 11 | Cis-1,2-Dichloroethylene |
| 12 | Chloroform |
| 13 | 1,1,1-Trichloroethane |
| 14 | Carbontetrachloroide |
| 15 | 1,2-Dichloroethane |
| 16 | Trichloroethylene |
| 17 | 1,2-Dichloropropane |
| 18 | Bromodichloromethane |
| 19 | trans-1,3-Dichloropropene |
| 20 | cis-1,3-Dichloropropene |
| 21 | 1,1,2-Trichloroethane |
| 22 | Tetrachloro ethylene |
| 23 | 1,2-Dibromoethane |
| 24 | Chlorobenzene |
| 25 | 1,3-Dichlorobenzene |
| 26 | 1,4-Dichlorobenzene |
| 27 | Benzylchloride |
| 28 | 1,2-Dichlorobenzene |
| 29 | Trans-1,2-Dichloroethene |

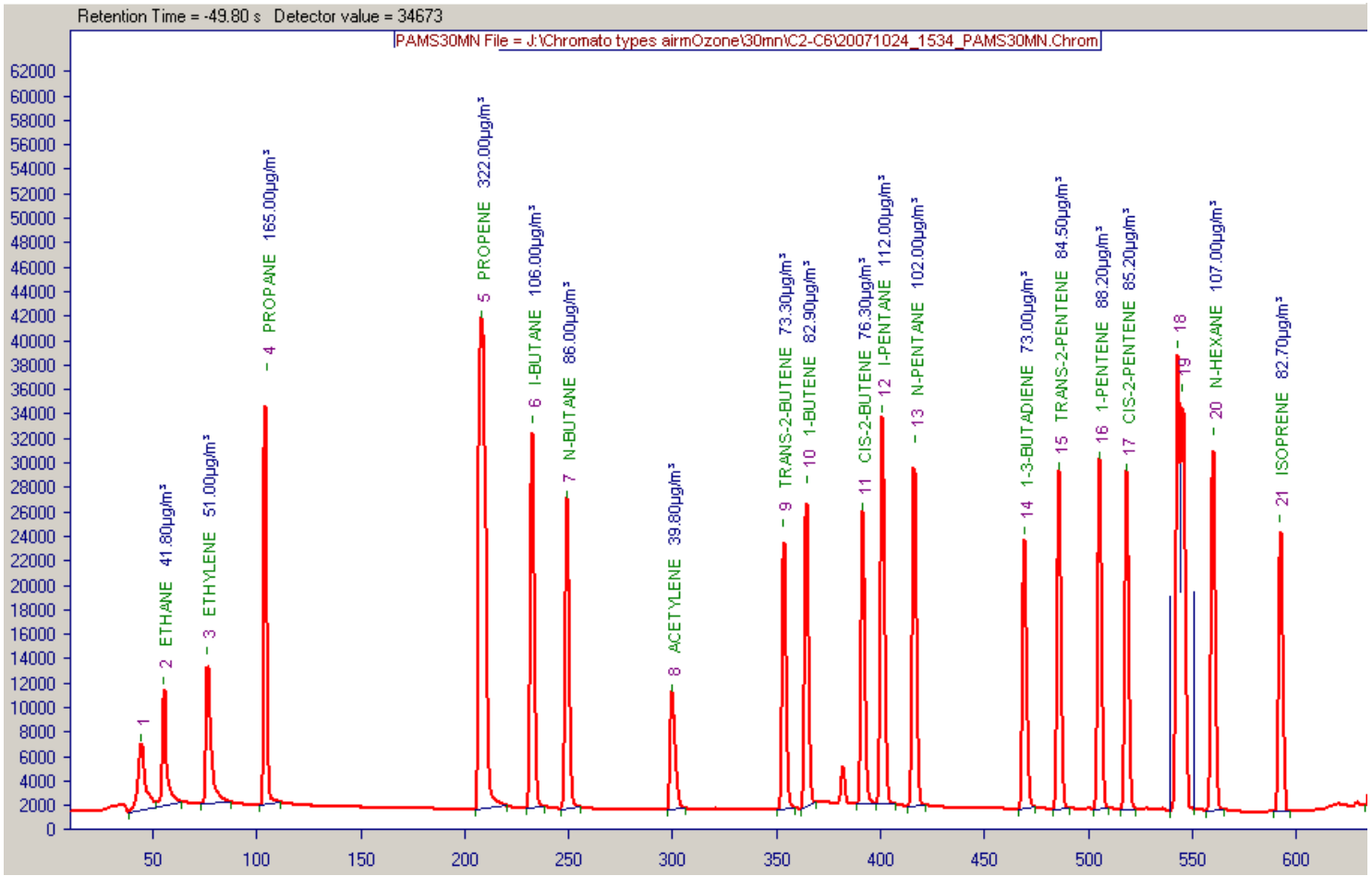
## O,N-VOC + 1,3-Butadiene

| | |
|---|---|
| 1 | **Acetaldehyde** |
| 2 | Methanol |
| 3 | Acrolein = Propenal |
| 4 | Propanal |
| 5 | Acetone |
| 6 | Acetonitrile |
| 7 | Methyl Ter Butyl Ether （MTBE） |
| 8 | Metharolein （2-Methyl Propenal） |
| 9 | N-Butanal （Butyraldehyde） |
| 10 | Methyl Vinyl ketone (MVK) |
| 11 | Methyl Ethyl ketone (MEK) |
| 12 | 2-pentanone (MPK) |
| 13 | N-pentanal |
| 14 | 3-Pentanone |
| 15 | N-Hexanal |
| 16 | 1,3-Butadiene |
| 17 | Isopropyl alcohol |
| 18 | Methyl-methacrylate |
| 19 | 2-Hexanone (MBK) |

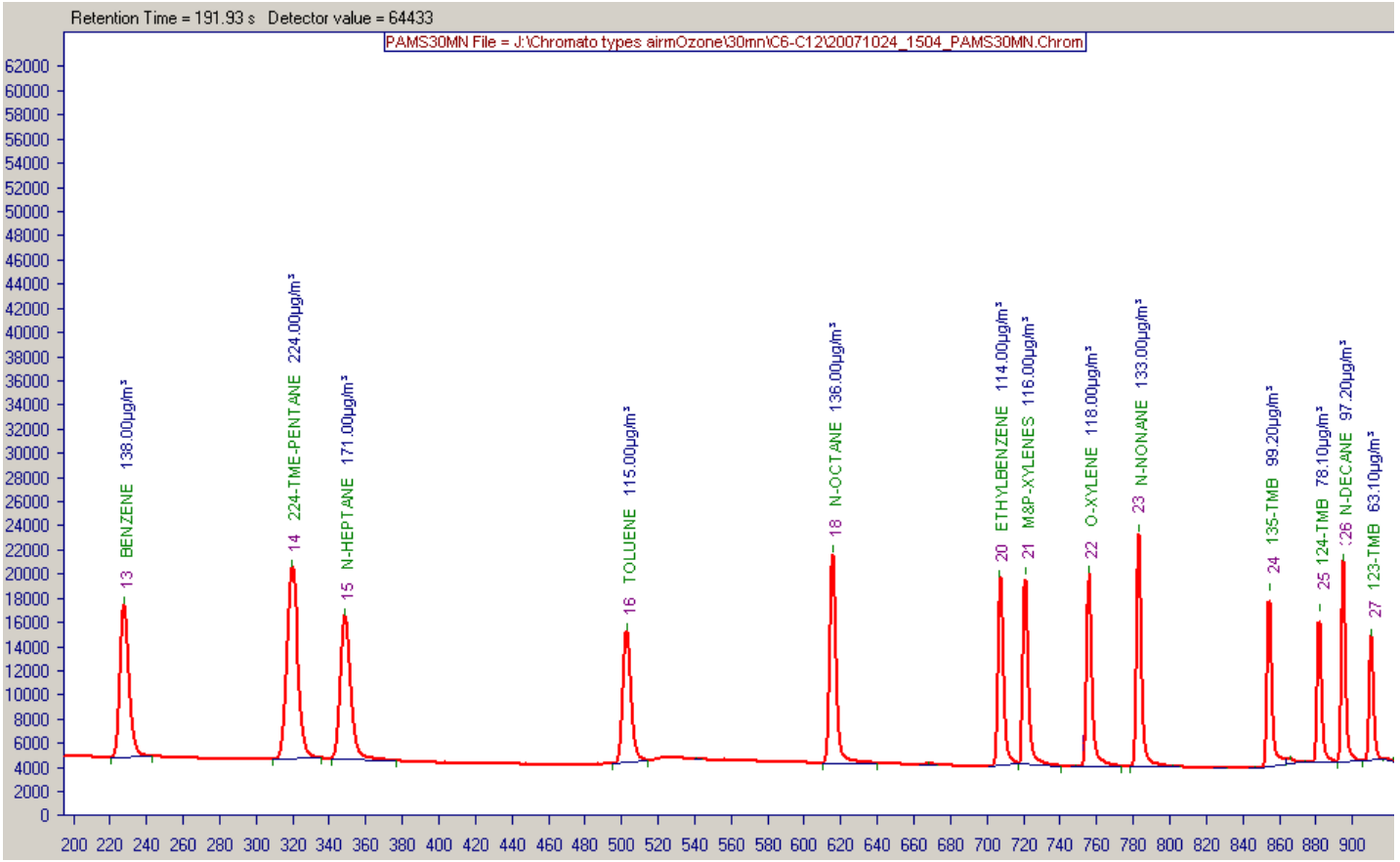
## Method 502-2/ Terpenes / TO15

| | |
|---|---|
| 1 | Alpha Pinene |
| 2 | Beta Pinene |
| 3 | Limonene |
| 4 | Carene |
| 5 | Tridecane |
| 6 | **Naphtalene** |
| 7 | Cyclopropane |
| 8 | Propadiene |
| 9 | Propyne |
| 10 | Ethanol |
| 11 | 1,2,4-Trichlorobenzene |
| 12 | Hexachloro 1,3-Butadiene |
| 13 | 1,2,3-Trichlorobenzene |
| 14 | 2-Methyl-2-Butene |
| 15 | 3-Methyl-1-Butene |
| 16 | 4-Methyl-1-Pentene |
| 17 | 2-Methyl-1-Pentene |
| 18 | Trans-2-Hexene |
| 19 | Cis-2-Hexene |

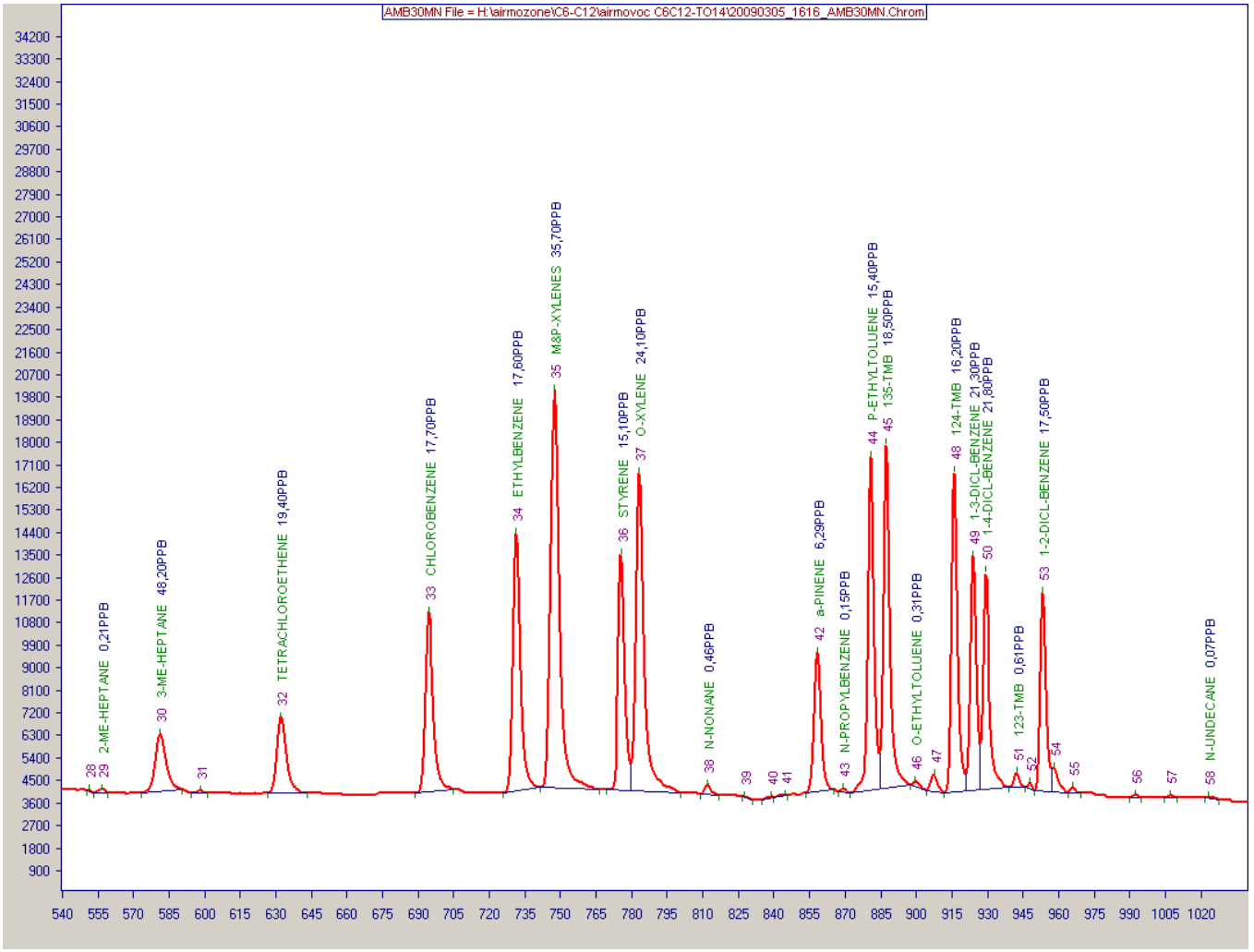
# Ozone precursors light hydrocarbons (C2-C6)



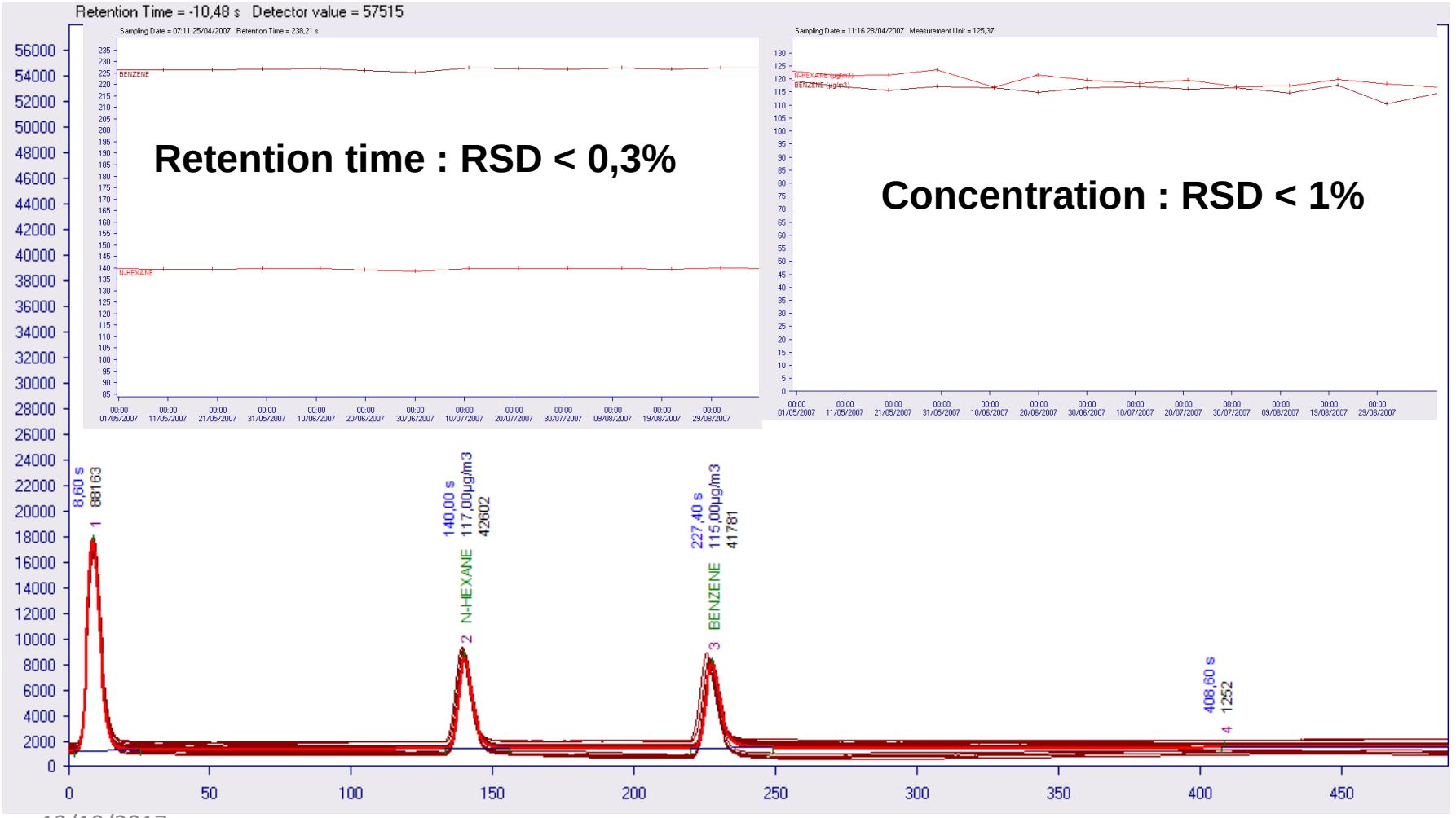
# Ozone precursors heavy hydrocarbons (C6-C12)



# Results Toxics Compounds TO14



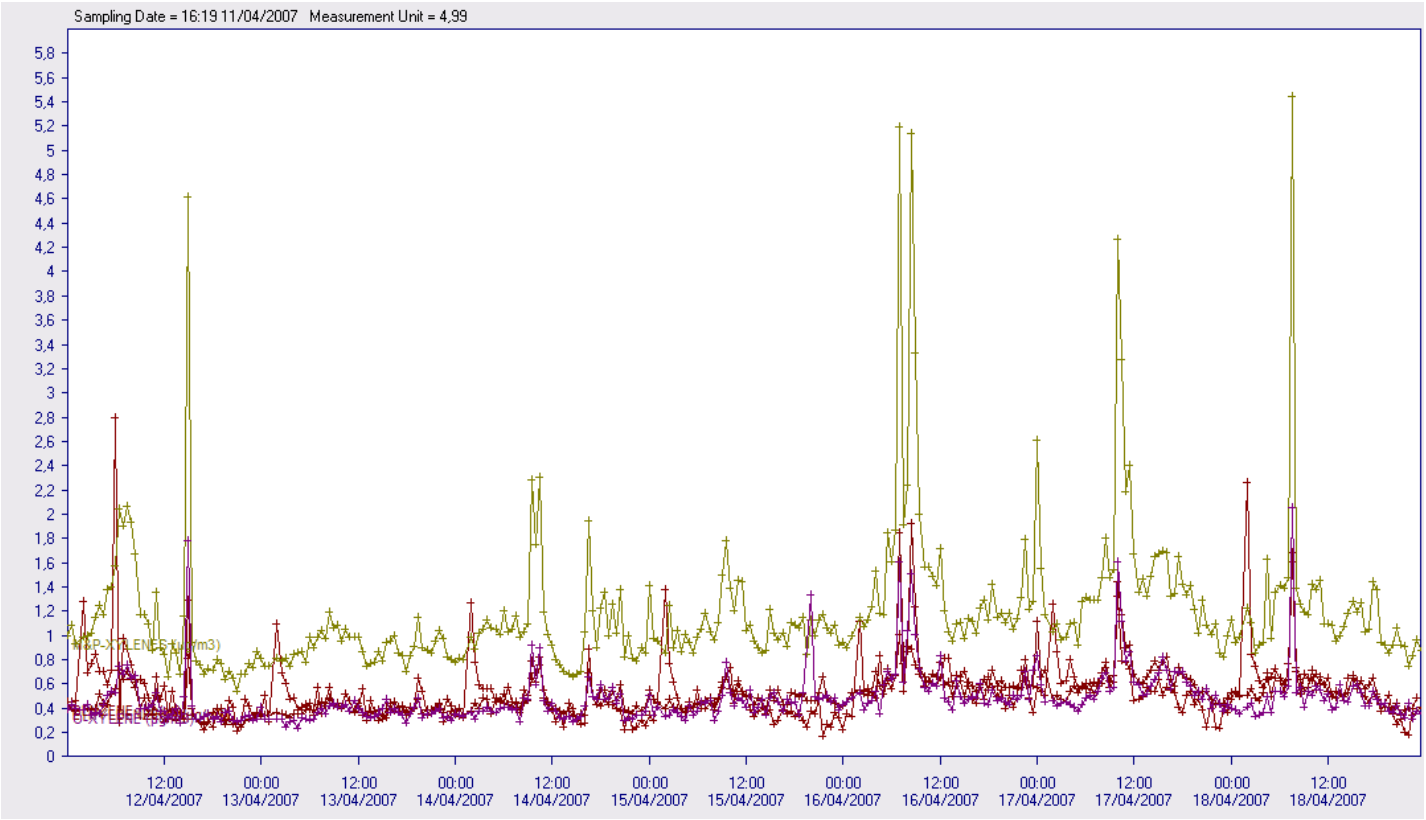
# Stability

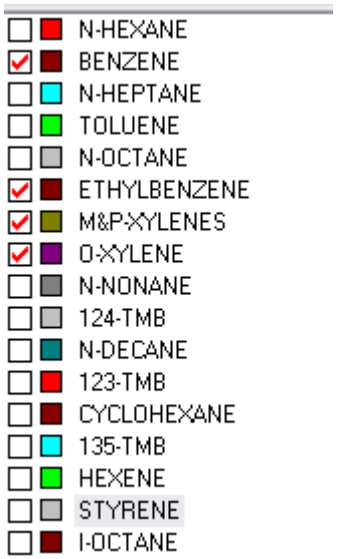



timestamp calibrations

# Week of analyses

**airmoVOC C6-C12 : Follow-up of concentration on a few compounds (in µg/m3) over one week (April 12 to 18, 2007) : Trend Area function of data processing Peak Viewer software.**

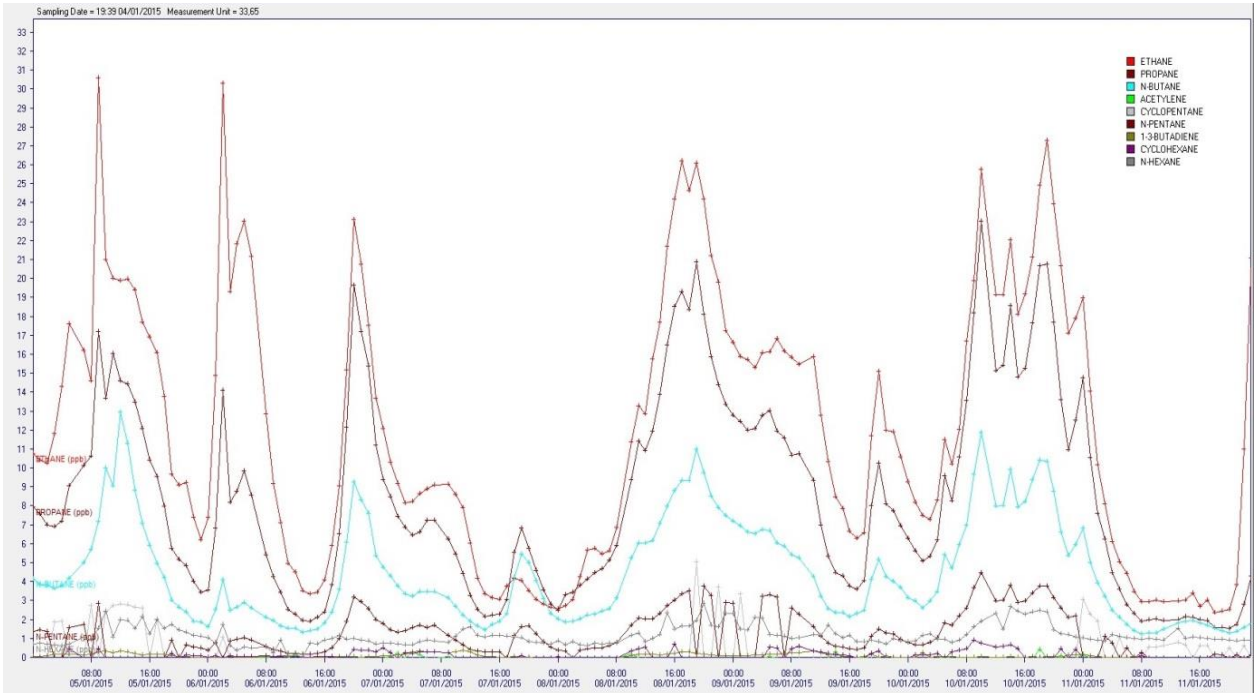


# airmoVOC C2-C6

## Results are studied weekly : automatic TREND

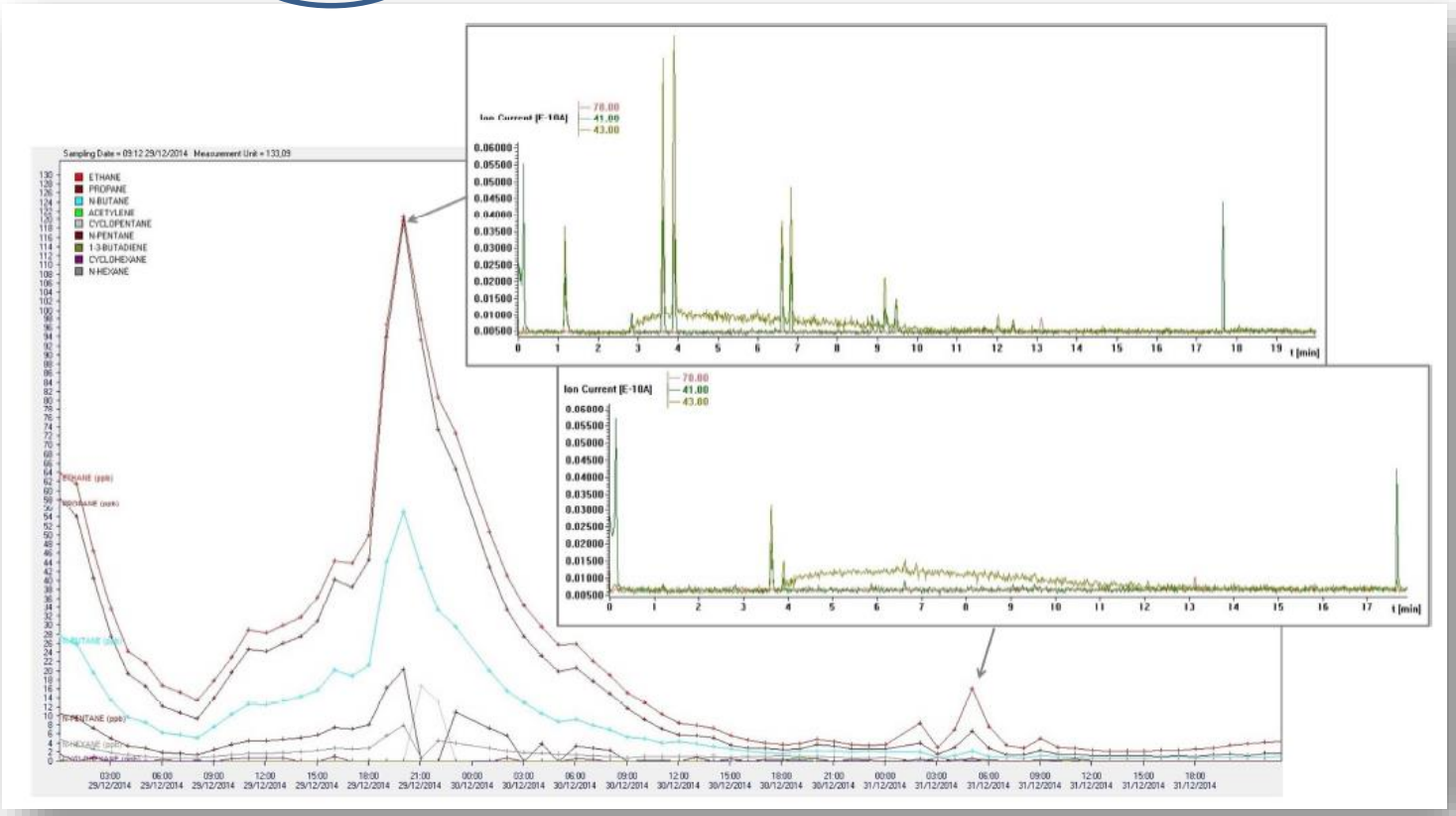
| Week 1 | ETHANE | PROPANE | N-BUTANE | ACETYLENE | CYCLOPENTANE | N-PENTANE | 1-3-BUTADIENE | CYCLOHEXANE | N-HEXANE |
|---|---|---|---|---|---|---|---|---|---|
| mean (ppb) | 12,02 | 8,47 | 4,55 | 0,02 | 0,33 | 1,19 | 0,14 | 0,14 | 1,21 |
| std dev | 7,12 | 5,32 | 2,77 | 0,07 | 0,88 | 1,17 | 0,11 | 0,21 | 0,53 |
| min (ppb) | 2,42 | 1,61 | 1,29 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,12 |
| max (ppb) | 30,67 | 23,08 | 12,99 | 0,49 | 5,12 | 4,54 | 0,44 | 0,95 | 2,90 |




Compounds evolution without problem of quantification identified from 0 to 36 ppb

# airmoVOC C2-C6

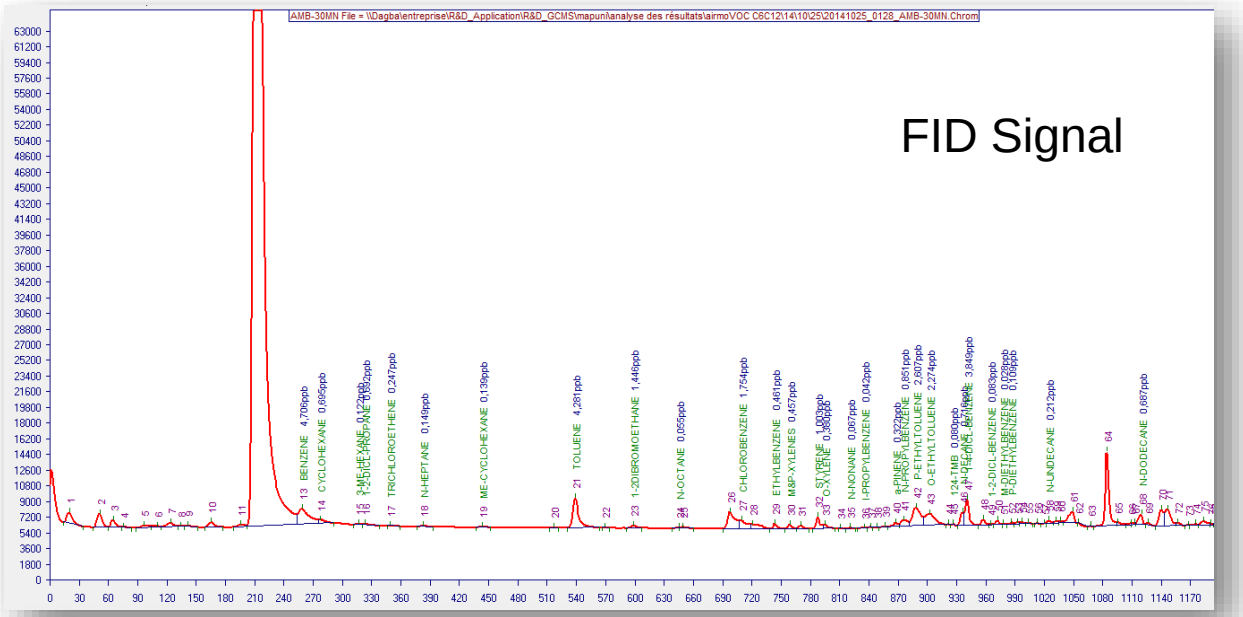
| Week 5 | ETHANE | PROPANE | N-BUTANE | ACETYLENE | CYCLOPENTANE | N-PENTANE | 1-3-BUTADIENE | CYCLOHEXANE | N-HEXANE |
|---|---|---|---|---|---|---|---|---|---|
| mean (ppb) | 22,26 | 18,75 | 9,25 | 0,03 | 0,49 | 2,67 | 0,15 | 0,16 | 1,45 |
| std dev | 25,87 | 24,81 | 11,43 | 0,14 | 2,56 | 4,00 | 0,10 | 0,35 | 1,50 |
| min (ppb) | 2,35 | 1,27 | 0,84 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| max (ppb) | 121,14 | 119,88 | 55,23 | 1,17 | 16,93 | 20,54 | 0,38 | 1,53 | 8,06 |



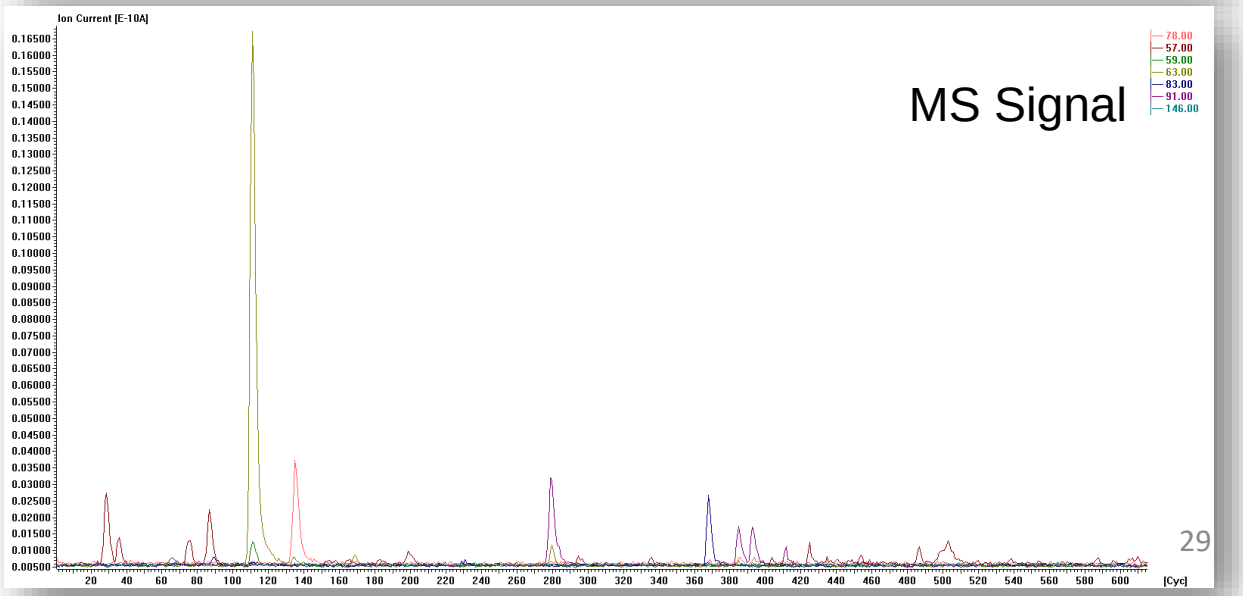

Double check with MS that increase measured by FID is due to the correct compound

# Unexpected compound identification

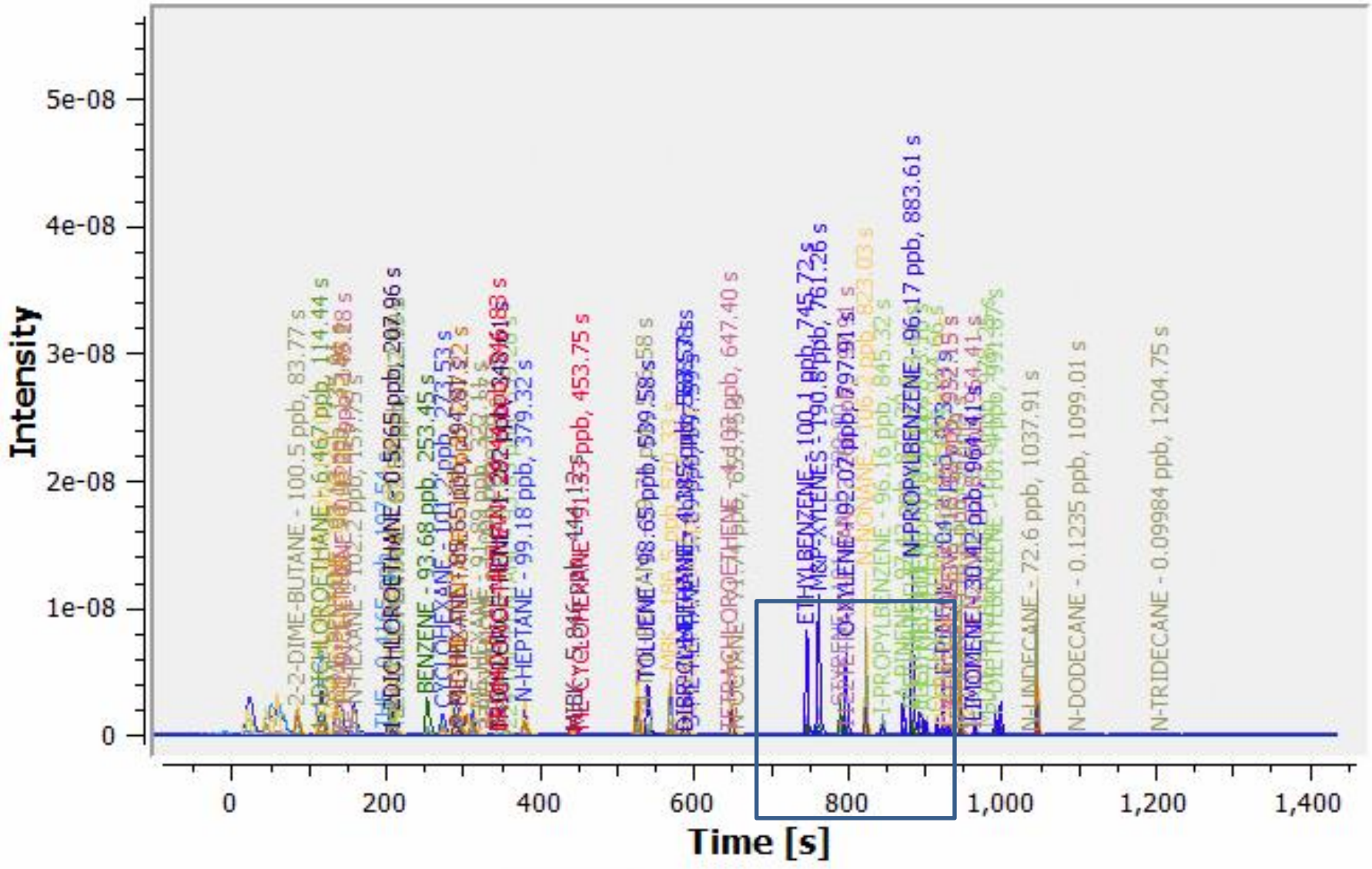
Signal saturation of an unexpected compound for the user



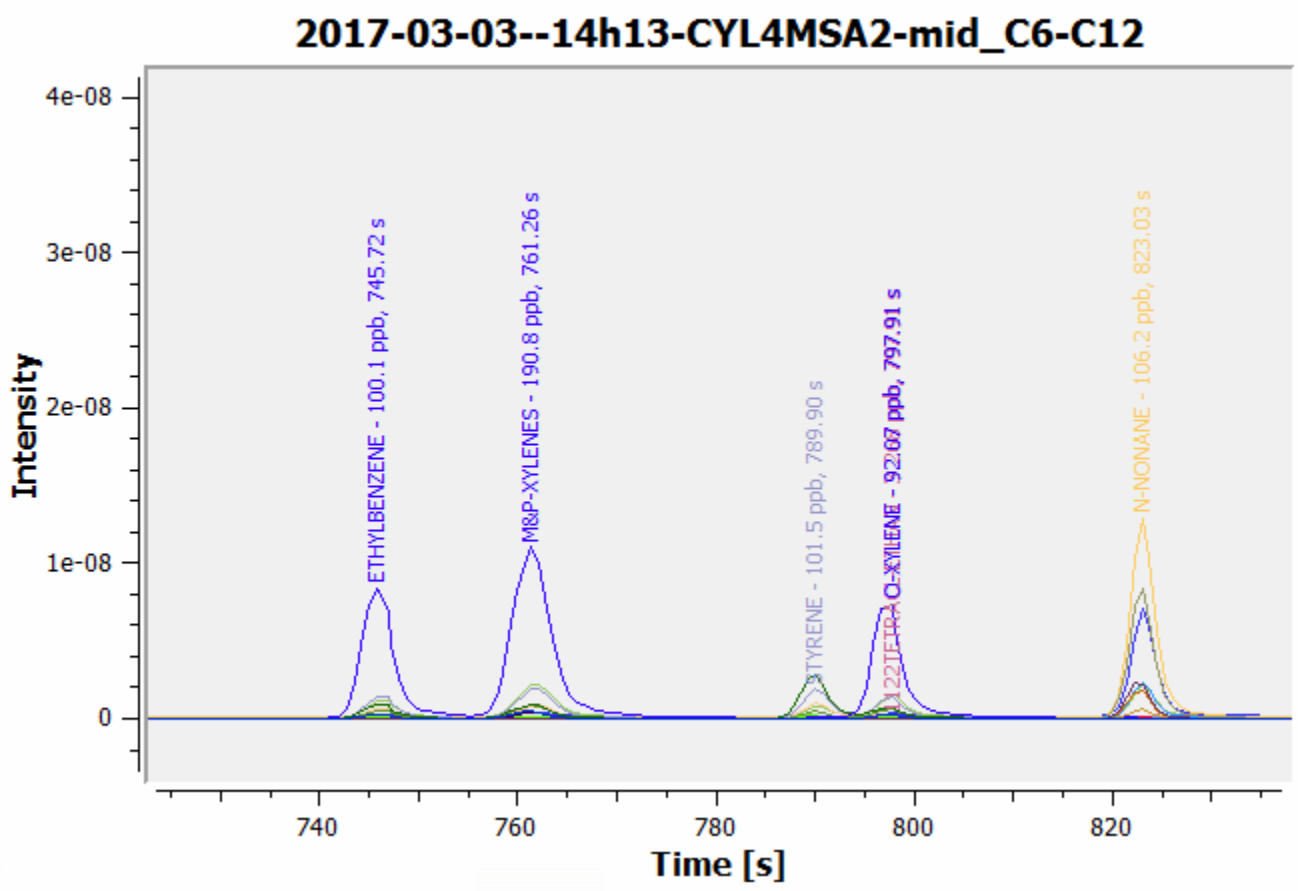

Mass spectrometer observed and quantified by SIM mode



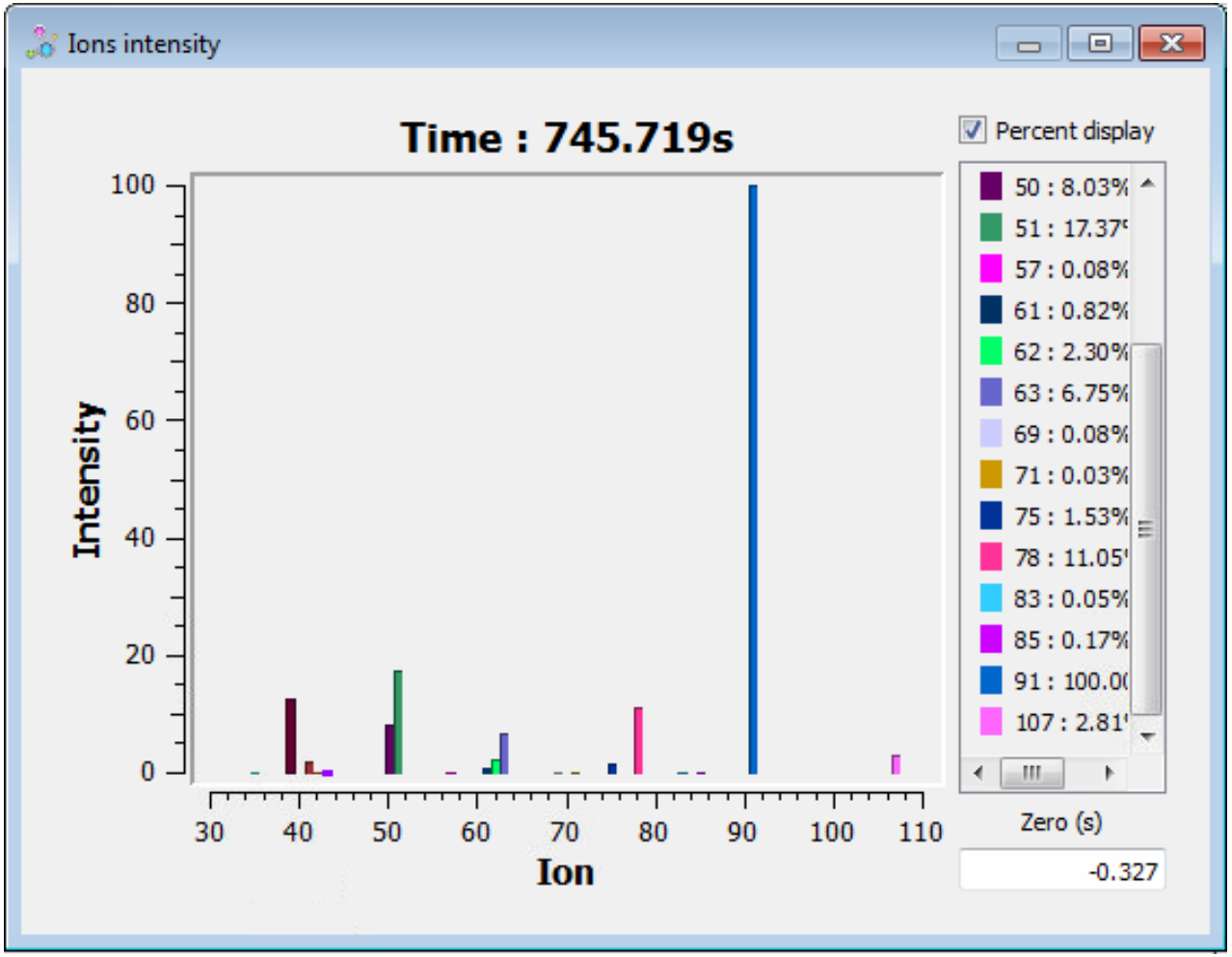
# Example of PAMS 56 monitoring



# Example of PAMS 56 monitoring



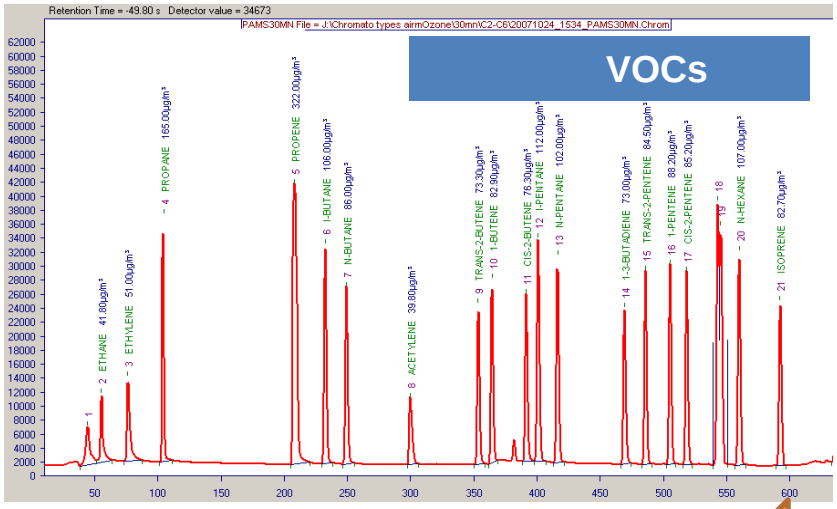
# Fragmentation MID ethylbenzene

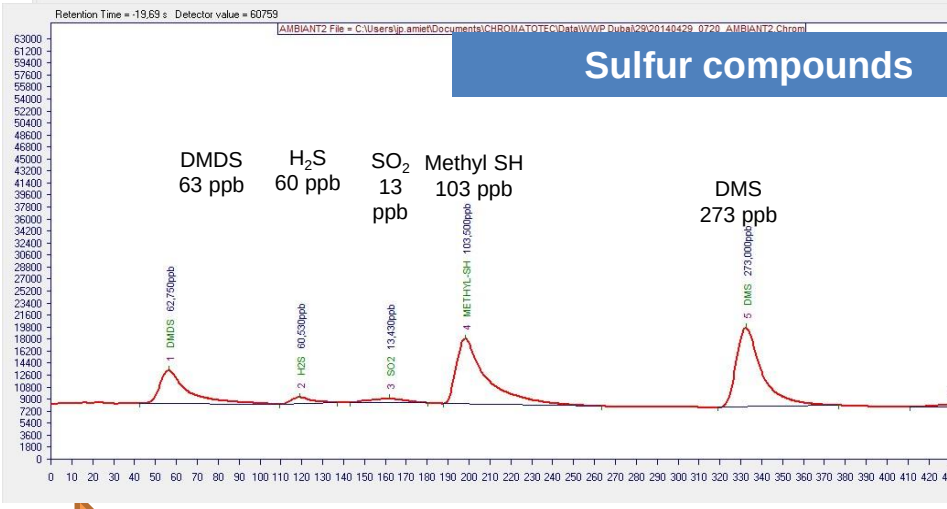


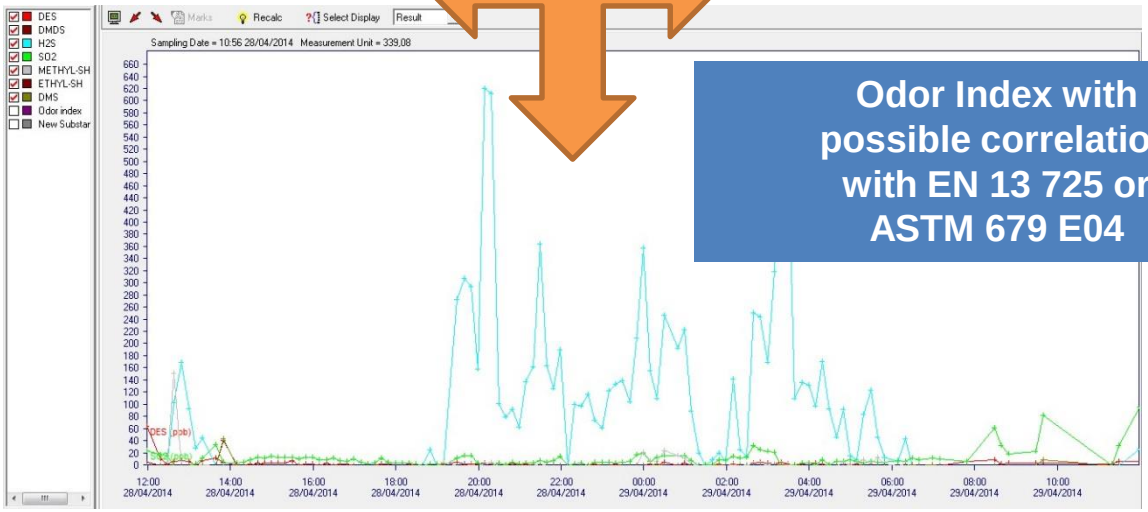
# Regarding odorants thresholds for VOCs

| | Compound | Characteristic odor | Olfactive odor threshold | |
|---|---|---|---|---|
| | | | µg/m³ | ppb |
| **Aldehydes** | Acetaldehyde | Fruit, apple | 50 to 300 | 28 to 167 |
| | Propionaldehyde | Rancid | # 20 | # 8.4 |
| | Butyraldehyde | Apple | 20 to 50 | 7 to 17 |
| | Valeraldehyde | Fruit | 20 to 70 | 5.7 to 20 |
| | Acetone | Sweet fruit | 119 000 | 50 000 |
| **Volatile Fatty Acids** | Acetic | Vinegar | # 900 | # 366 |
| | Propionic | Rancid | # 80 | # 26 |
| | Butyric | Rancid butter | 4 to 50 | 1 to 14 |
| | Valeric | Perspiration | # 5 | # 1.2 |

# Odor index
## can be defined to obtain global odor fingerprint trend



# Dedicated solution for odorants & chemicals impact on neighborhood with vigiOdor

- Solution to manage measurement units with alerts and warning
- Validation of results including embedded permeation tube
- Capabilities to work from ppb to ppm with same equipment
- Correlation done with portable olfactometer or direct observatoire using complaints / sensory observation
- Integration with sensory panel
- Reliable results in WWTP
- Capabilities to integrate full package (dispersion & complaints management) to check impact and validity of prediction
- Option: Correlation with EN 13725 in WWTP

# vigiODOR

**A global odor package including:**

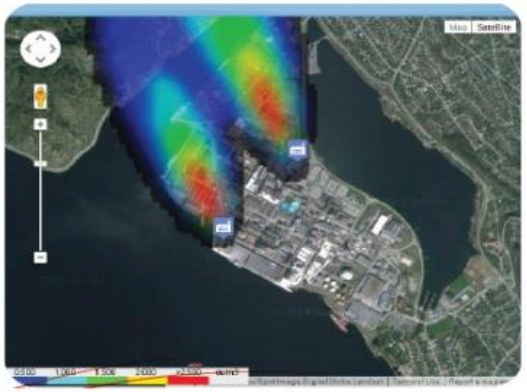
- Chemical & odorants Monitoring Systems
- Odor Modelling Software (modular 2D, 3Dcalculator)
- On site sensory evaluation (olfactometry)
  - Portable analyzer
  - Dynamic olfactometer EN 13725, ASTM 679
- Local weather tower
- Complaints management tools

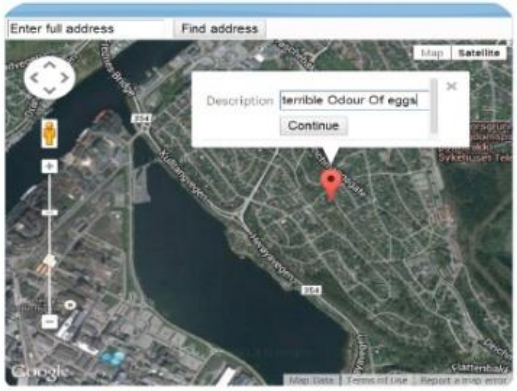
**Results**

- Odors Sources and Quantification
- Optimum Number of Analyzers & Positions
- Monitoring Specific Compounds

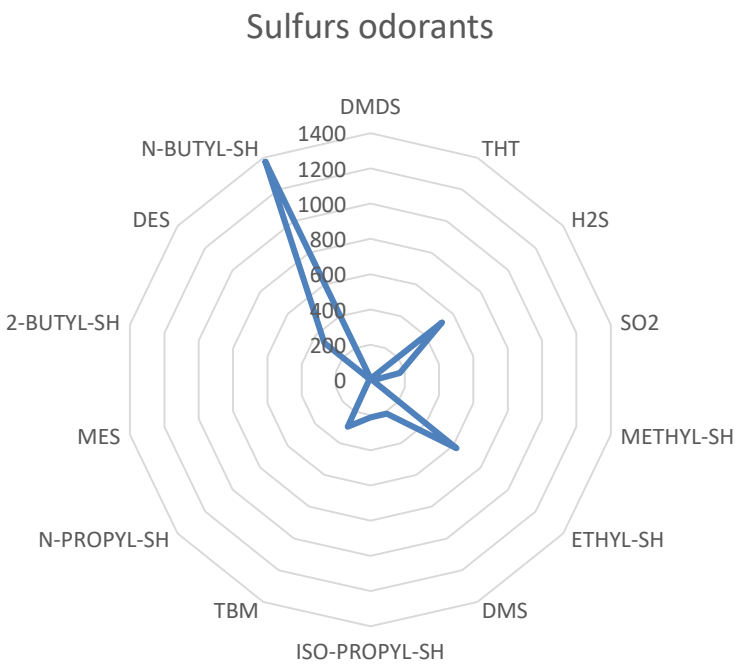
# vigiODOR / plum'Air

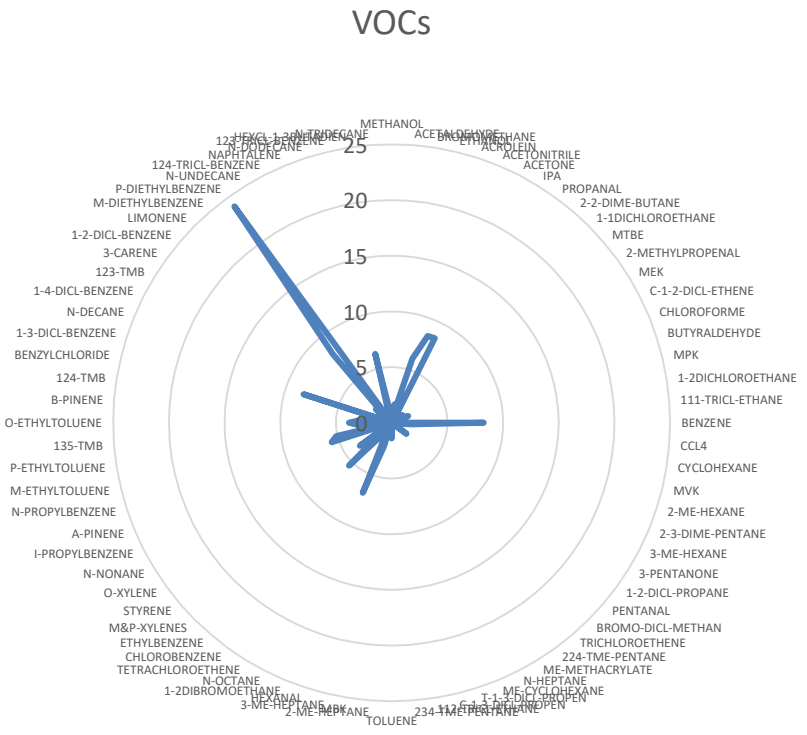
- 2 dedicated solutions
  - Plumair
    - Chemical impact
  - vigiODOR
    - Odor impact
- Modular solutions
  - Capabilities to integrate several analyzers
    - Chromatotec solutions
    - Nox, Sox, PM2.5, PM 10
    - Meteo weather station
  - Management of complaints to correlate with perception of neighborhood



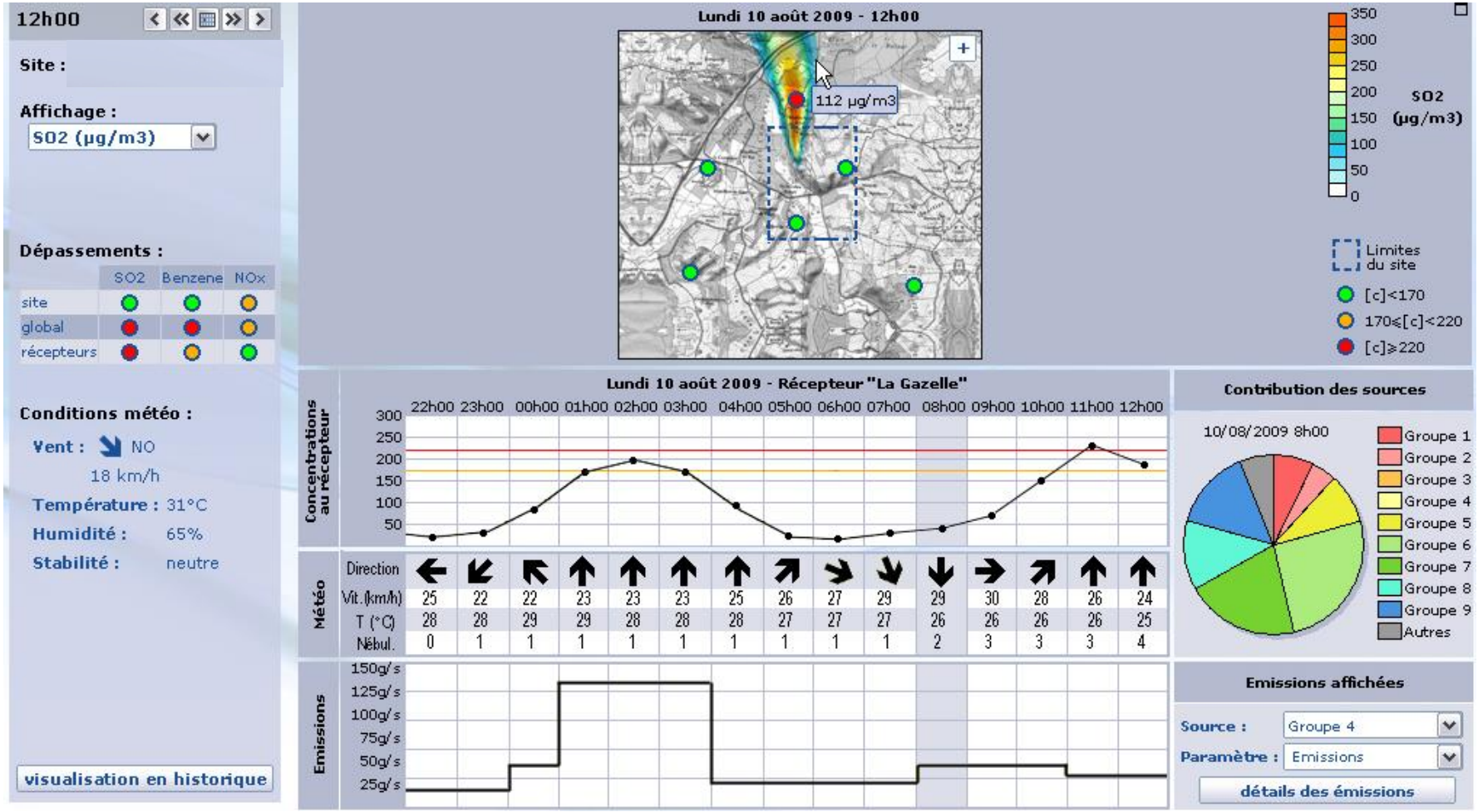


# Global odorants fingerprints



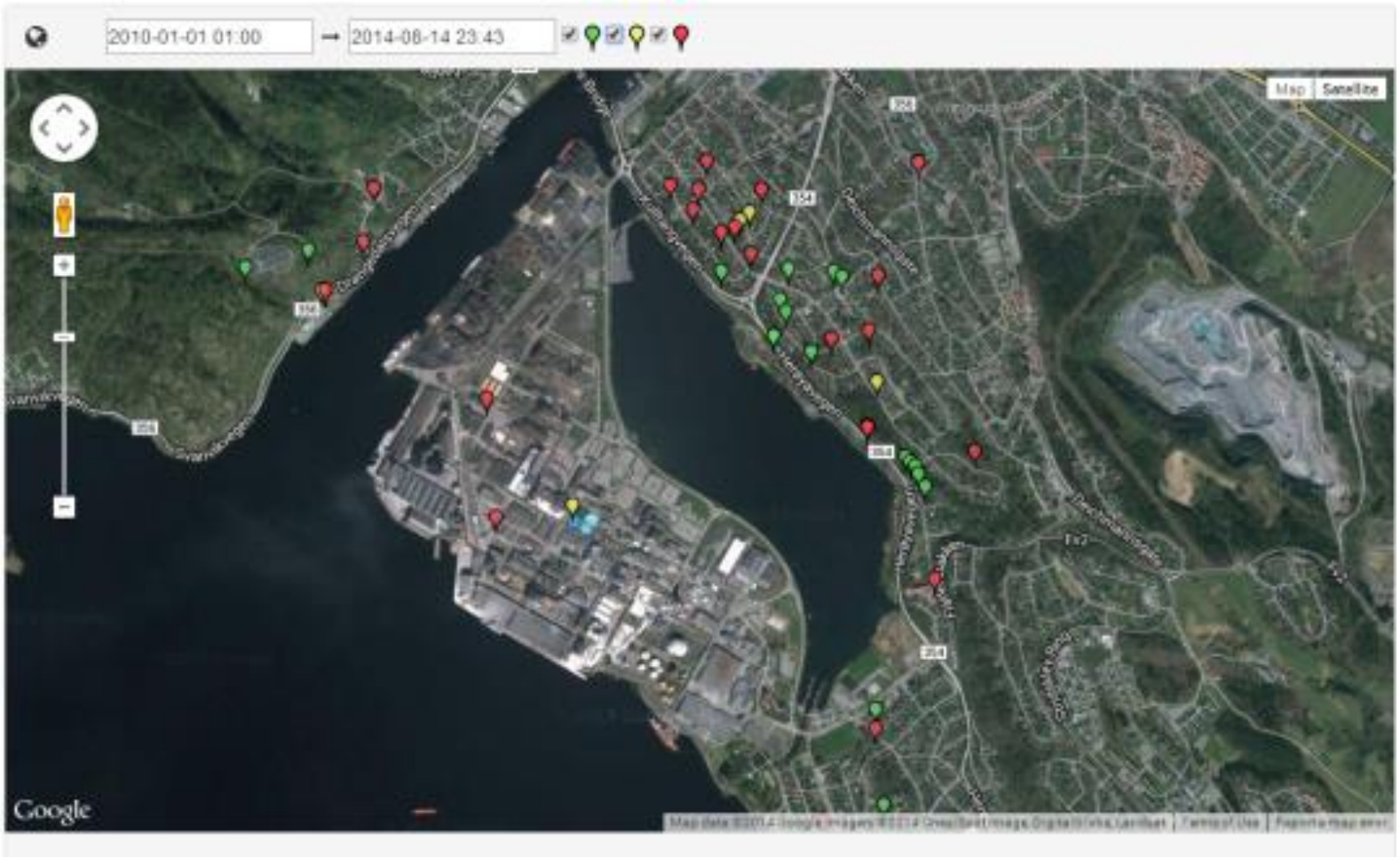
# vigiODOR


12h00
Site :
Affichage :
SO2 (µg/m3)
Dépassements :
SO2 Benzene NOx
site
global
récepteurs
Conditions météo :
Vent : NO
18 km/h
Température : 31°C
Humidité : 65%
Stabilité : neutre
visualisation en historique
Lundi 10 août 2009 - 12h00
112 µg/m3
350
300
250
200
150
100
50
0
SO2 (µg/m3)
Limites du site
[c]<170
170≤[c]<220
[c]≥220
Lundi 10 août 2009 - Récepteur "La Gazelle"
Concentrations au récepteur
22h00 23h00 00h00 01h00 02h00 03h00 04h00 05h00 06h00 07h00 08h00 09h00 10h00 11h00 12h00
300
250
200
150
100
50
Météo
Direction
Vit.(km/h) 25 22 22 23 23 23 25 26 27 29 29 30 28 26 24
T (°C) 28 28 29 29 28 28 28 27 27 27 26 26 26 26 25
Nébul. 0 1 1 1 1 1 1 1 1 1 2 3 3 3 4
Emissions
150g/s
125g/s
100g/s
75g/s
50g/s
25g/s
Contribution des sources
10/08/2009 8h00
Groupe 1
Groupe 2
Groupe 3
Groupe 4
Groupe 5
Groupe 6
Groupe 7
Groupe 8
Groupe 9
Autres
Emissions affichées
Source : Groupe 4
Paramètre : Emissions
détails des émissions

# vigiODOR

**RESULTS**

- **Automatic management of complaints**



# Conclusions

- Very large range of products available and designed according to Market's needs
  - VOC, Sulfurs, nitrogenous
  - 24h /7 days measurements
- Large range of concentration level from ppt to ppb and ppm
- Turnkey solutions:
  - Instruments
  - Multiplexers
  - Air generators
- Capability to work on hazardous area:
  - ATEX Ex II 3G Ex pz IIC T4

# Conclusions

- Unique technology for sulfur quantification at low concentration levels
- Modular and innovative solutions according to your customer's needs
- Equipments 100 % Hand made and control  with French Quality
- Solutions recognized as performant with amount of certifications

CHROMATOTEC® GROUP

EXPERTS IN GAS ANALYSIS

# Thanks for your attention

Contact : mickael.gezat@chromatotec.com

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