Online Analytical Solutions Experts

Continuous monitoring systems for polycyclic aromatic hydrocarbons in ambient air : SVOCs

Outline

- Introduction
- airmo C6-C20+
- Calibration system
- Field campaign
- Solids and liquids analysis with airmo C6-C20+

SVOCs: PAHs, Pesticides, alkanes …

- Semivolatile Organic Compounds (SVOCs) are
  - not as volatile as VOCs
  - Hardly noticeable through smell
- PAH: 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	C10H8	91-20-3	2	128	218
2	Acenaphthylene	ACN	C12H8	208-96-8	3	152	280
3	Acenaphthene	ACL	C12H10	83-32-9	3	154	279
4	Fluorene	FLR	C13H10	86-73-7	3	166	298
5	Anthracene	ANT	C14H10	120-12-7	3	178	340
6	Phenanthrene	PHN	C14H10	85-01-8	3	178	340
7	Fluoranthene	FLT	C16H10	206-44-0	4	202	384
8	Pyrene	PYR	C16H10	129-00-0	4	202	390
9	Benzo(a)anthracene	BAA	C18H12	56-55-3	4	228	437
10	Chrysene	CHY	C18H12	218-01-9	4	228	448
11	Benzo(a)pyrene	BAP	C20H12	50-32-8	5	252	495
12	Benzo(b)fluoranthene	BBF	C20H12	205-99-2	5	252	481
13	Benzo(k)fluoranthene	BKF	C20H12	207-08-9	5	252	480
14	Benzo(ghi)perylene	BGP	C22H12	191-24-2	6	276	550
15	Indeno[1.2.3-cd]pyrene	ICP	C22H12	193-39-5	6	276	536
16	Dibenz(a.h)anthracene	DBA	C22H14	53-70-3	6	278	524

- In Europe. ambient air legislation targets Benzo(a)pyrene
  - With annual target value of 1 ng/m^3

PAHs

- PAHs in the atmosphere are distributed between gas and particle phase
  - 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
    - $^{\bullet}OH$
    - $^{\bullet}NO_3$
    - photolysis at a lesser extent

L. Pozzoli. S. Gilardoni. M.G. Perrone. G. de Gennaro. M. De Rienzo. D. Vione. Ann. Chim. 94 (2004) 17.

PAHs

PAH	SINKS	ATMOSPHERIC LIFETIME
Naphthalene	$^{\bullet}OH$ » $^{\bullet}NO_3$, O_3	6.8 daylight hours
1-Methylnaphthalene	$^{\bullet}OH$ » $^{\bullet}NO_3$, O_3	2.8 daylight hours
2-Methylnaphthalene	$^{\bullet}OH$ » $^{\bullet}NO_3$, O_3	2.8 daylight hours
Acenaphthylene	$^{\bullet}NO_3 > O_3 > {}^{\bullet}OH$	6 nighttime minutes 1 daylight hour
Acenaphthene	$^{\bullet}NO_3 > {}^{\bullet}OH$ » O_3	1.2 nighttime hours 1.5 daylight hours
Fluorene	$^{\bullet}OH > {}^{\bullet}NO_3$ » O_3	9.1 daylight hours
Phenanthrene	$^{\bullet}NO_3 > {}^{\bullet}OH$ » O_3	4.6 nighttime hours 11.2 daylight hours

- Light compounds are very sensitive to the amount of $^{\bullet}OH$
- The main source is the photolysis of ozone ($\lambda < 320$ nm)
  - $O_3 + h\nu \rightarrow O_2 + O(^1D)$
  - $O(^1D) + H_2O \rightarrow 2\ {}^{\bullet}OH$
- Radicals react very rapidly
  - Negligible tropospheric concentration of •OH can be found during the night

L. Pozzoli. S. Gilardoni. M.G. Perrone. G. de Gennaro. M. De Rienzo. D. Vione. Ann. Chim. 94 (2004) 17.
B. J. Finlayson-Pitts. J. N. Pitts. Atmospheric Chemistry. Wiley. New York. 1986.

PAHs

Report from June 2018

Risk factor	Polluant
5.1	1.3-butadiene
1.4	Manganese
0.9	Hydrogen sulfide
0.88	Acrylonitrile
0.86	1.1.2-trichloroethane
0.7	Copper
0.4	Trichloroethylene
0.3	Vanadium
0.2	Cobalt
0.088	Antimony
0.087	Naphthalene

Agency recommends to monitor the priority compounds

anses
agence nationale de sécurité sanitaire
alimentation, environnement, travail
Connaître, évaluer, protéger

https://www.actu-environnement.com/ae/news/qualite-air-polluants-anses-butadiene-puf-carbone-suie-31570.php4

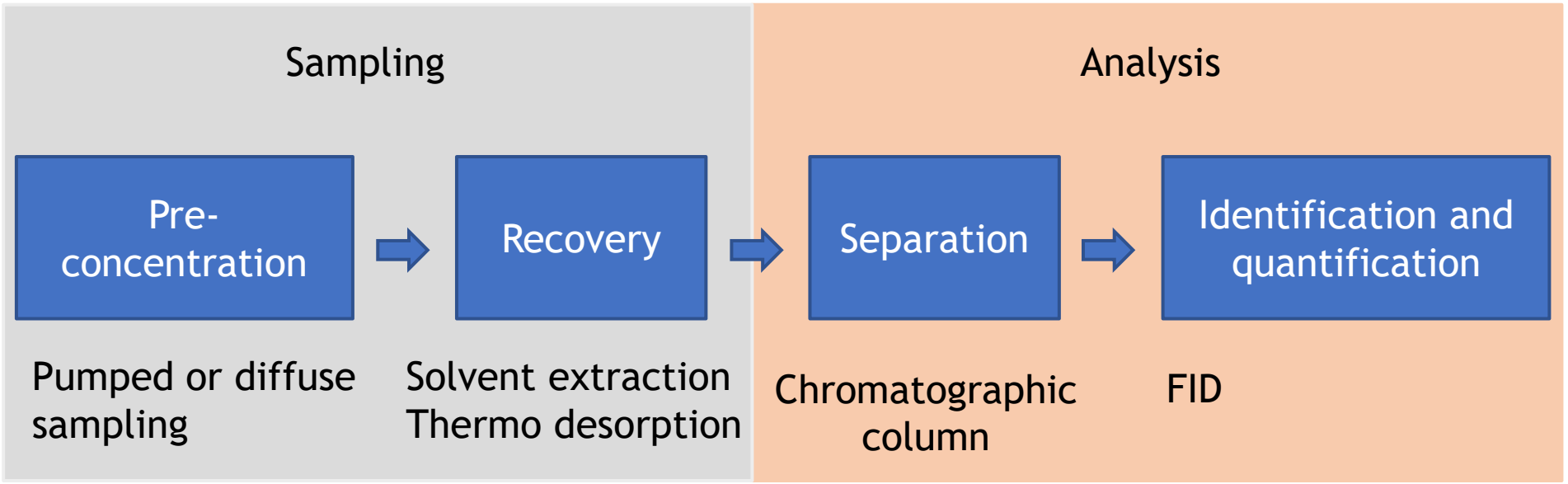
PAHs

- Very toxic
- Produced naturally and by human activities
- Gaseous or solid
- Lifetimes of light compounds in the gaseous phase is short
- To control their emissions and effects on people's health
  - Need to monitor continuously PAHs
  - Time between measurements < 1 hour
    - Vehicle exhaust
    - Industrial process

Techniques for determination of PAHs and sVOCs

- Concentration in air
  - 10 – 300 ng/m^3 for Naphthalene
  - 0.05 – 1 ng/m^3 for 3 to 6 rings
  - Pre-concentration required

- Very complex gas mixture
  - Separation needed before identification and quantification



Sampling

- Solvent extraction
  - Worldwide used and reference for PAH measurement
  - Time consuming
  - Labor-intensive procedures
  - Toxic organic solvents
  - Sampling and analysis require analytical engineer

- Thermo desorption
  - No analytical engineer needed
  - Easy to automate
  - Reliable

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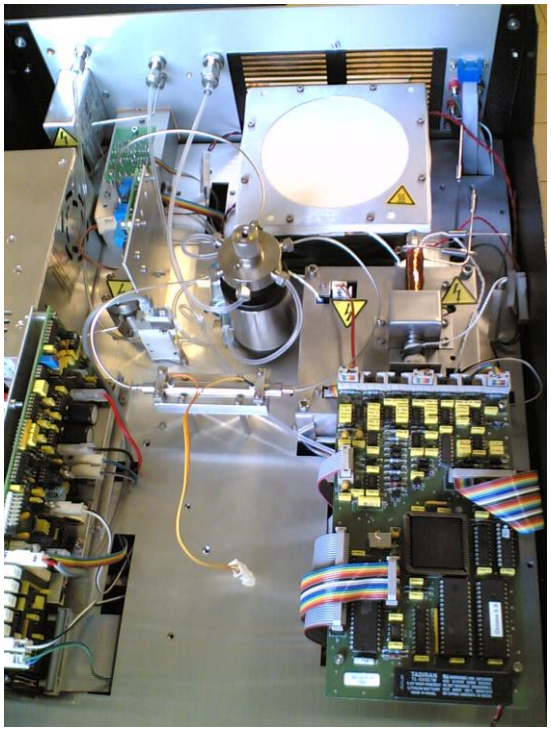
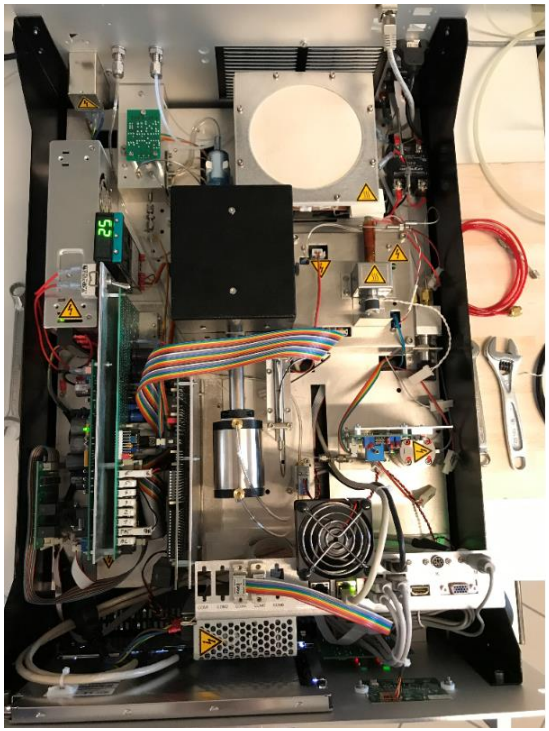
airmoVOC C6-C20+

airmoVOC C6-C12

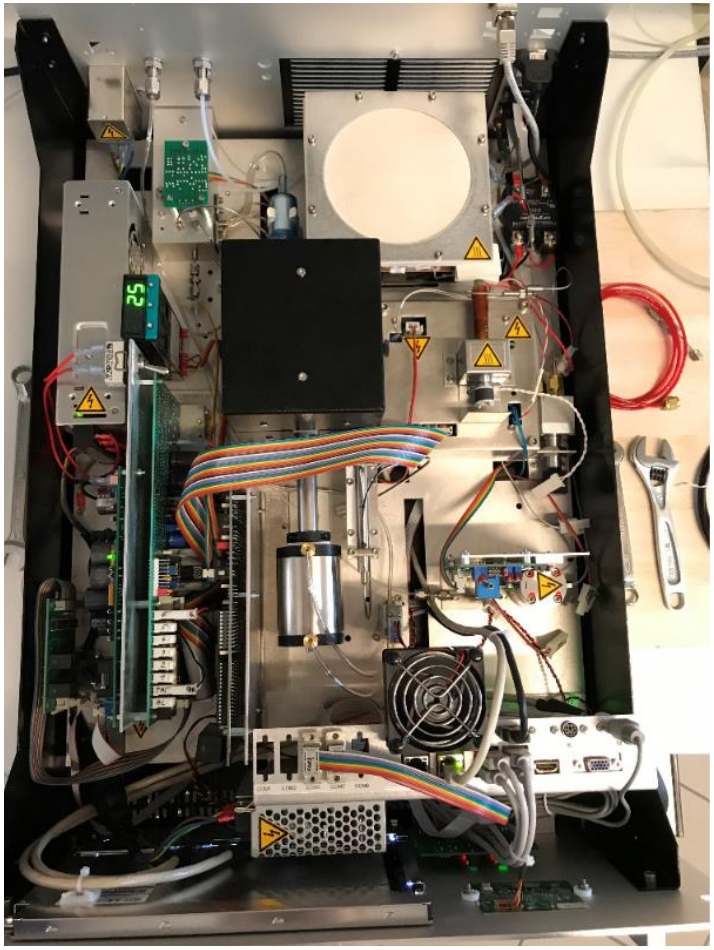


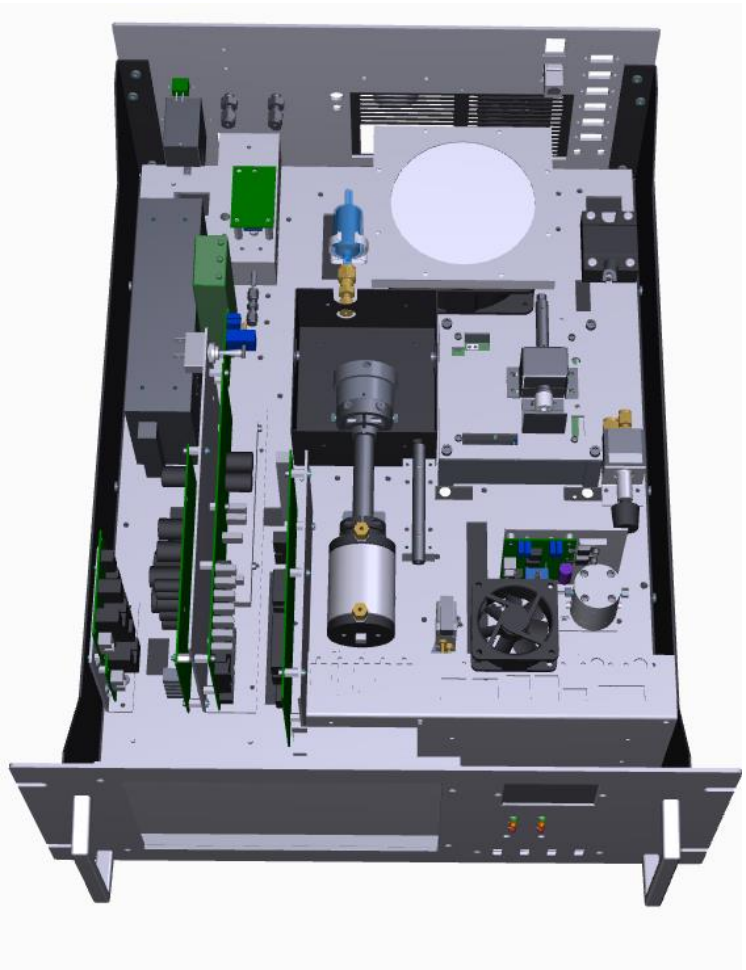
airmoVOC C6-C16



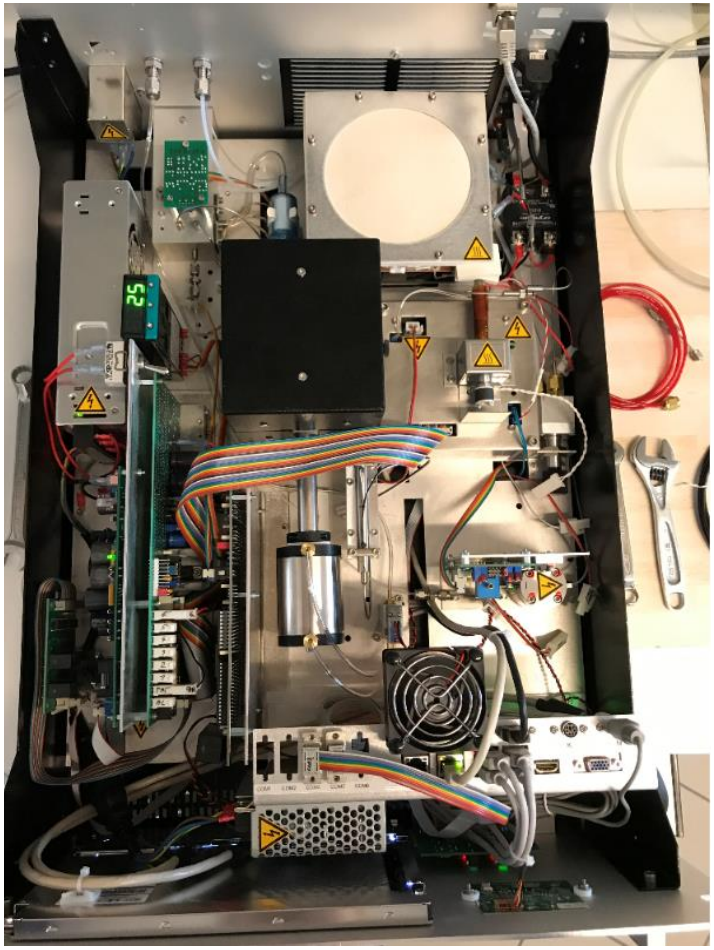
- Column: Apolar MXT
- Oven : 37 – 350 °C
- Detector:
  - FID
    - T : 202 °C
- Sampling line
  - Inox
  - 150 °C
- Carrier gas: H_2
- Trap: Carbo trap mixture

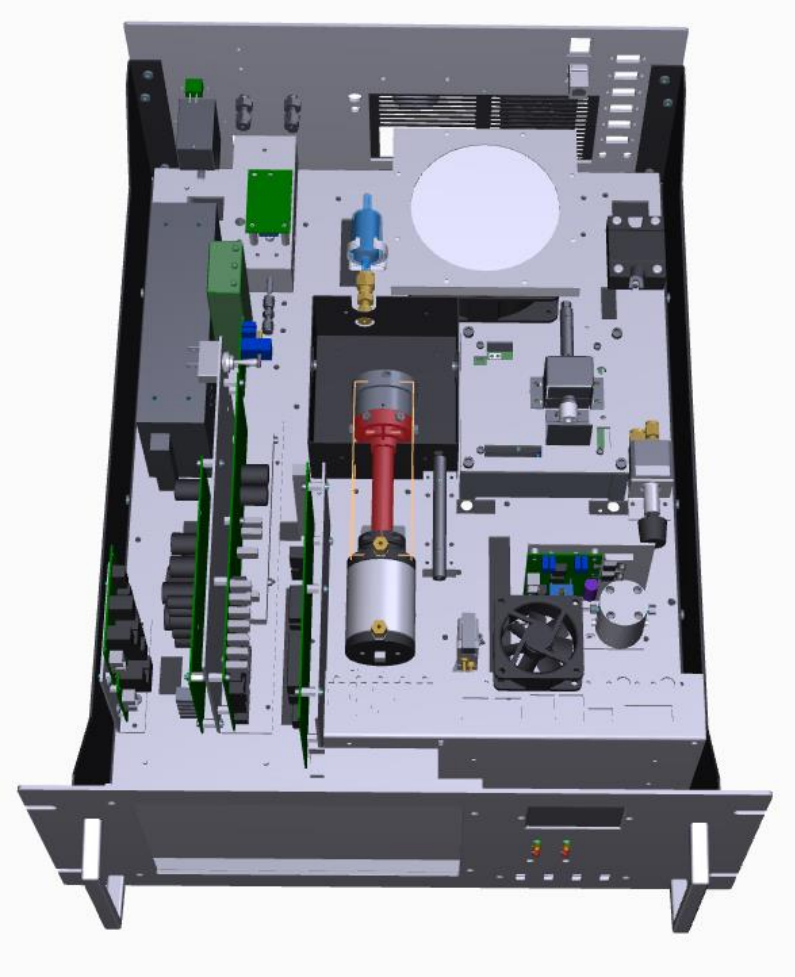
airmoVOC C6-C20+





airmoVOC C6-C20+





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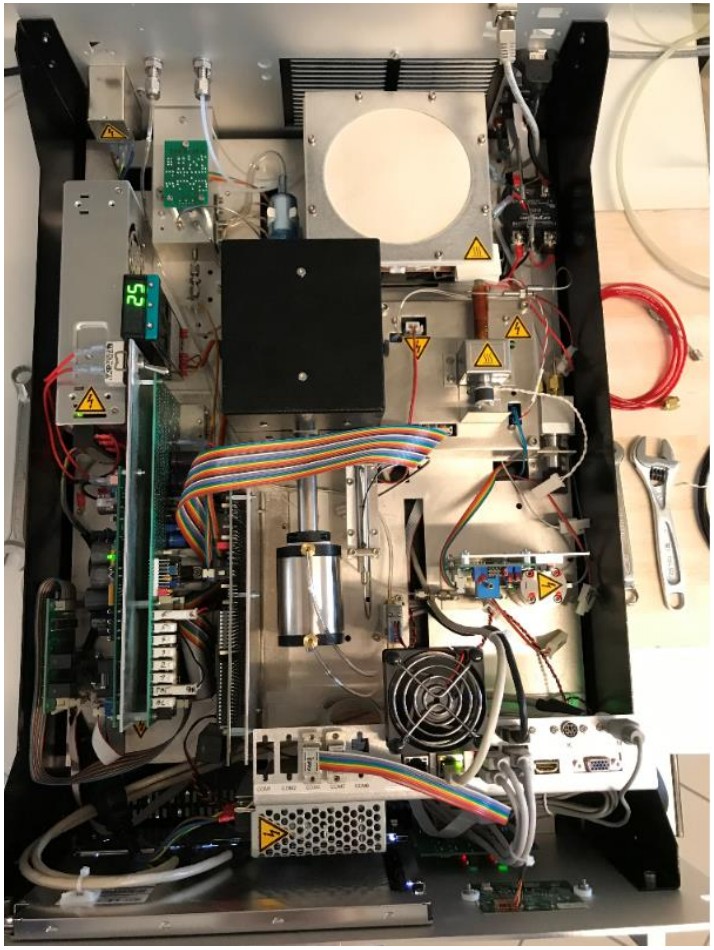

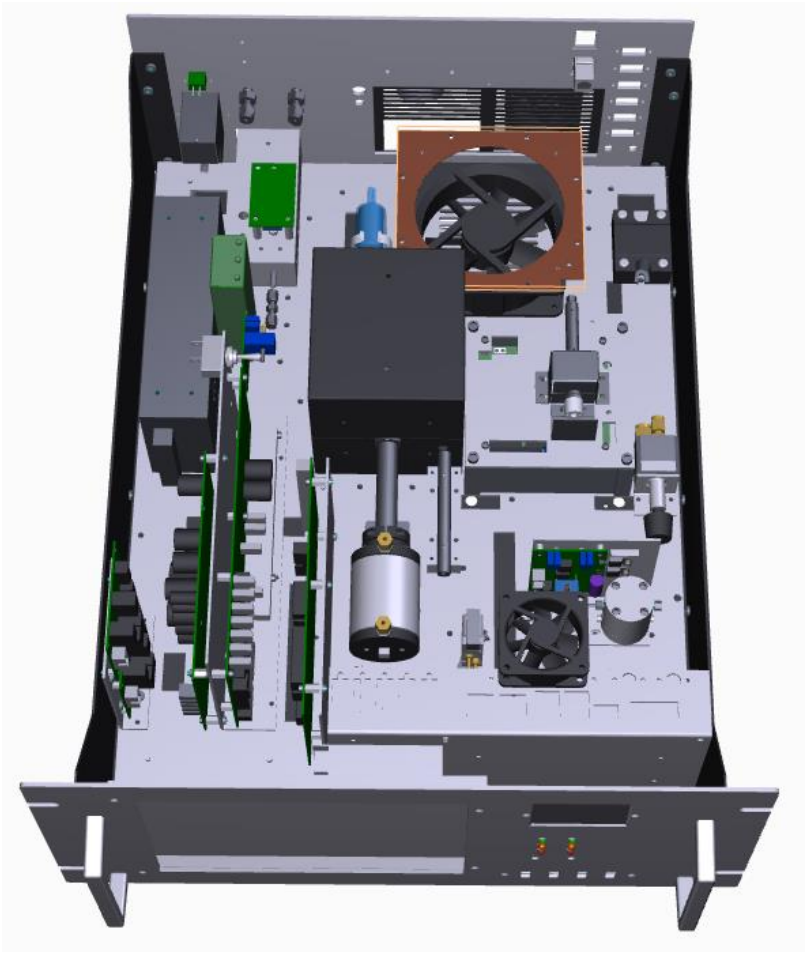

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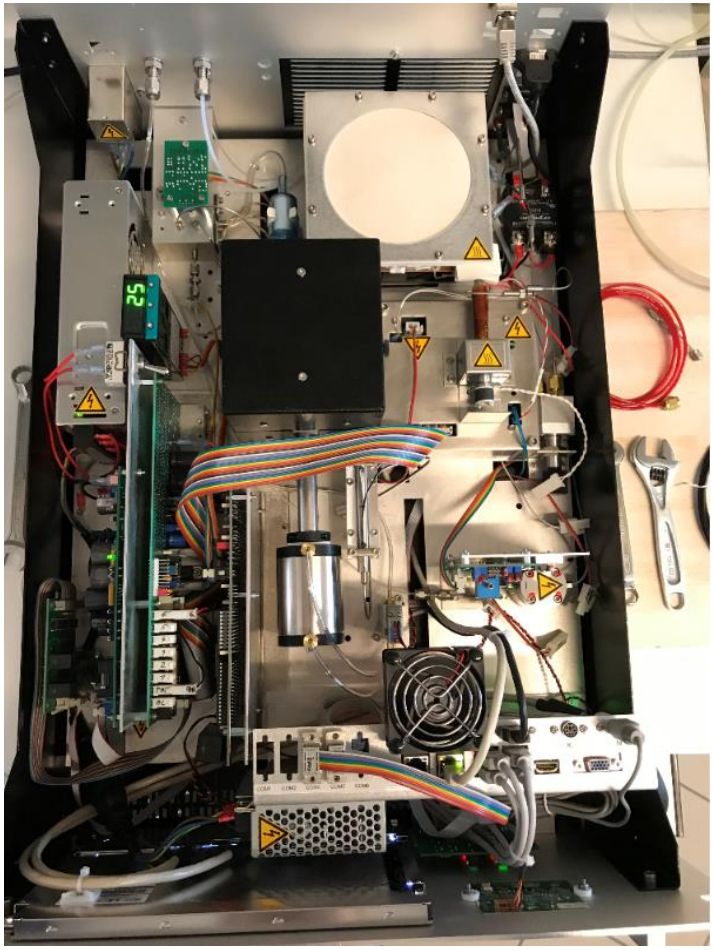

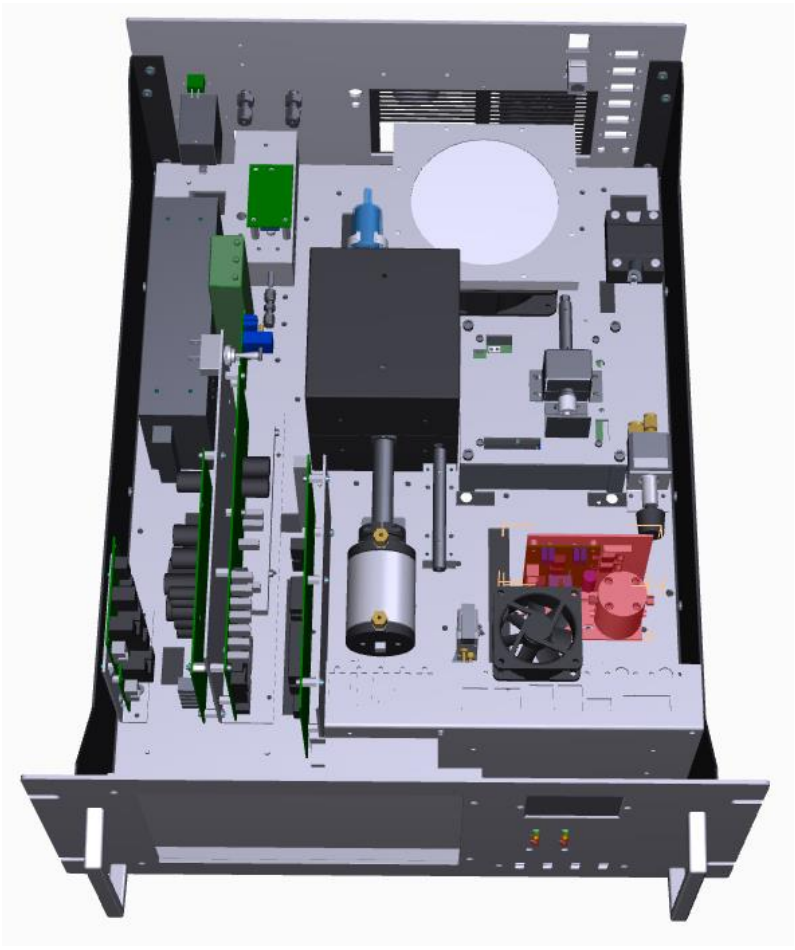

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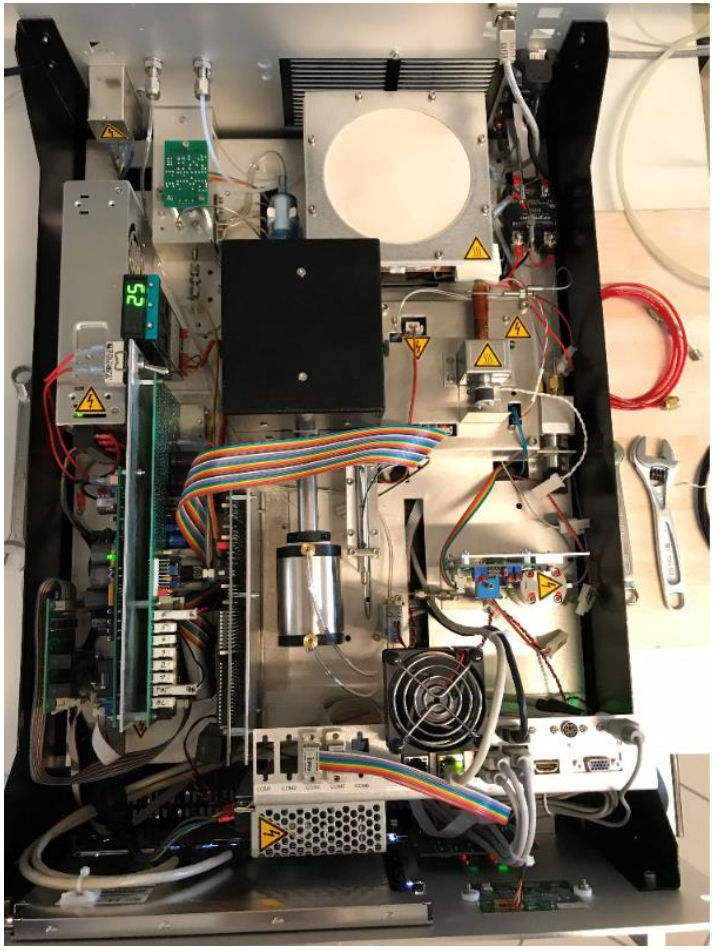
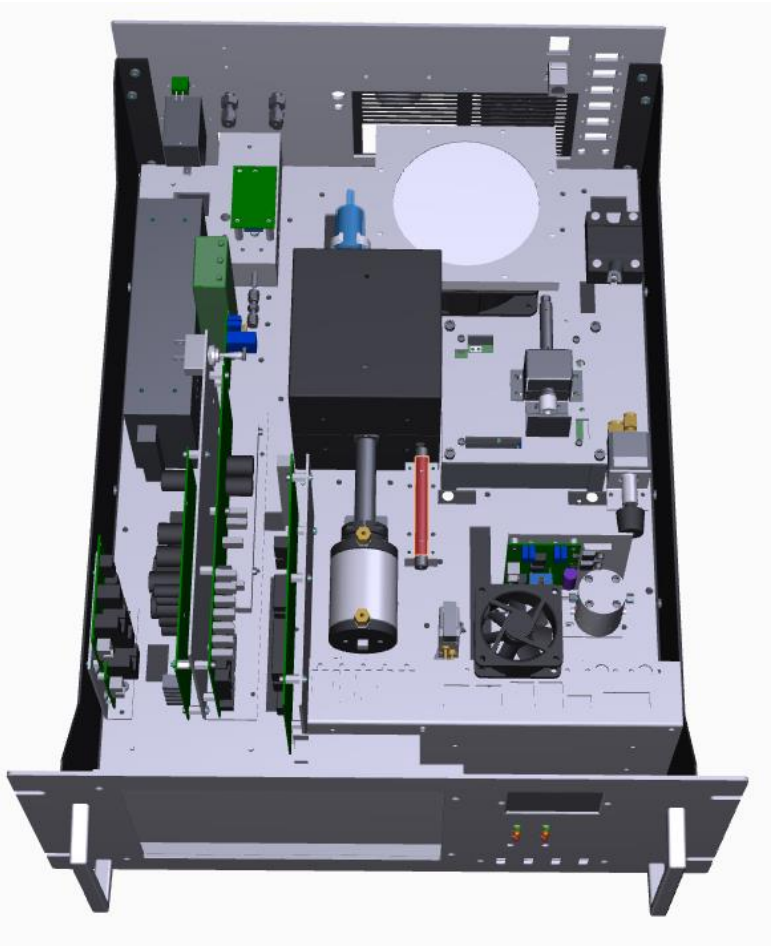
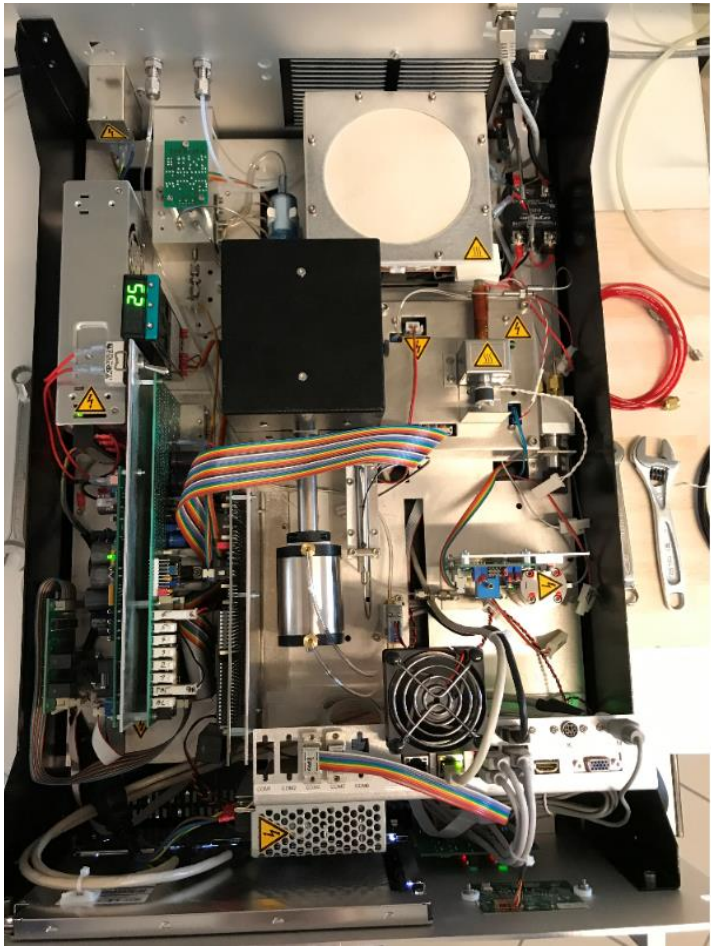
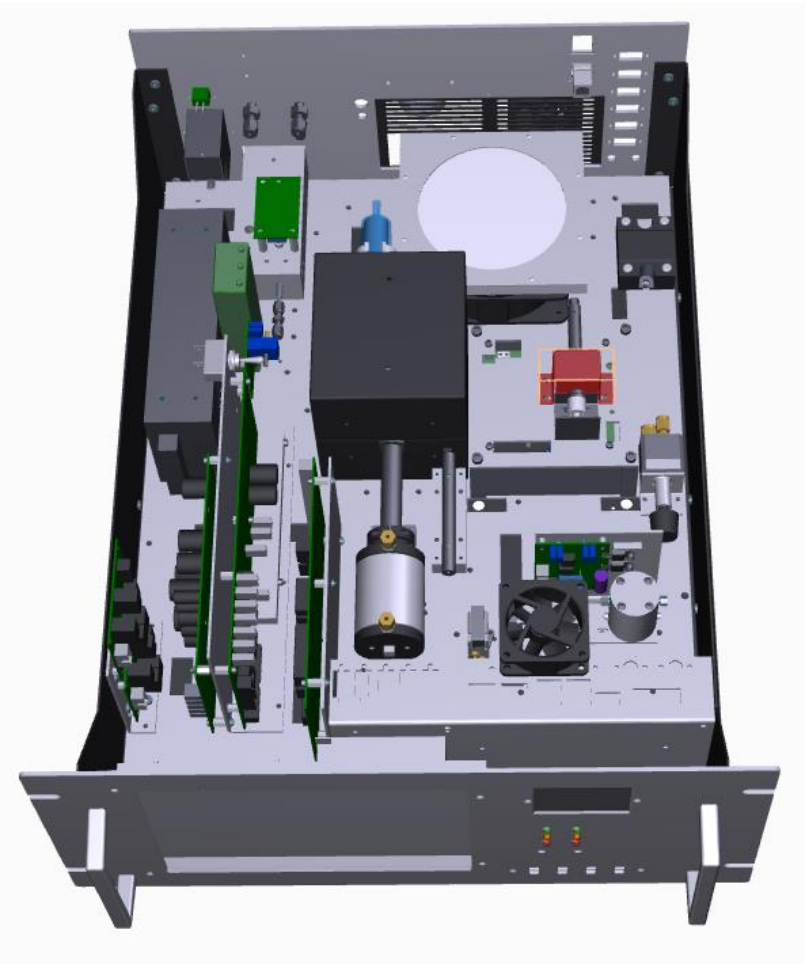


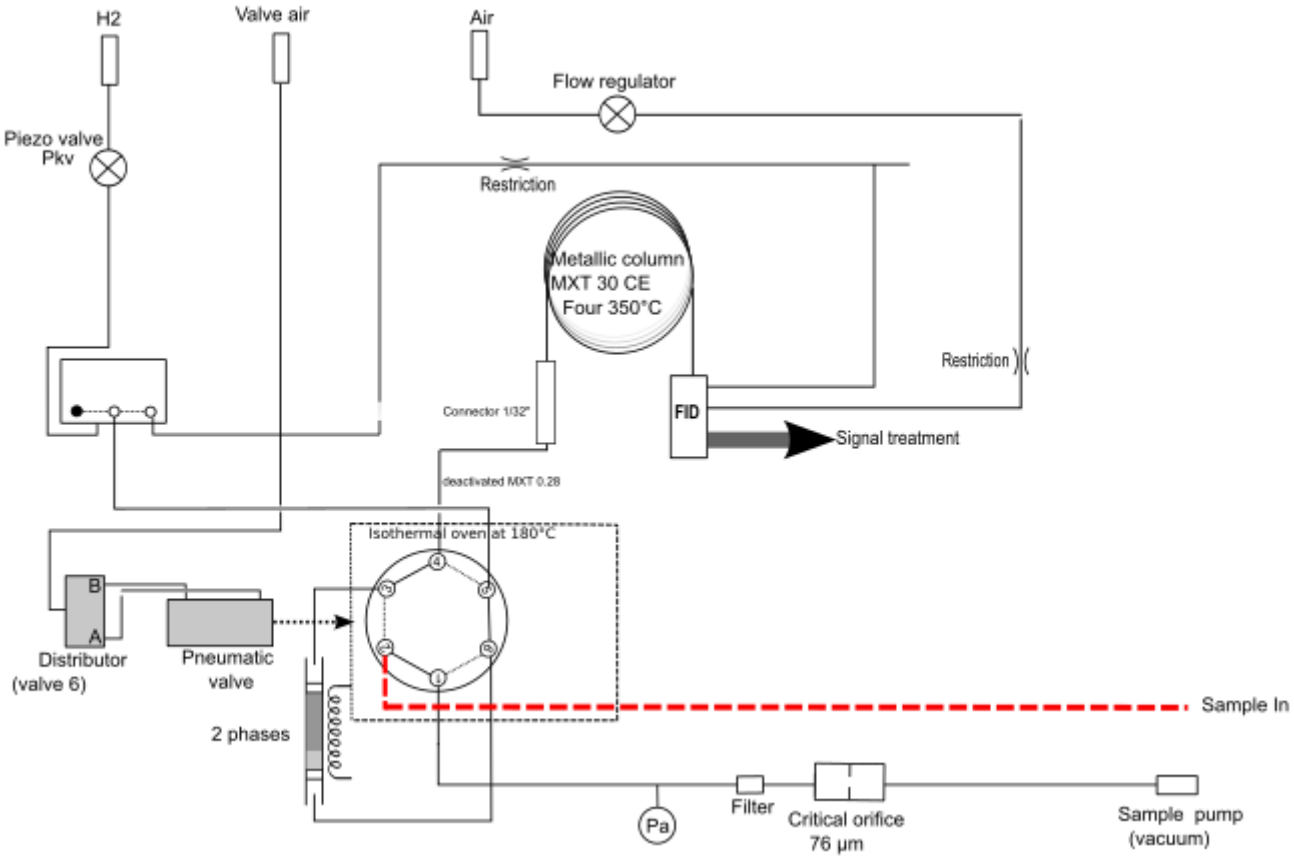


airmoVOC C6-C20+





airmoVOC C6-C20+



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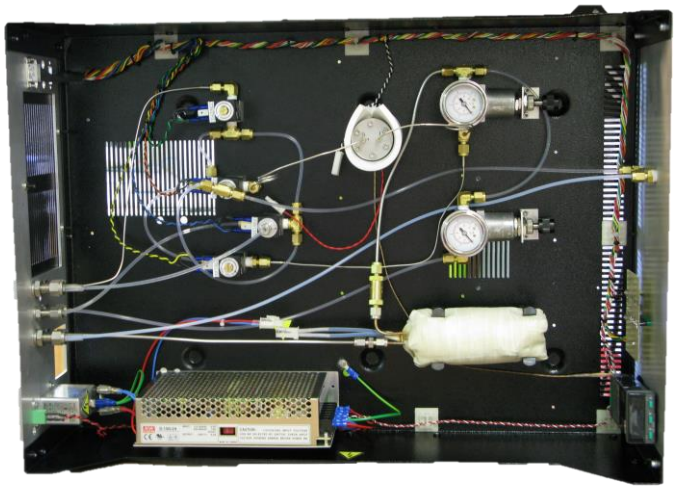
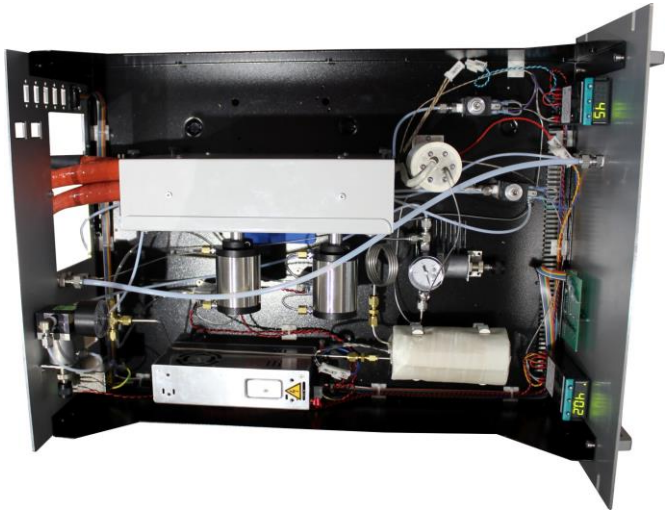
airmoCAL PAH

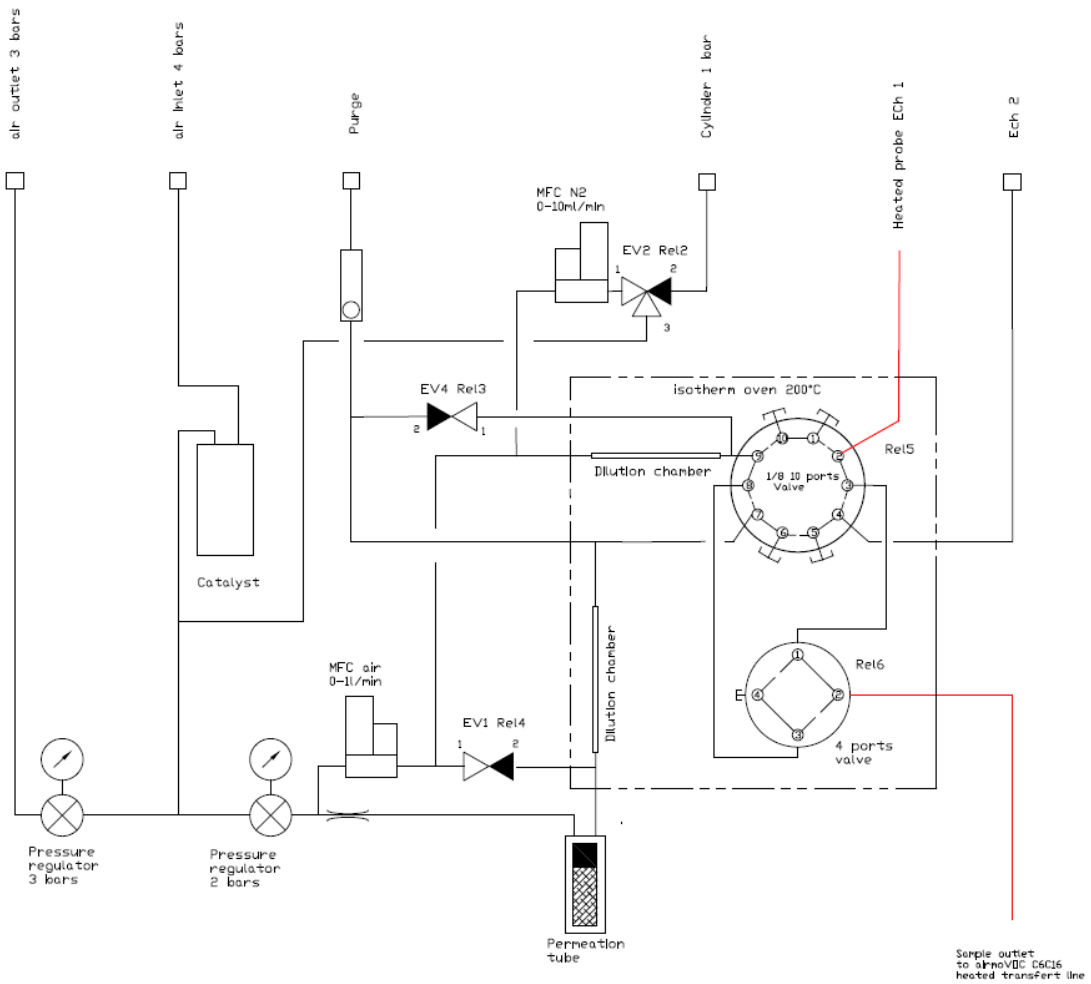


airmoCAL
- Selection of 4 samples
  - Sample analysis
  - Calibration with permeation tubes
  - Calibration with cylinder
  - Zero analysis
- Purge of sampling line

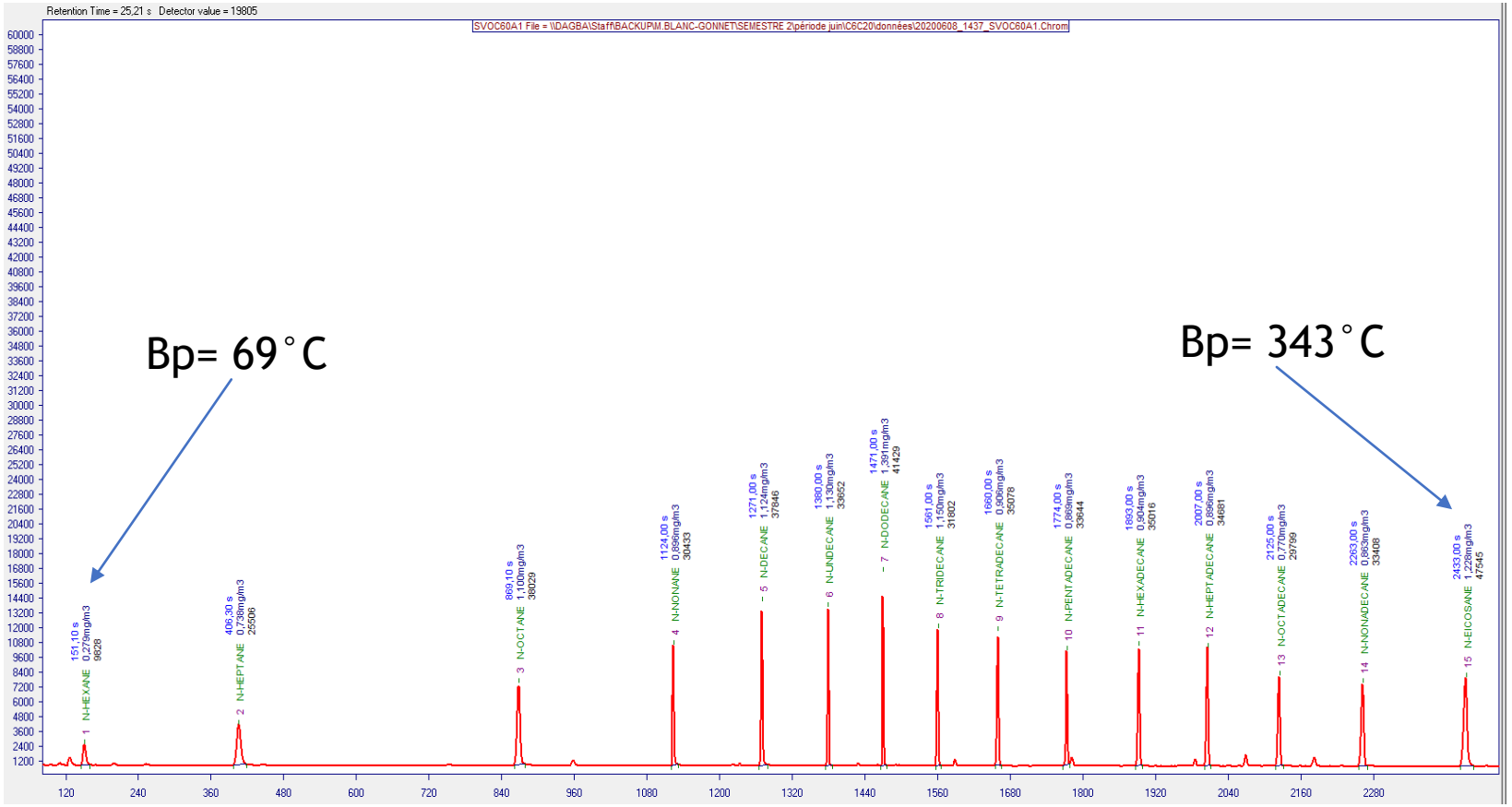


airmoCAL PAH
- Selection of 5 samples
  - Sample analysis
  - Calibration with permeation tubes
  - Calibration with cylinder
  - Zero analysis
  - (Liquid injection)
- Heated sampling inlet
- Heated mixture outlet
- Heated selection valve at 200 °C

airmoCAL 200

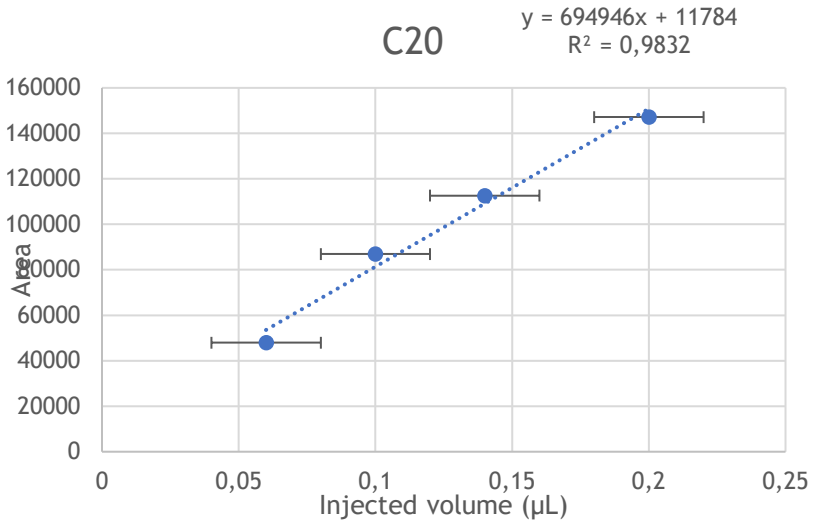


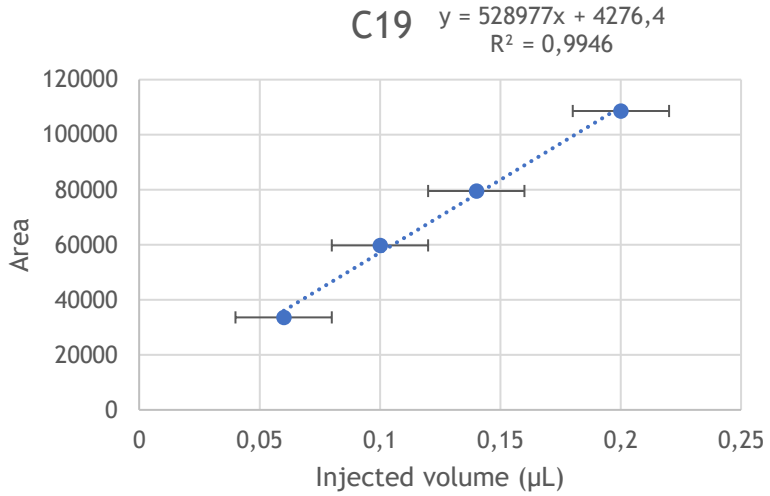
airmoVOC C6-C20+: linear alkanes



Injection C6-C20+ (0,06µL)

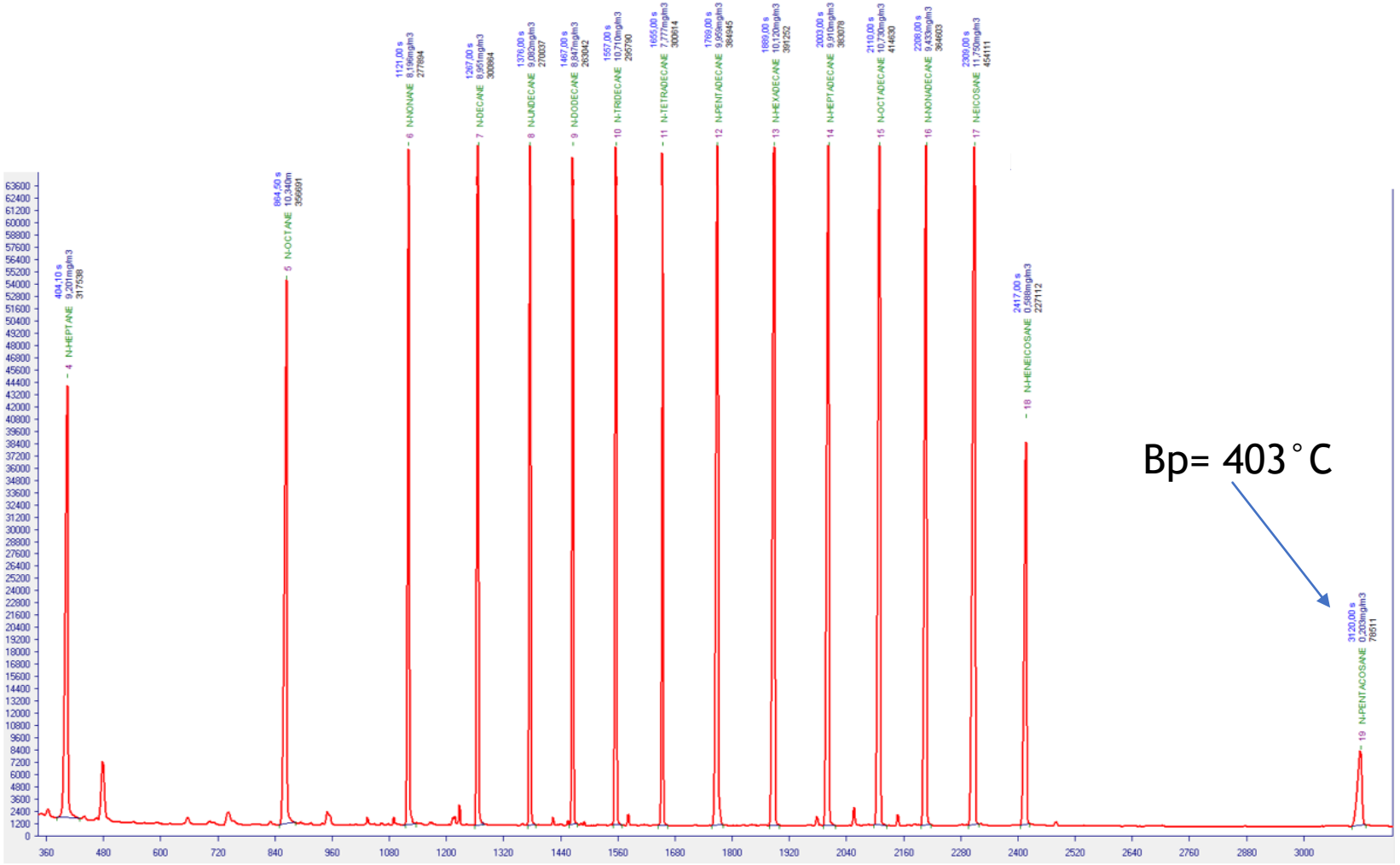
Linearity from C6 to C20





Substance	r²
C6	0.98
C7	0.96
C8	0.98
C9	0.99
C10	0.98
C11	0.97
C12	0.97
C13	0.96
C14	0.97
C15	0.97
C16	0.97
C17	0.98
C18	0.99
C19	0.99
C20	0.98

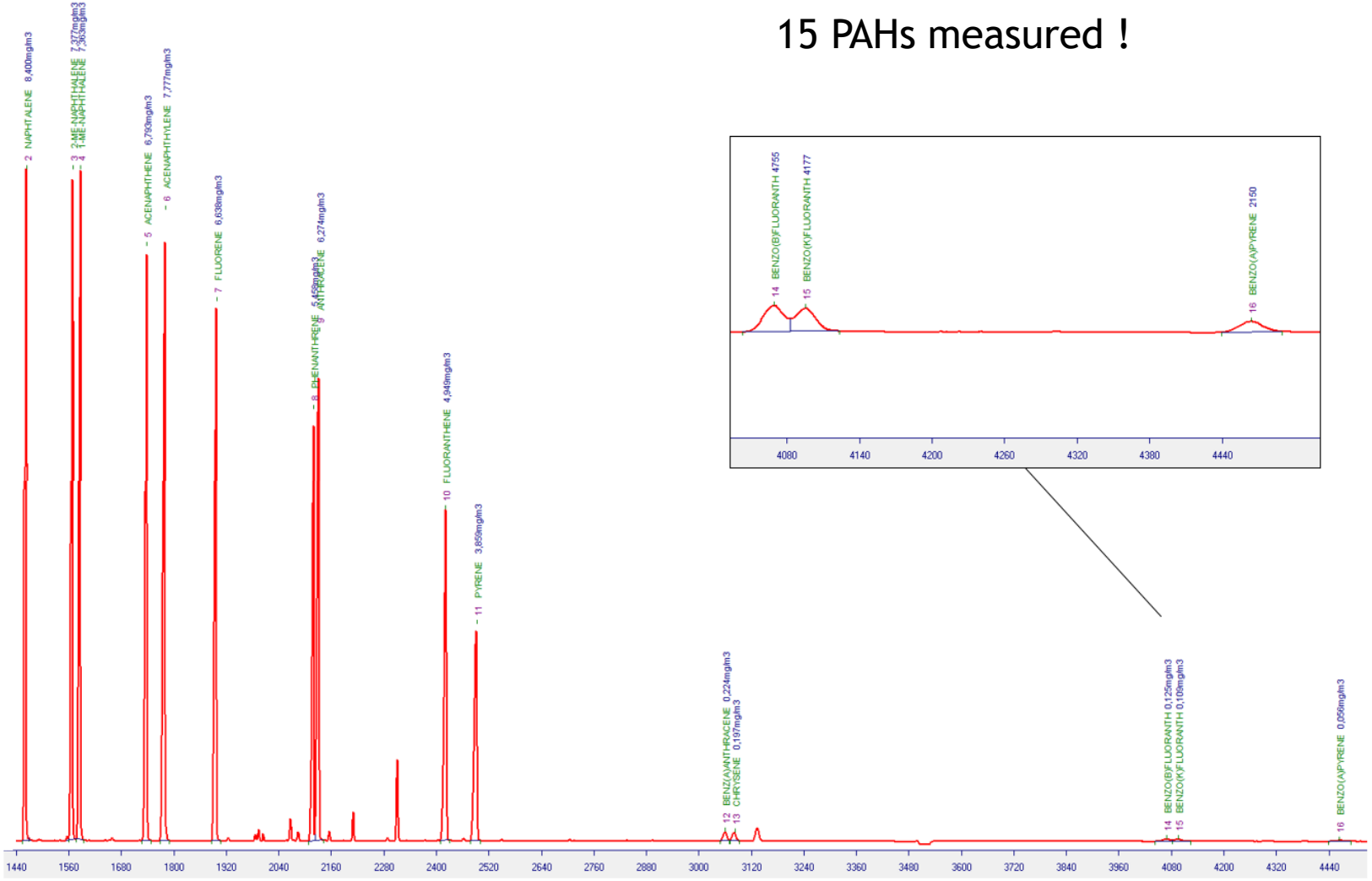
Injection of linear alkanes up to C25



Injection of PAHs up to benzo a pyrene

CHROMATOTEC® GROUP
Online Gas Analyzer Experts

15 PAHs measured !



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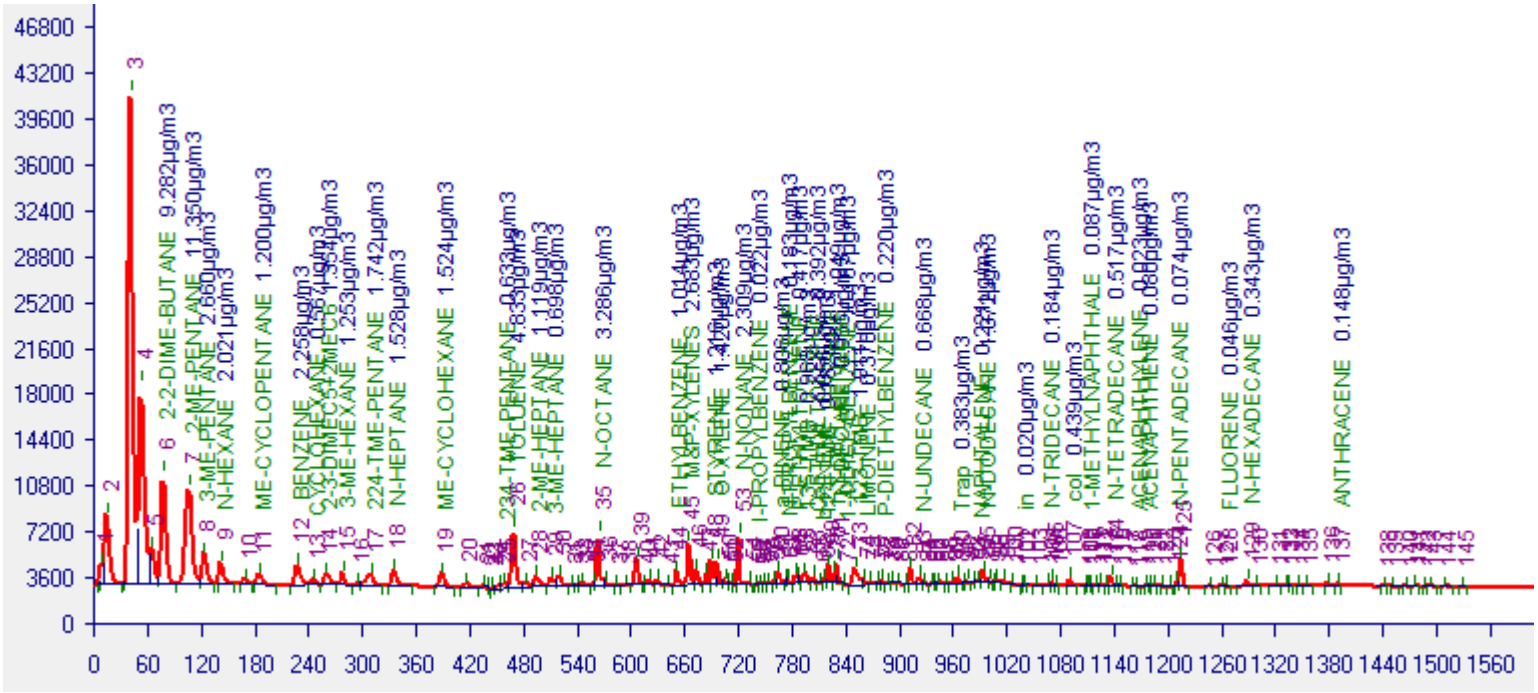
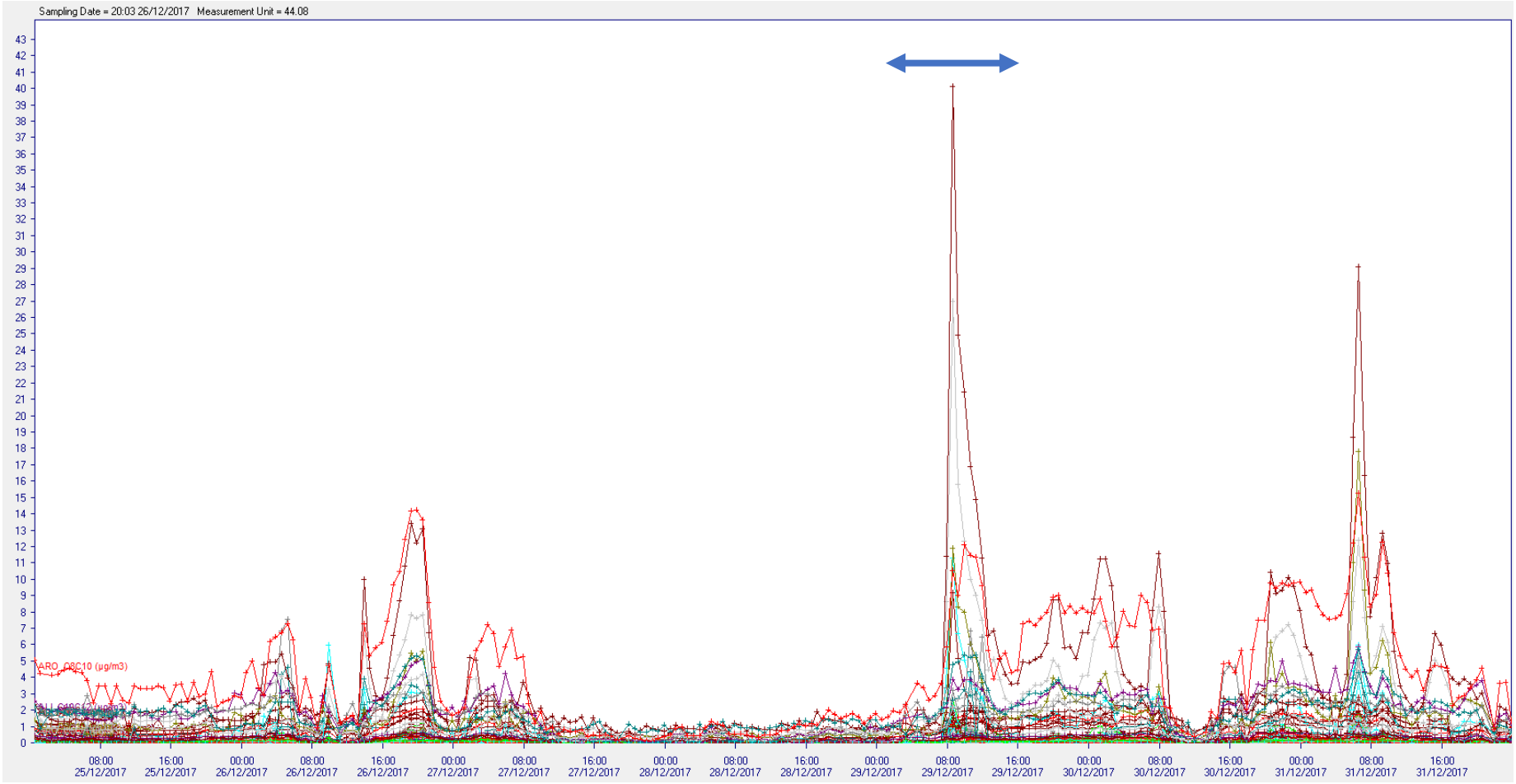
Field campaign

- Study of ambient air around decontamination area
- Location: South of France
- 1 month monitoring

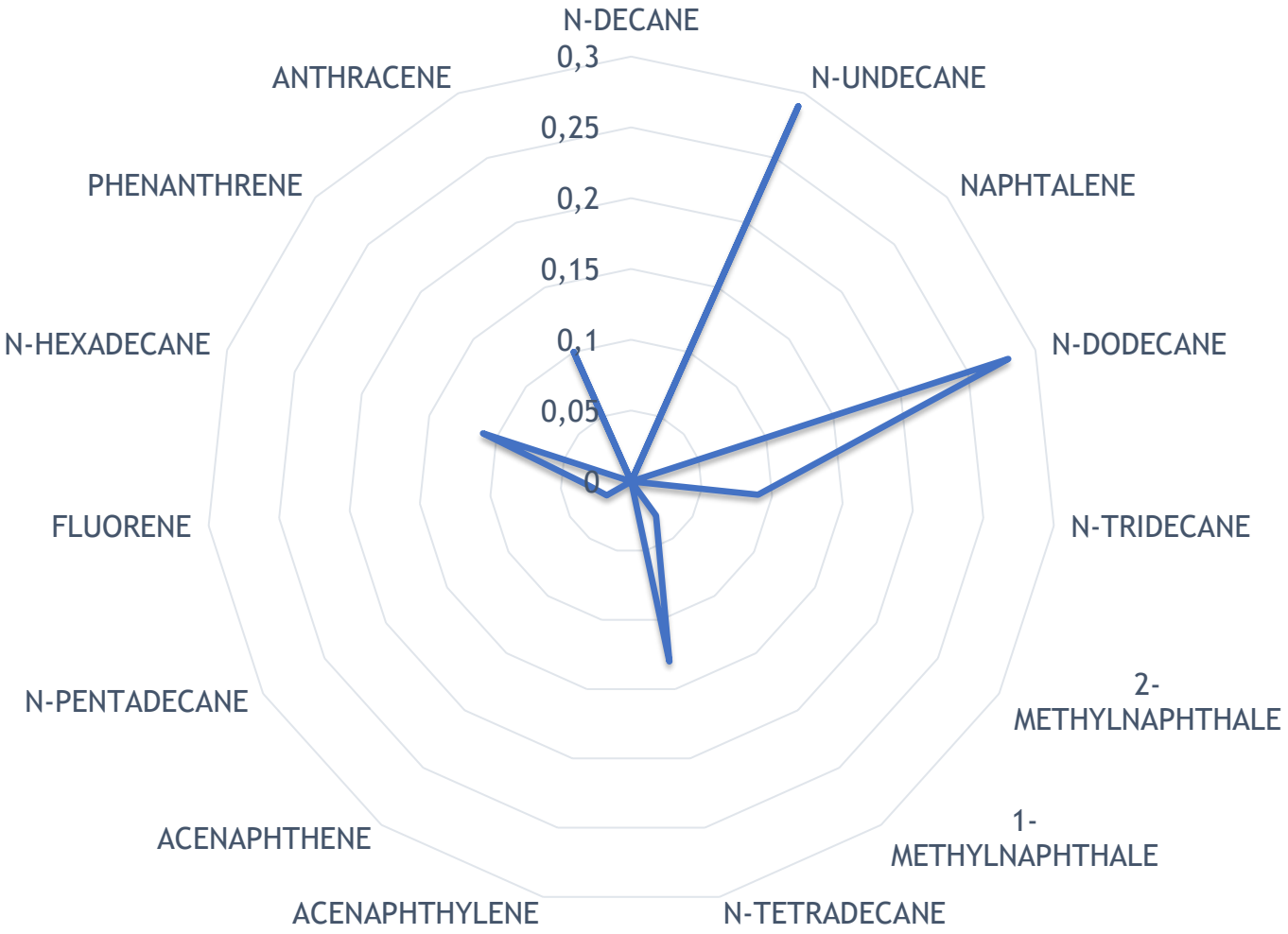
Ambiant air analysis



Ambiant air analysis



Compounds contribution



Some references for sVOCS

AIR LANGUEDOC-ROUSSILLON
Membre agréé du réseau Atmo

AIR LR & ORAMIP deviennent Atmo OCCITANIE votre parten'air

2016 1 field campaign airmoVOC C6C16
French air quality monitoring network

กรมควบคุมมลพิษ
POLLUTION CONTROL DEPARTMENT

2016 2 GCMS C10C20
Thailand Pollution Control Department

Guangzhou city EMC

2016 1 GCMS C10C20
Guangzhou City EMC

2017 1 airmoVOC C6C16
Indian Physical Research Laboratory

IMT Lille Douai
École Mines-Télécom
IMT-Université de Lille

2018 1 airmoVOC C6C16
French air quality monitoring reference laboratory

CHROMATOTEC®

Some references for sVOCS

2018 1 airmoVOC C6C16
French University on atmospheric chemistry

2018 1 airmoVOC C6C16 + DET QMS
French Research center on atmospheric chemistry

2019 airmoVOC C6C16 – Houston Lab

2020 airmoVOC C6C16
Ecole des Mines de Douai – second unit with upgrade

2020 airmoVOC C6C20
ULCO France – second unit – happy customer !

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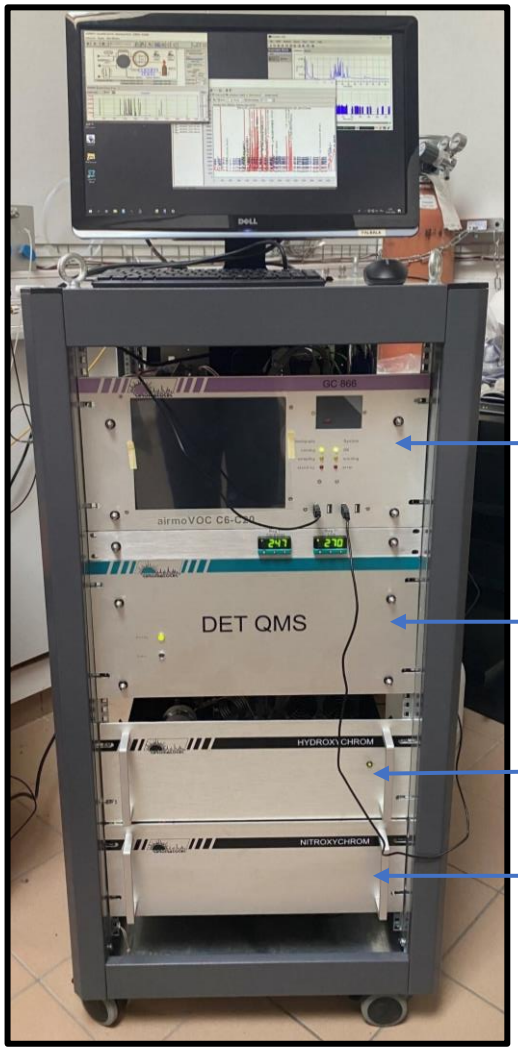
Analyze sVOC in the plastic beads
Must be < 1 ppm (W/W)

Manual pre-concentration

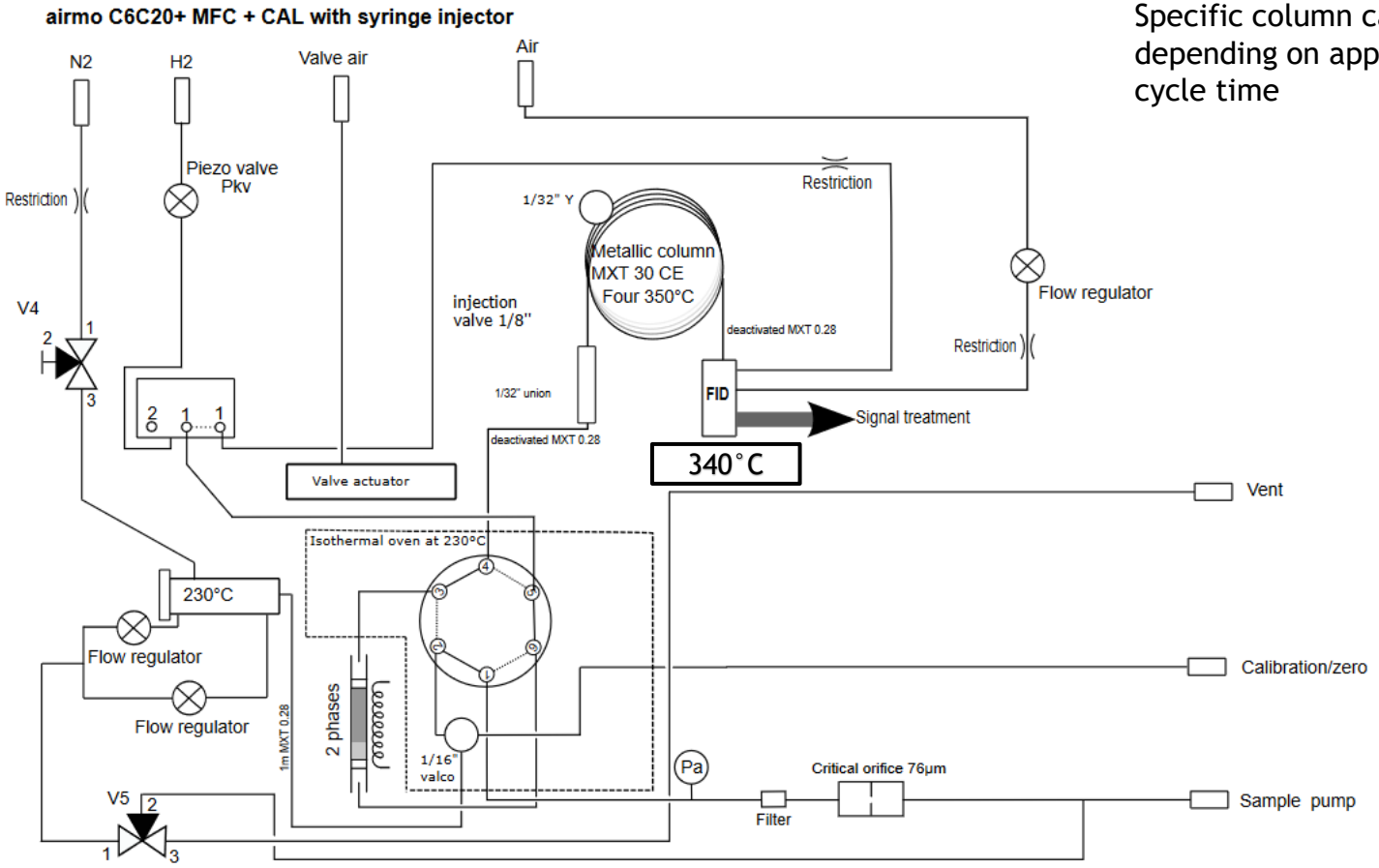
Analysis on laboratory GCMS

GC / MS C6C20+



Injector

airmoVOC C6-C20+

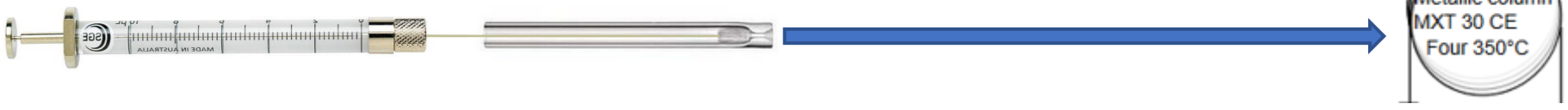


Specific column can be used depending on application and cycle time

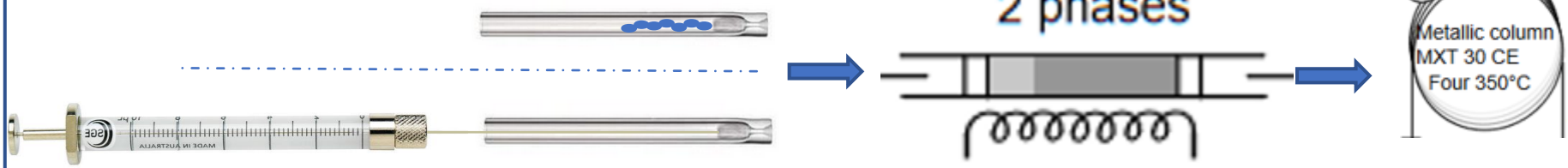
Sample injection

Liquid and solid analyses

Sample injection

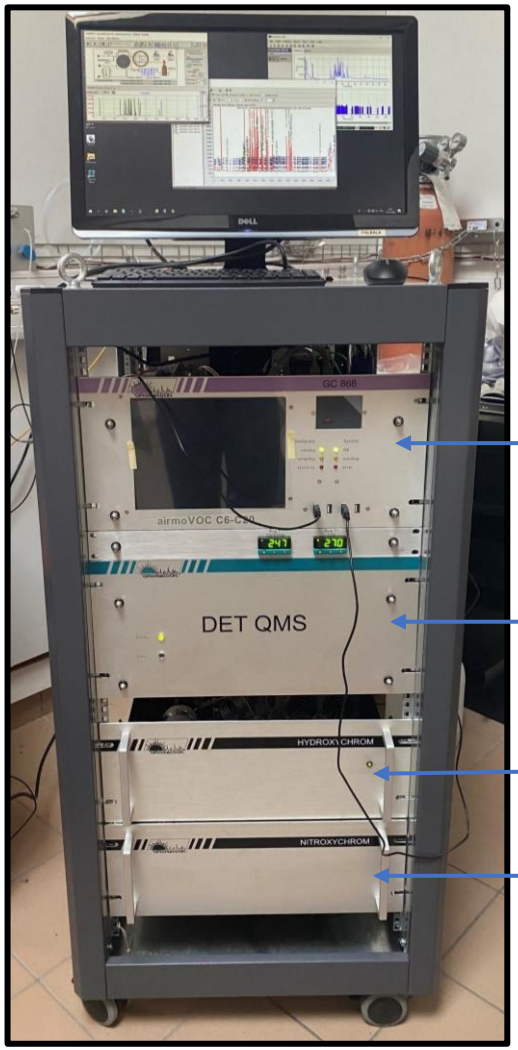


Liquid analysis



Liquid and solid analyses (and calibration for gaseous sample)

GC / MS C6C20+



airmoVOC C6C20+

DETQMS

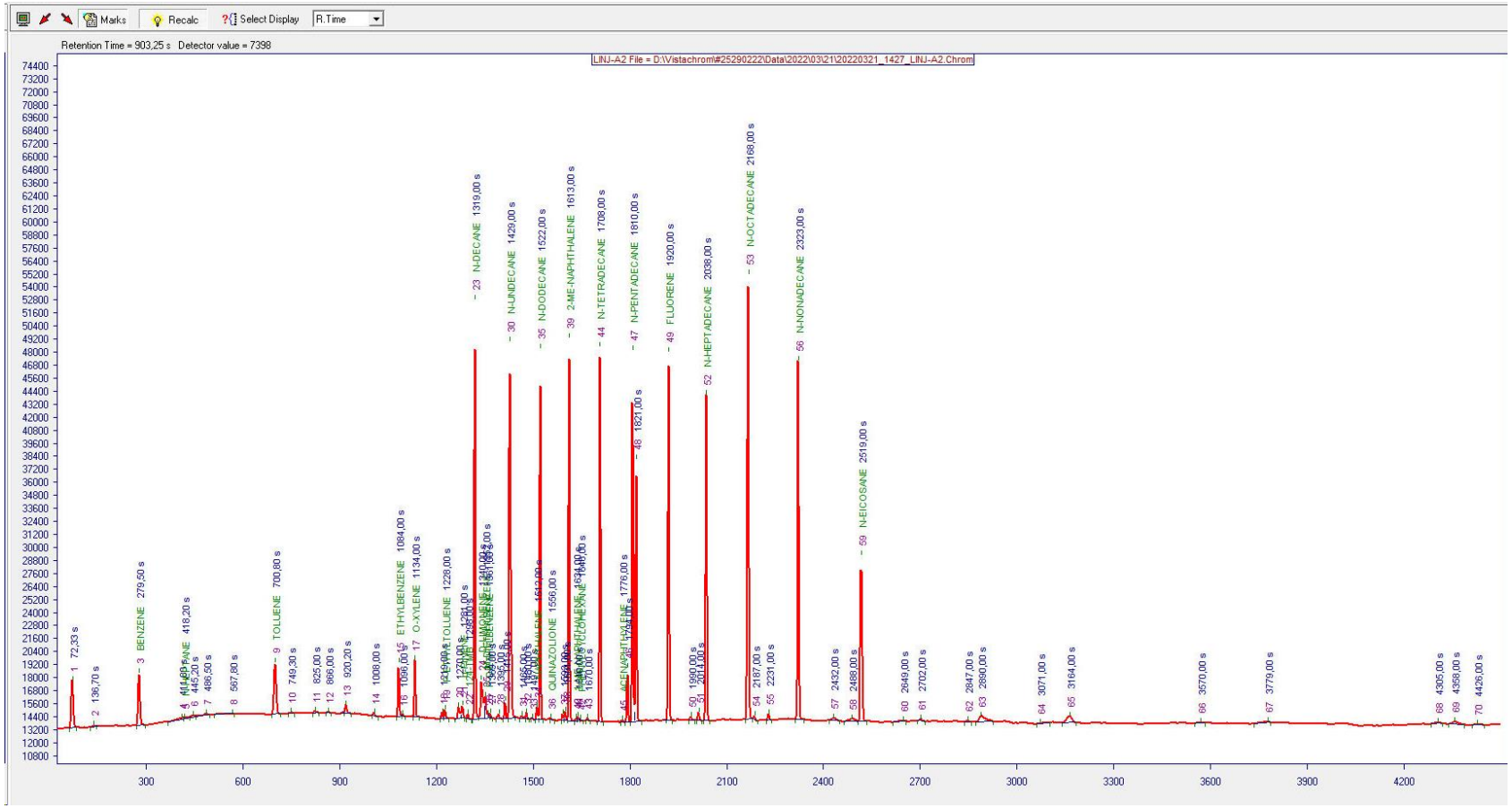
HYDROXYCHROM

NITROXYCHROM

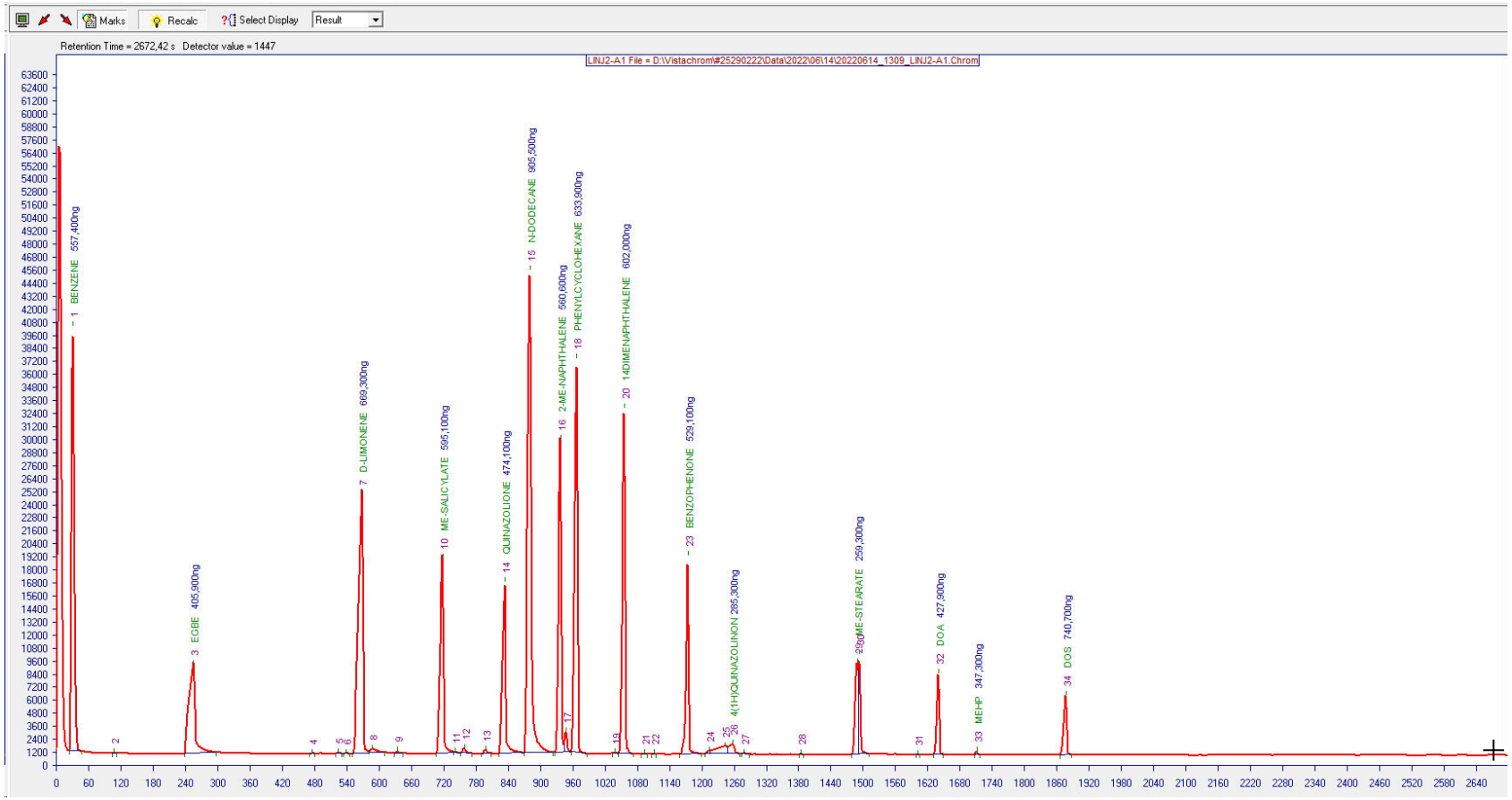
Injector

Sample injection

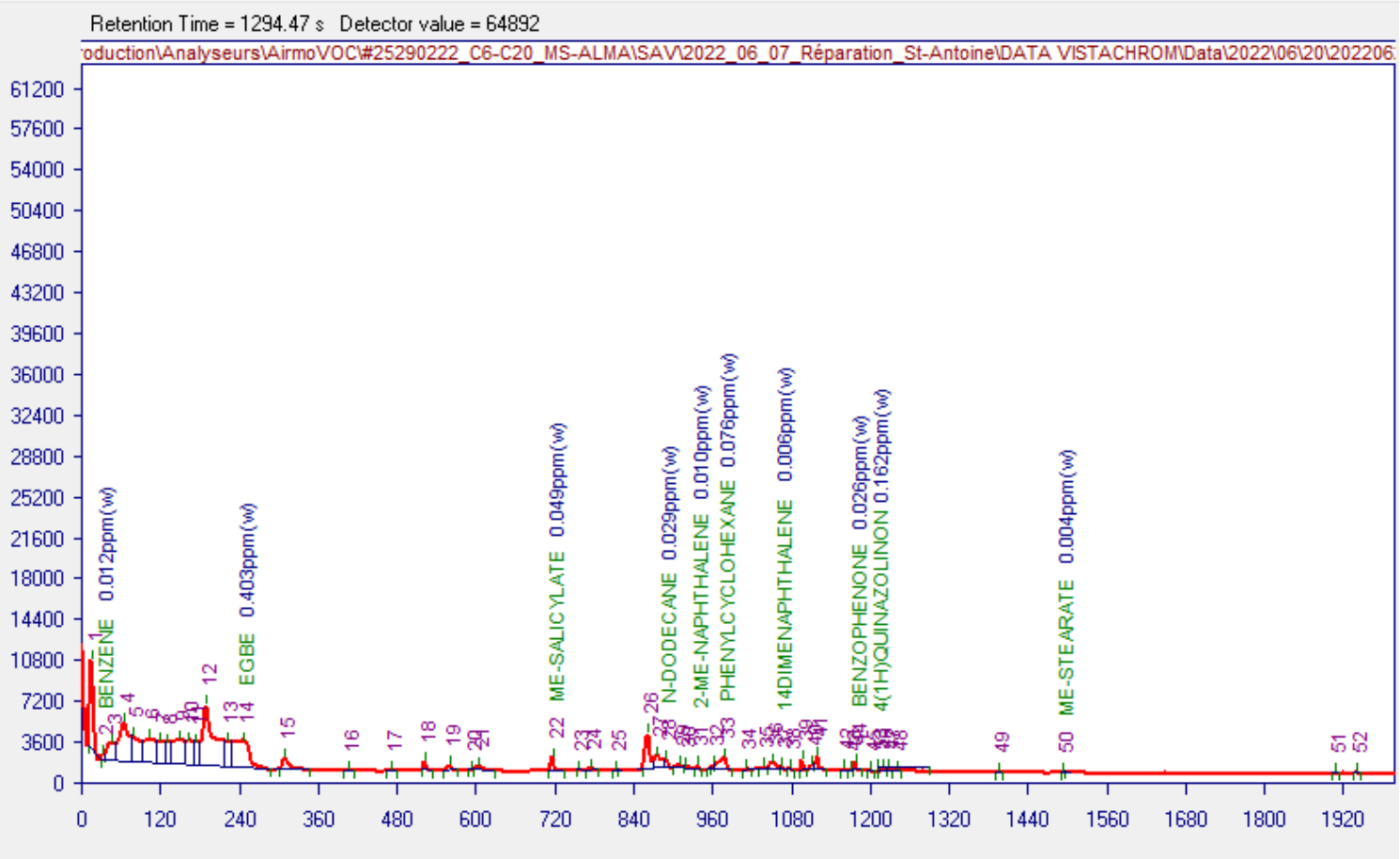
Liquid analysis



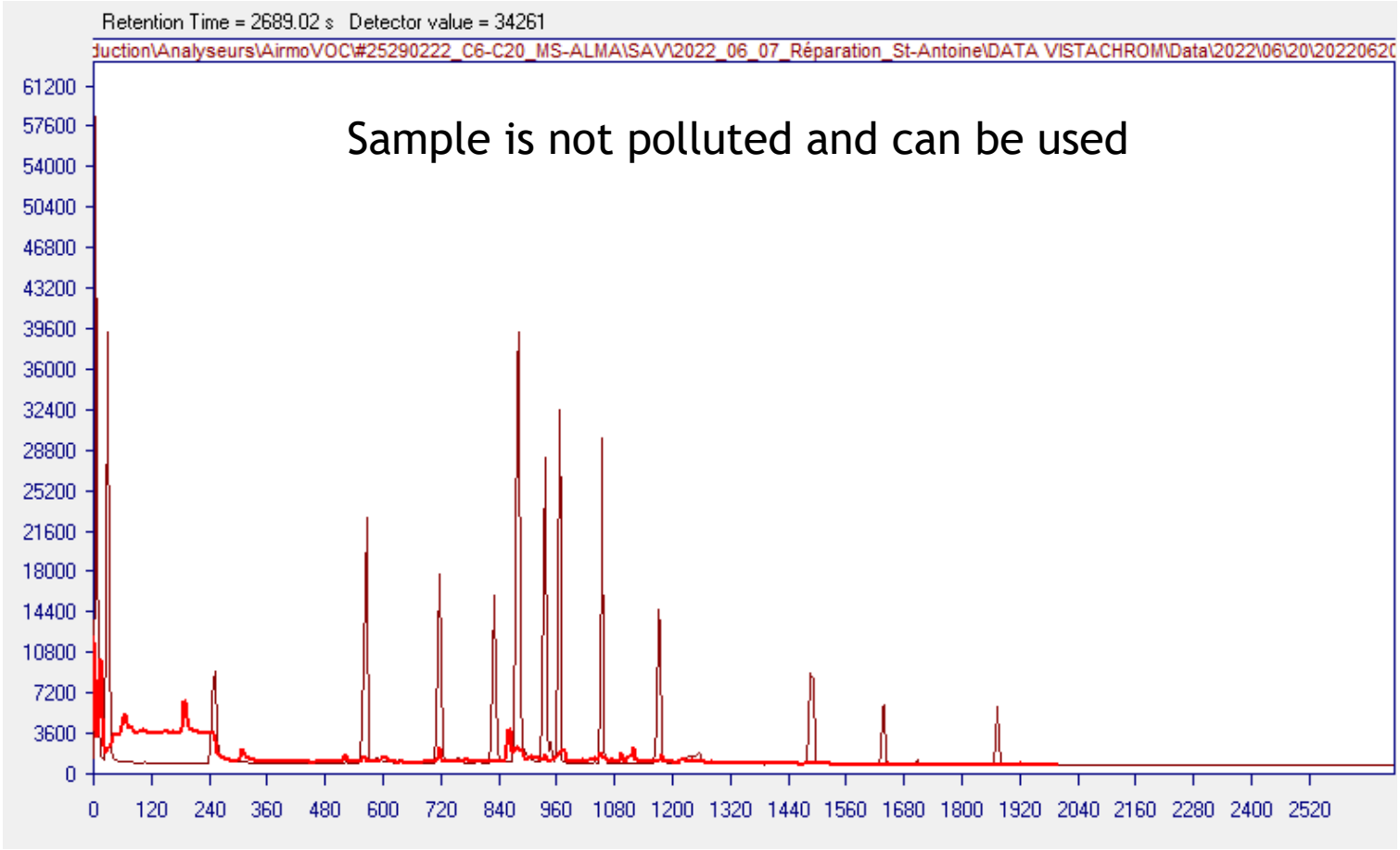
Liquid analysis



Solid analysis

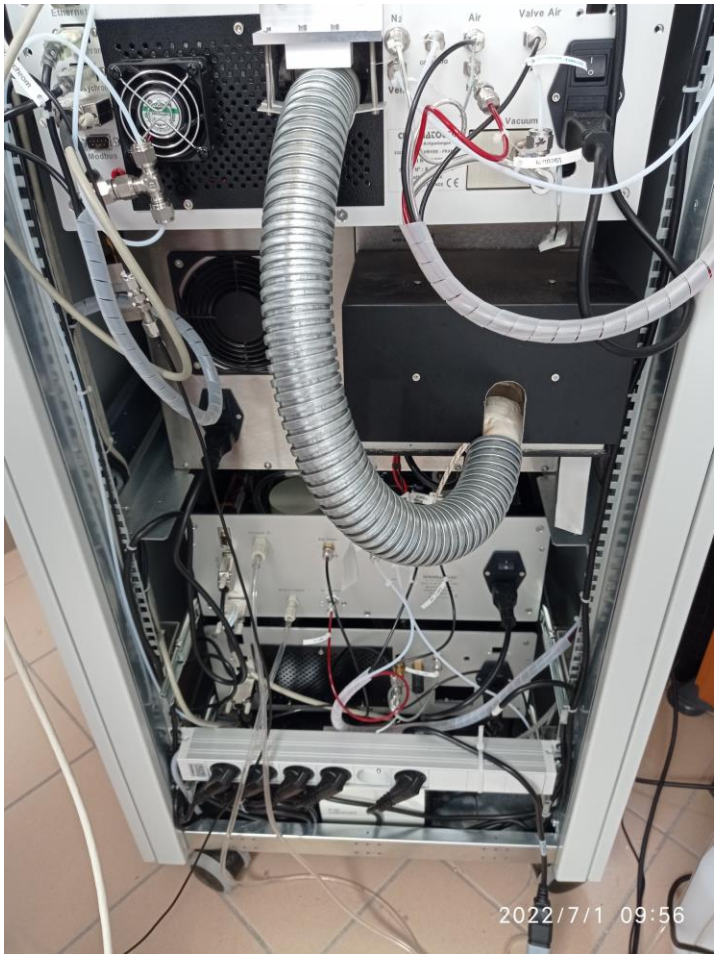


Solid analysis



Mass spectrometer

- Specific transfer line
  - New design
  - Heated up to 270°C
- Specific system for silica to tube heating for inlet MS
- Improved QC for transmission of heavy ions



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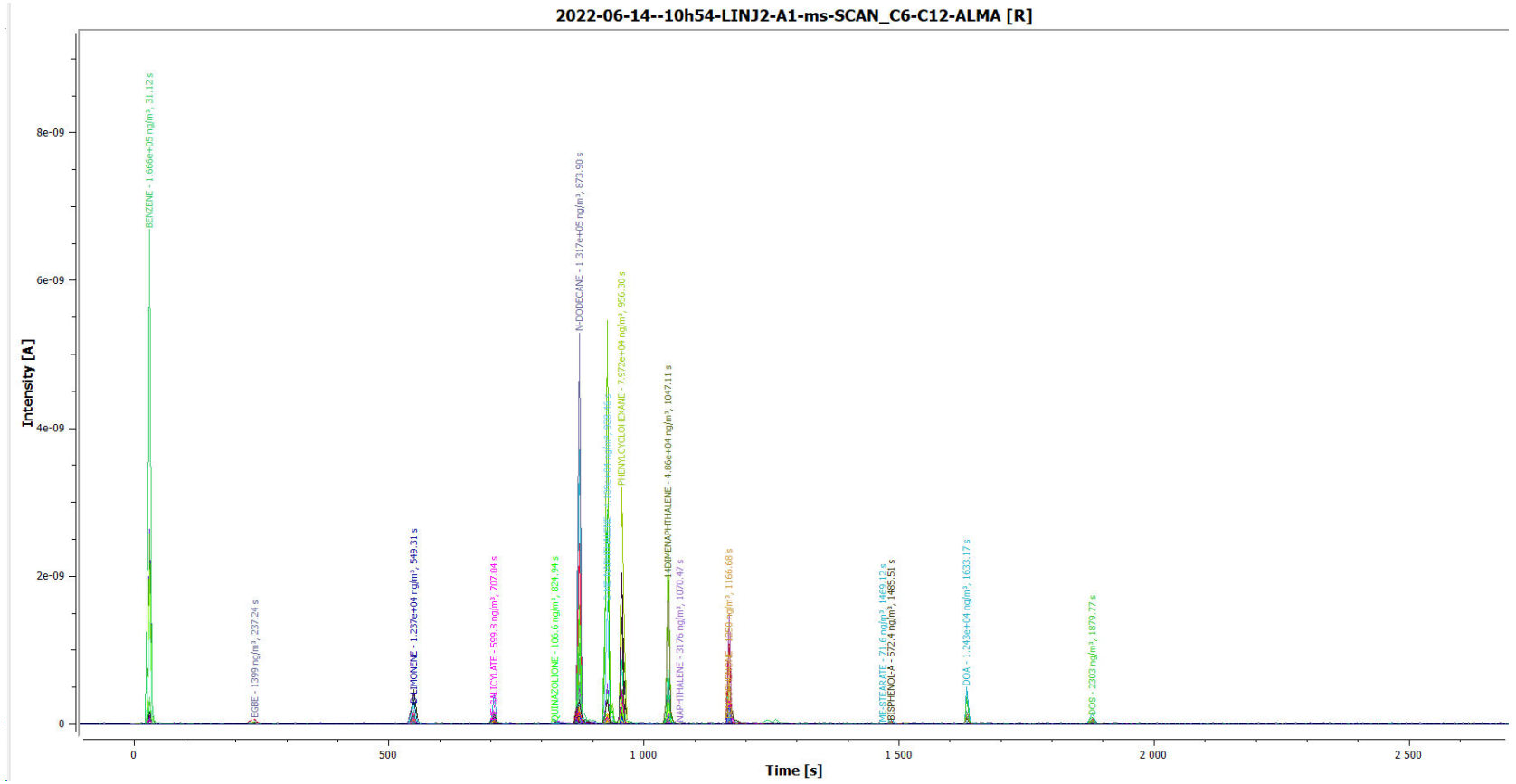
- Improved QC for transmission of heavy ions

Mass spectrometer



Conclusion

- System can analyze gas, liquid and solid samples
- Injector, Oven and FID can be heated up to 350°C
- Analytical system used for QC
  - Easy to handle and operate
  - Can run 24h/7days
- Mass spectrometer can be added to the system
  - heated line up to 270°C
  - 0-300 uma

Online Analytical Solutions Experts

Thanks for your attention