“Hydrocarbon Index” : A fully miniaturised and automated method

VEOLIA ENVIRONNEMENT
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Summary

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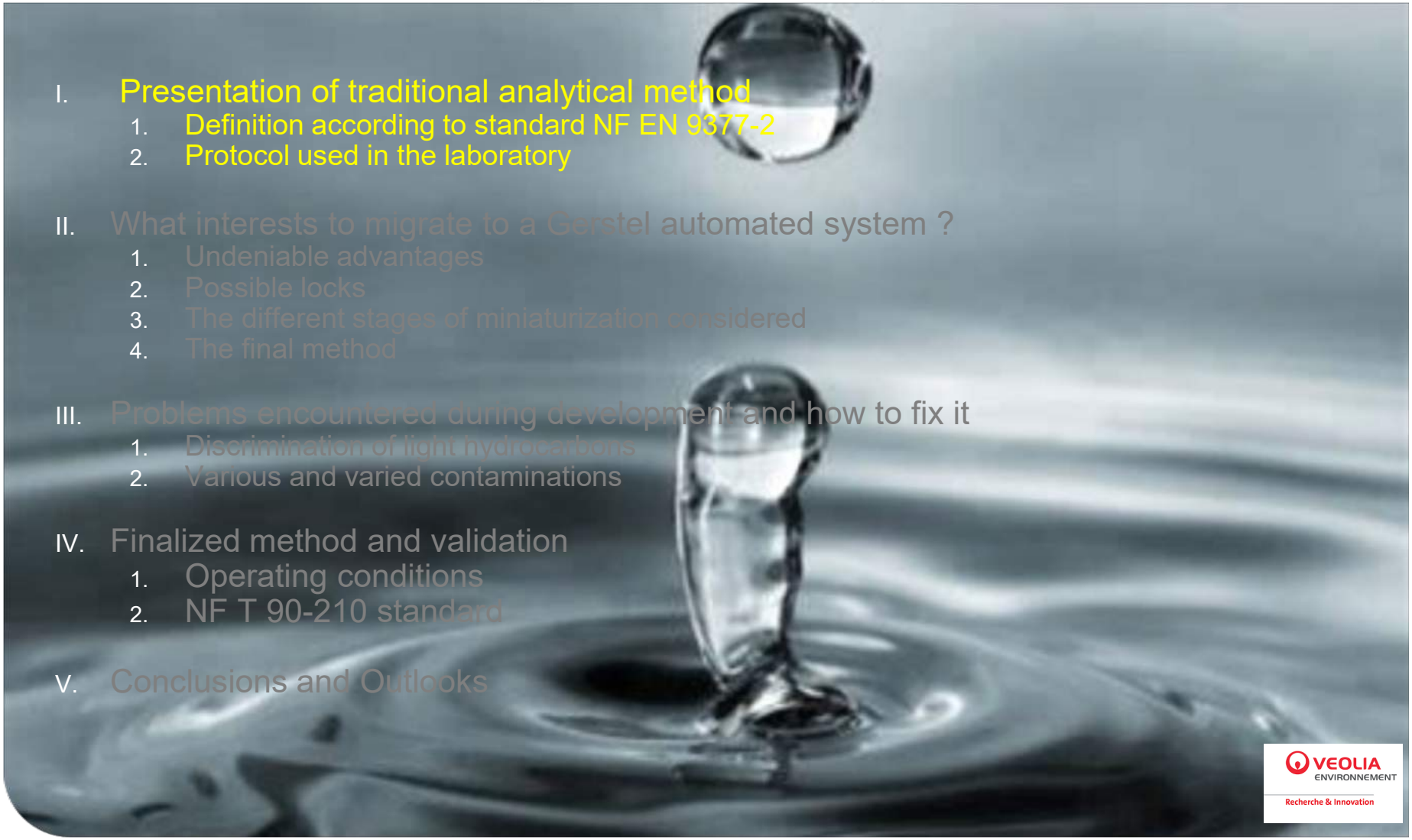
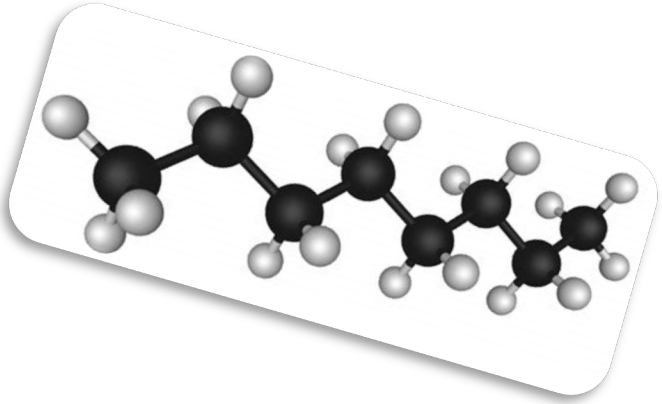


Hydrocarbons what is it?

A **Hydrocarbon** is an organic compound containing exclusively carbon (**C**) and hydrogen (**H**) atoms. They consequently have a formula of type: C_nH_m

1. Apolar compounds (hydrophobic, lipophilic)
2. Linear aliphatics saturated or not (alkanes, alkenes, alkynes, ...)
3. Branched aliphatics (methyl propane, ...)
4. Alicyclic (cyclopropane, cyclobutane, cyclohexene, ...)
5. Aromatic (benzene, PAHs, ...)
6. Substituted alkyl aromatics (methyl, ethyl, propyl, butyl, etc. group)

The so-called "volatile" hydrocarbons between C_5 and C_{10} are not included (standard XPT 90-124)



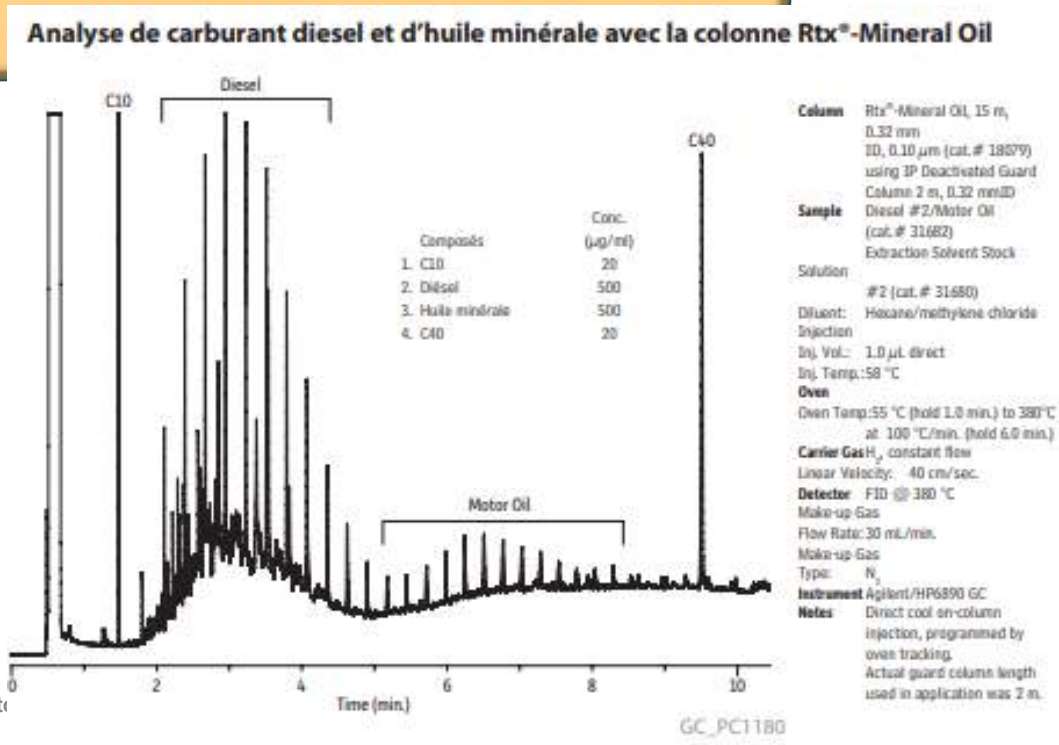
EN ISO 9377-2 standard of December 2000

1. Set of compounds extractable by a solvent or a mixture whose BP is between 36 and 69 ° C.
2. Substances not absorbed on Florisil®
3. Retention time between C_{10} and C_{40}
4. 2 different types A and B of mineral oils containing no additive:

"Type A must show discrete peaks on the chromatogram (eg a Diesel)"
"Type B must have a boiling range> Type A and with unresolved signals and of which 325 ° C <BP <460 ° C (eg lubricating/motor oil)"

Restek Rtx Mineral Oil
30m x 0,32mm x 0,15µm

- Low bleeding
- Very good resolution
- Robustness



Veolia's Lab

CAE Laboratory
Saint Maurice
(94, Val de Marne)

Central laboratory of Veolia

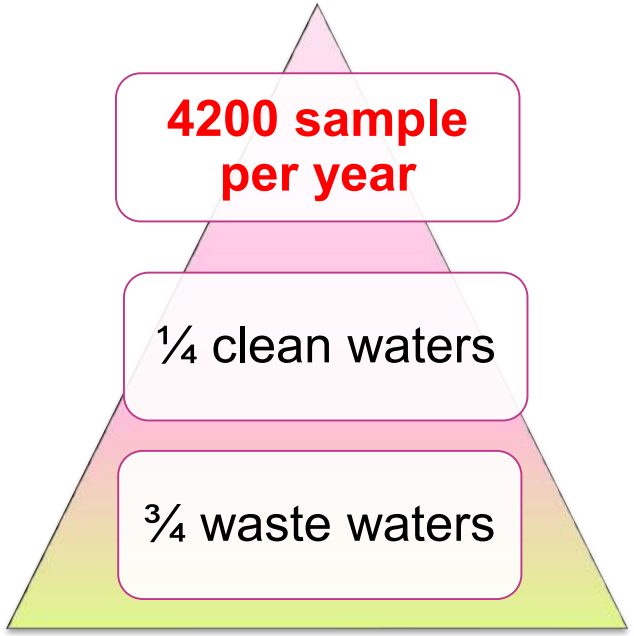
- Control Quality laboratory
- 3 sections Organic, Mineral and Microbiological Chemistry
- Cofrac accreditation since 2000 for 110 parameters (NF EN ISO / IEC 17025

Détermination of Hydrocarbon Index : WHY ?

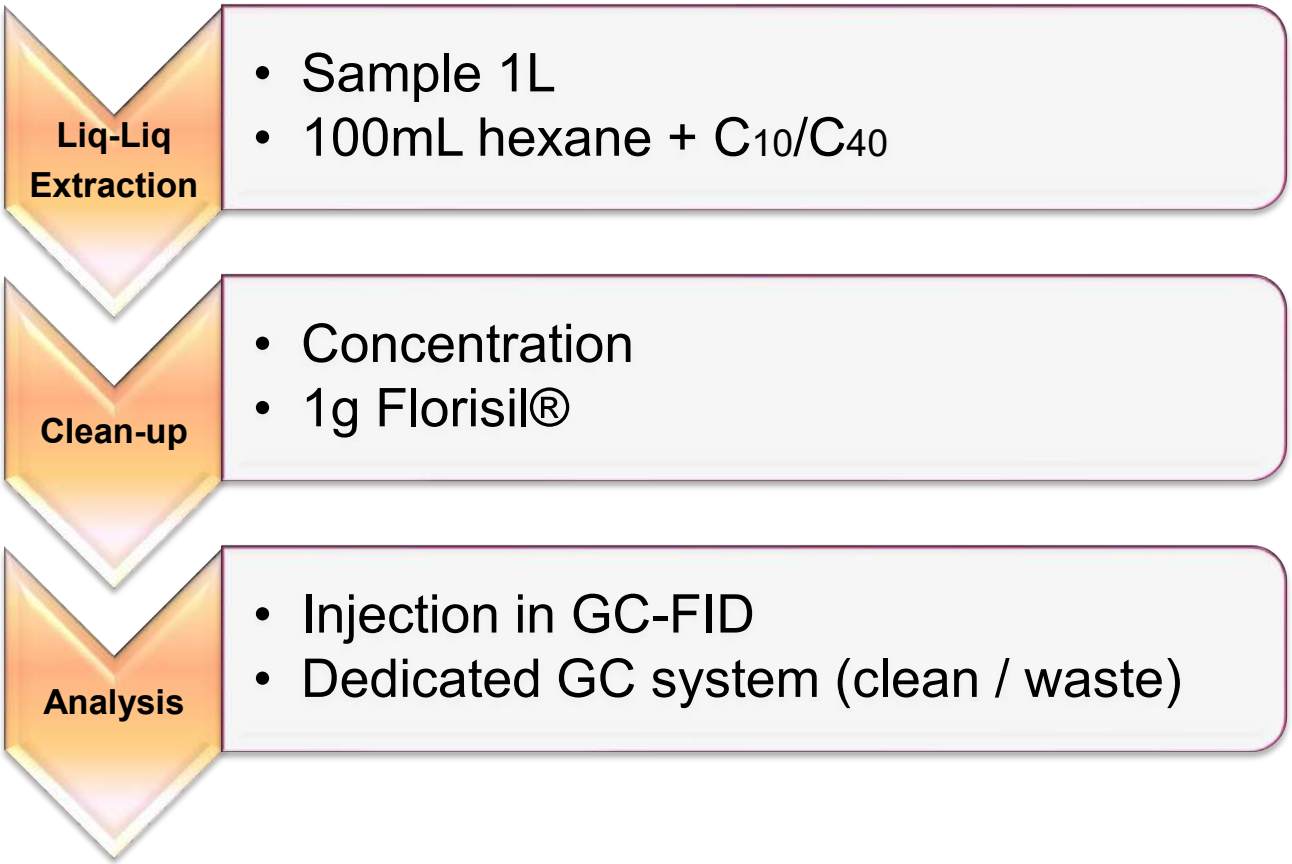
Regulatory controls
Pollution of resources
Self-monitoring of our operators

Limit of Quantification

- Tap water: 0,05 mg/L
- Raw water: 0,1mg/L
- Waste water: 0,2 mg/L



Protocol used in the laboratory in 3 steps



If we look in more detail ...

For 12 positions: 6:45

Setup of separatory funel

-

Rincing with Hexane

-

Setup samples + H2S04

-

100mL hexane

30mn

Liquid-Liquid Extraction

30mn

Solvent recovery

-

Freezing (2H minimum)

60mn

Rinse tube concentration

-

Concentration to 1mL

90mn

Setup of clean-up positions

-

Conditioning Florisil®

-

Elution of extract

60mn

Concentration of Purified extract from 5 to 1mL

45mn

vials and analysis by GC-FID

-

Data processing

90mn

some key figures

For 200 analysis

- Technician time: estimate 5 working days
- Rinsing glassware + extraction: 200 x 170mL = 34L of Hexane

- Tech cost 250 €
- Hexane cost 396 €
- Clean-up cost 667 €
- Recycling chemical product cost 31 €
- Gas cost (concentration, GC) 172 €

1516€ so 7,58€ per sample

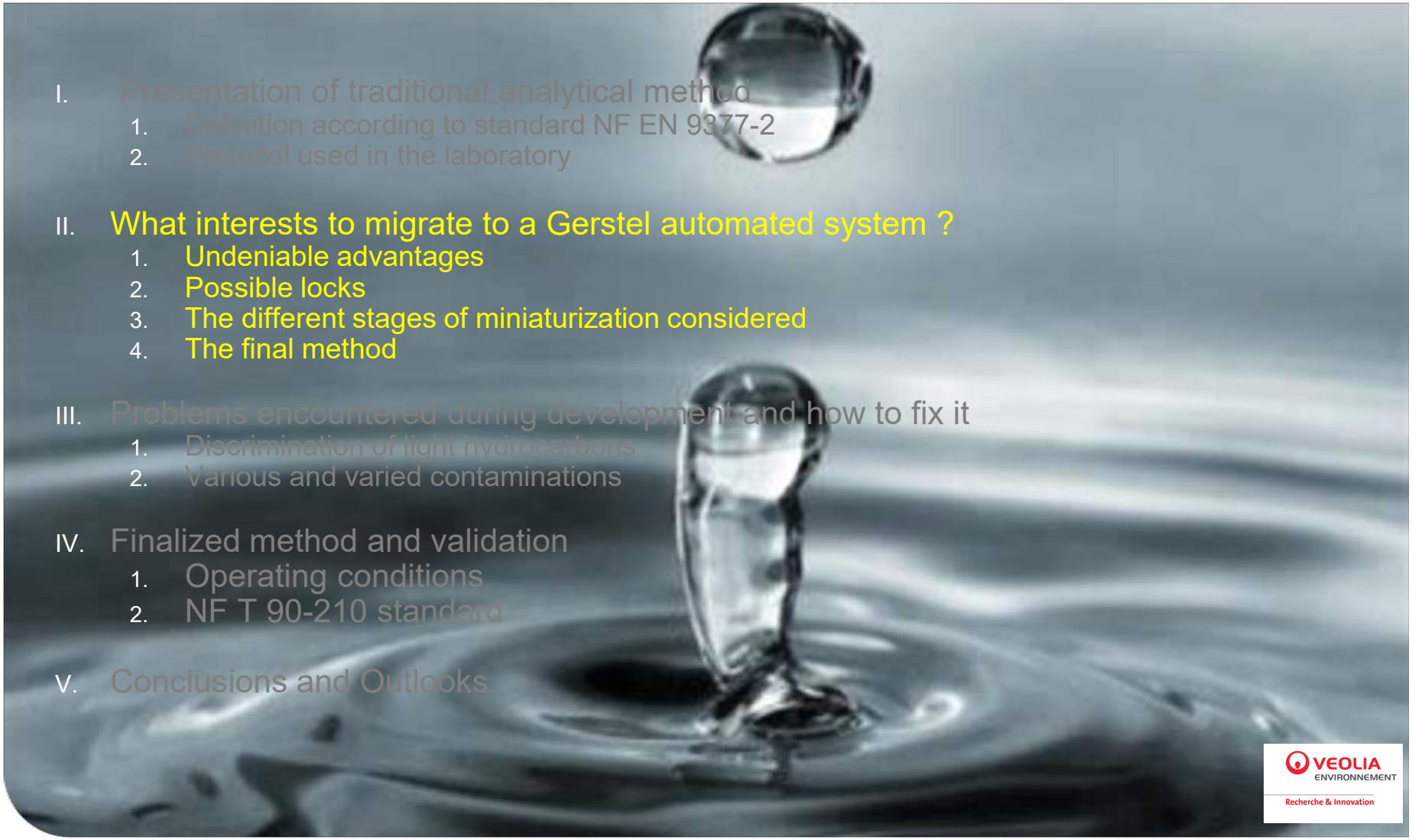
And over a year, we estimate the total cost to 32k€ for 4200 samples

Advantages and Disadvantages

- Simple
- Several systems according matrix
- Industrial waste waters
- Waste water

- technician time
  (too many preparation steps)
- Solvent volume used
- Clean-up and recycling waste costs
- Productivity
- Security : Hexane

Summary



An evidence …


Increased productivity
Green Lab
Miniaturization & Automating
Consumable cost
Security

Posssible Locks

Limite of quantification:

Tap water: 0,05 mg/L

Raw water / river / surface : 0,1 mg/L

Waste water: 0,2 mg/L

RIC / VERI partnership

Matrix :

Emulsions Issues (WW)

& Clean-up (from cartridge to ?)

Automating cost

Protocol adopted

Sampling : 9mL
Ajustement to pH ~2 (HCl) and add of 0,9g $MgSO_4$
Add of 0,9mL of extracting agent (Hexane+C_{10}&C_{40})

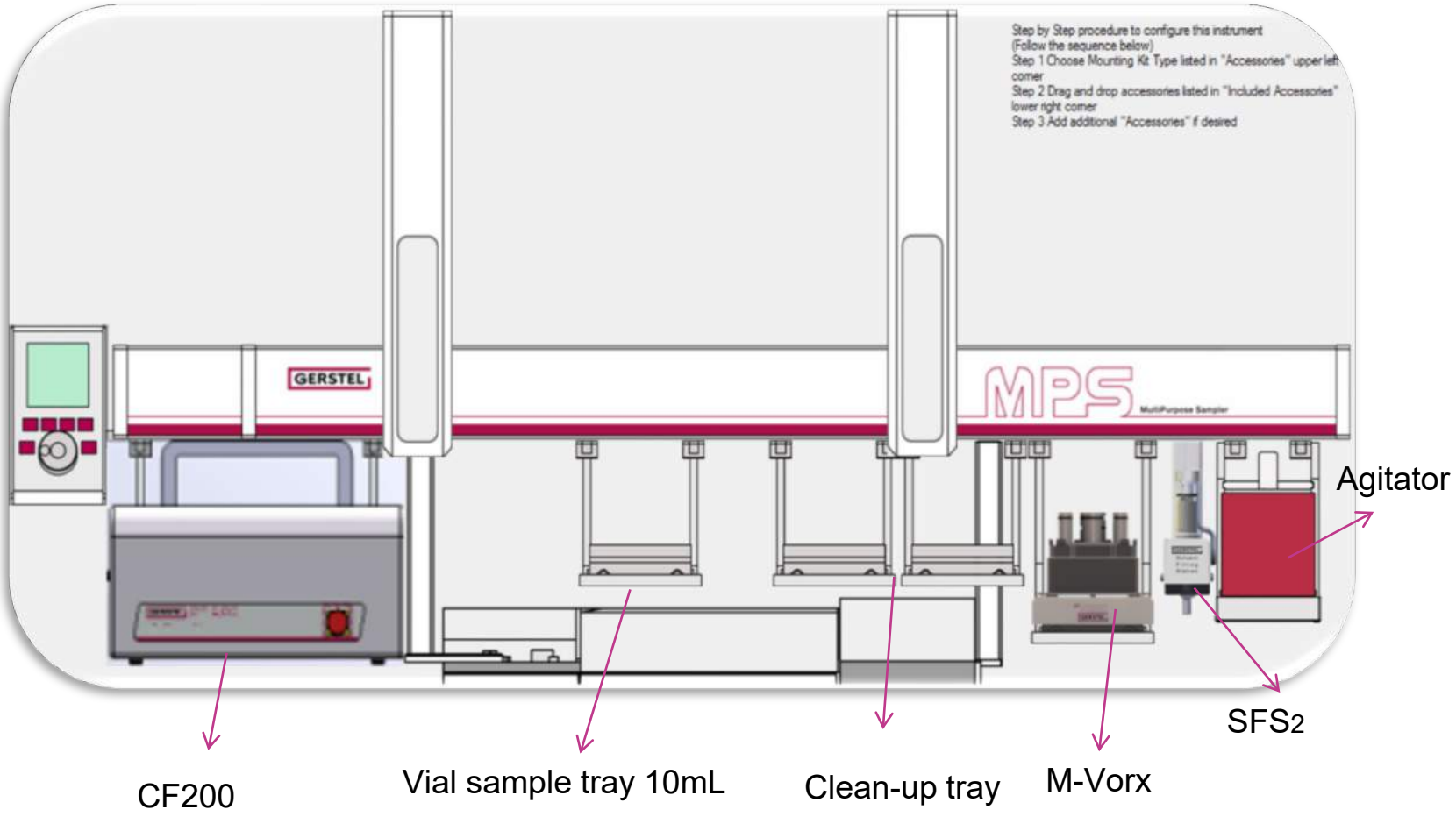
LLE by agitation 60mn @ 700 rpm

Centrifugation (CF200) 2mn @ 2000 rpm

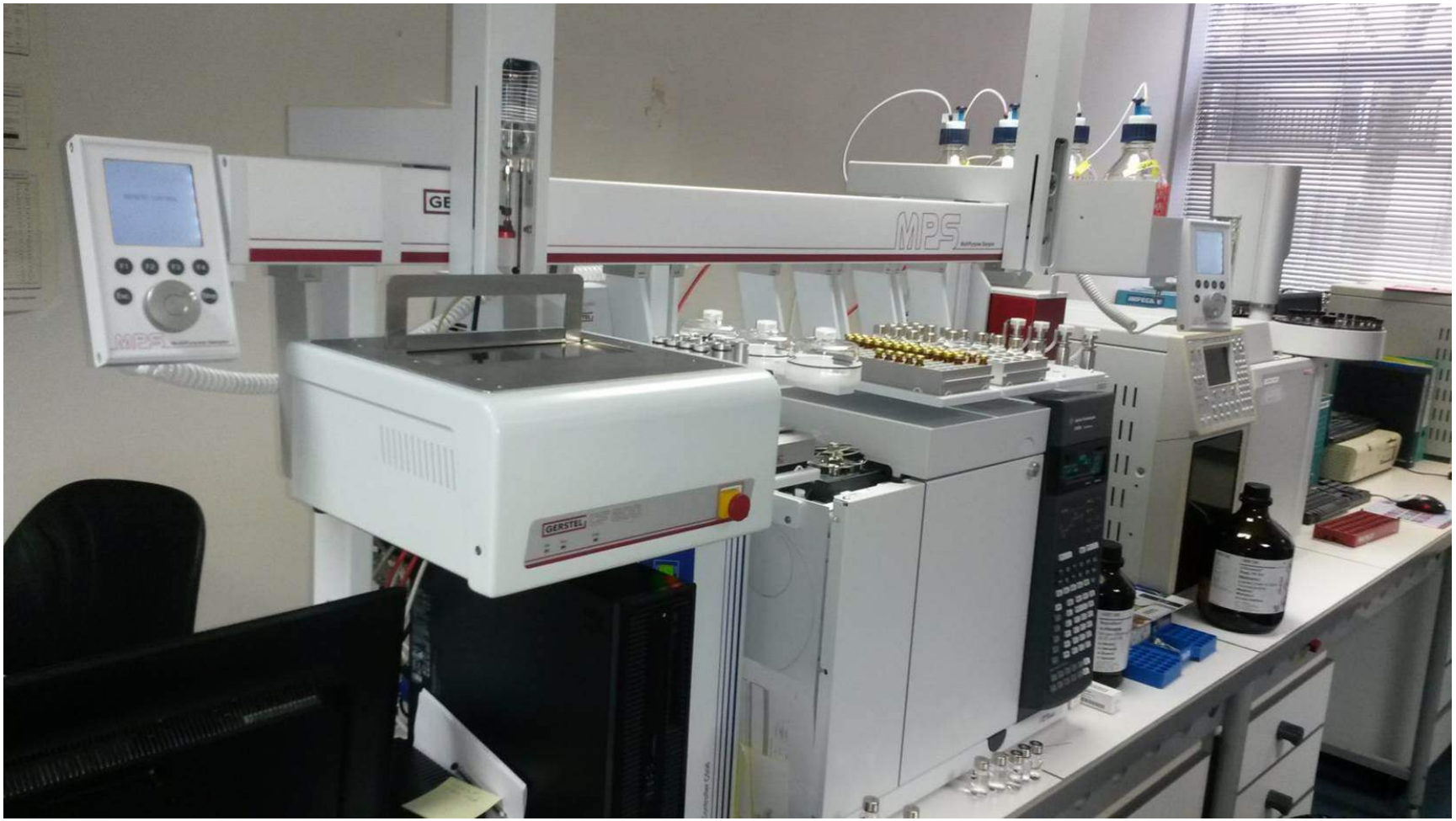
Drying and Purification in situ in a custom bottle made by Restek containing 30mg of Florisil® and 20mg of Na2SO4
(m-Vorx 2mn @ 1000 rpm)

Injection in PTV-LVI of 50µL in GC-FID Agilent 7890

Equipment

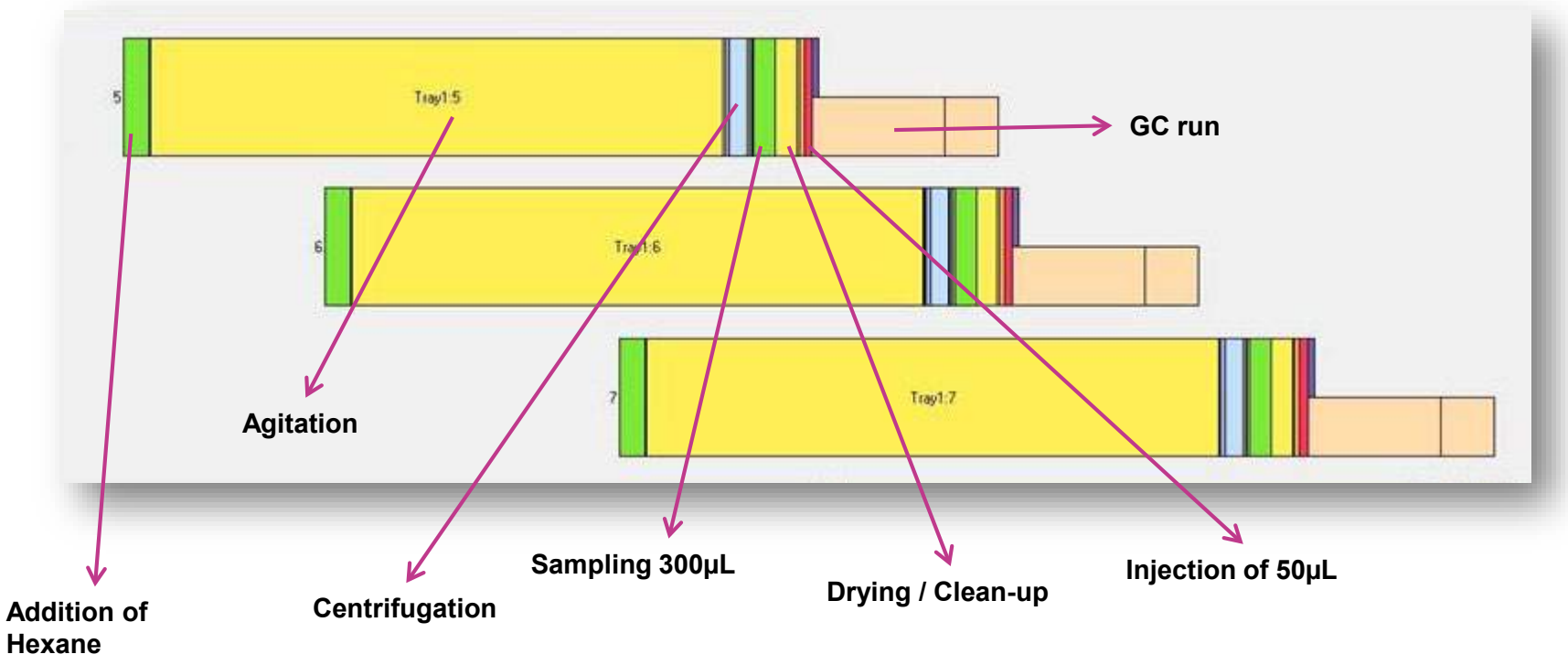

Step by Step procedure to configure this instrument
(Follow the sequence below)
Step 1 Choose Mounting Kit Type listed in "Accessories" upper left corner
Step 2 Drag and drop accessories listed in "Included Accessories" lower right corner
Step 3 Add additional "Accessories" if desired
GERSTEL
MPS
MultiPurpose Sampler
Agitator
SFS2
CF200
Vial sample tray 10mL
Clean-up tray
M-Vorx

Equipment



Séquence détaillée

8 samples in ~4h
ie 32 minutes / sample, preparation included



Undeniable Advantages

Volume Reduction

- 190 x less of solvent
- Test sample 9mL vs 1L

Time saving

Costs and Productivity

18 x less

Security

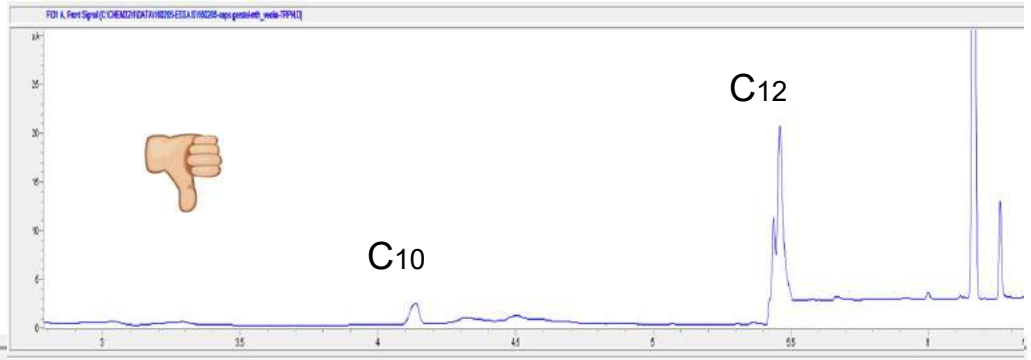
Less solvent better health

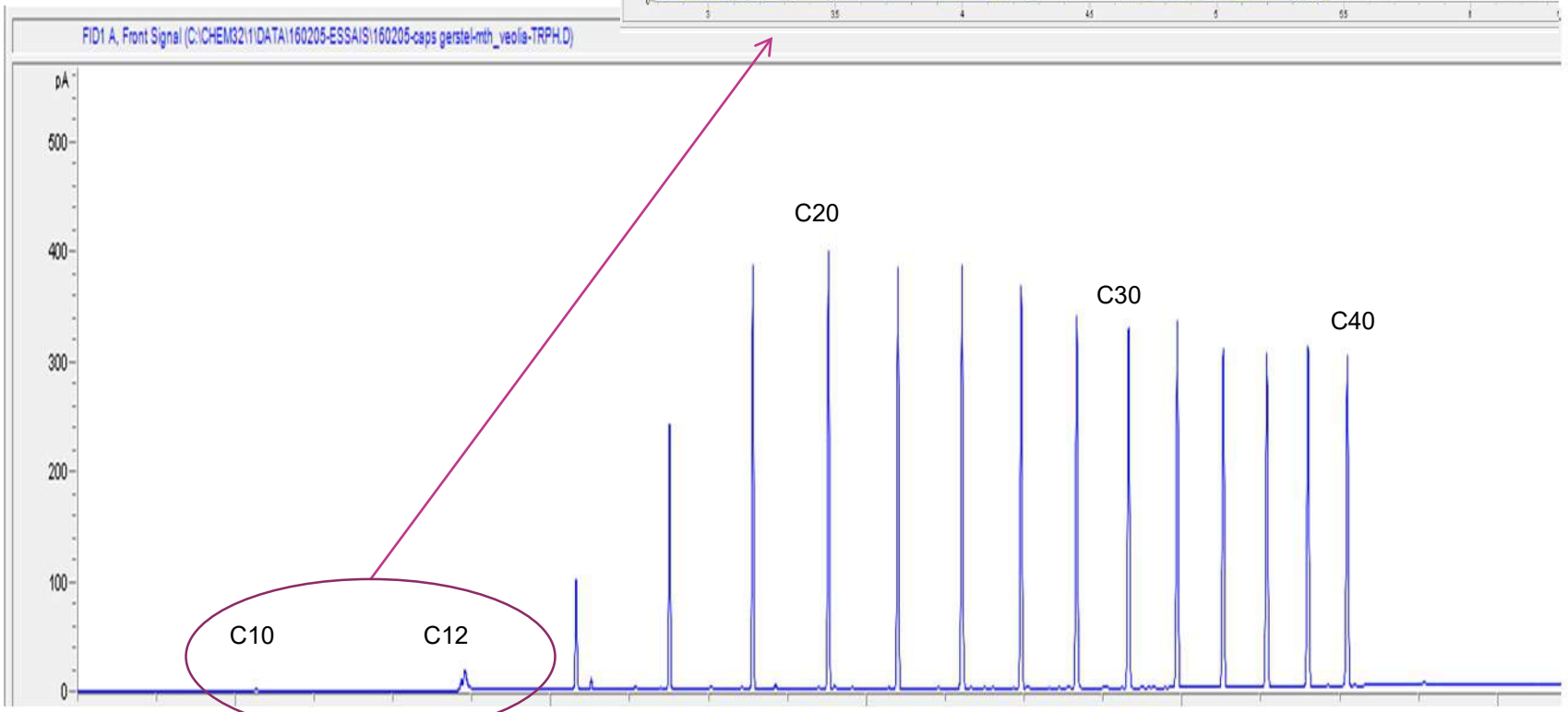
GREEN CHEMISTRY

Summary

Difficulties encountered: discrimination of light hydrocarbons

C_{40}/C_{20}: 0,8

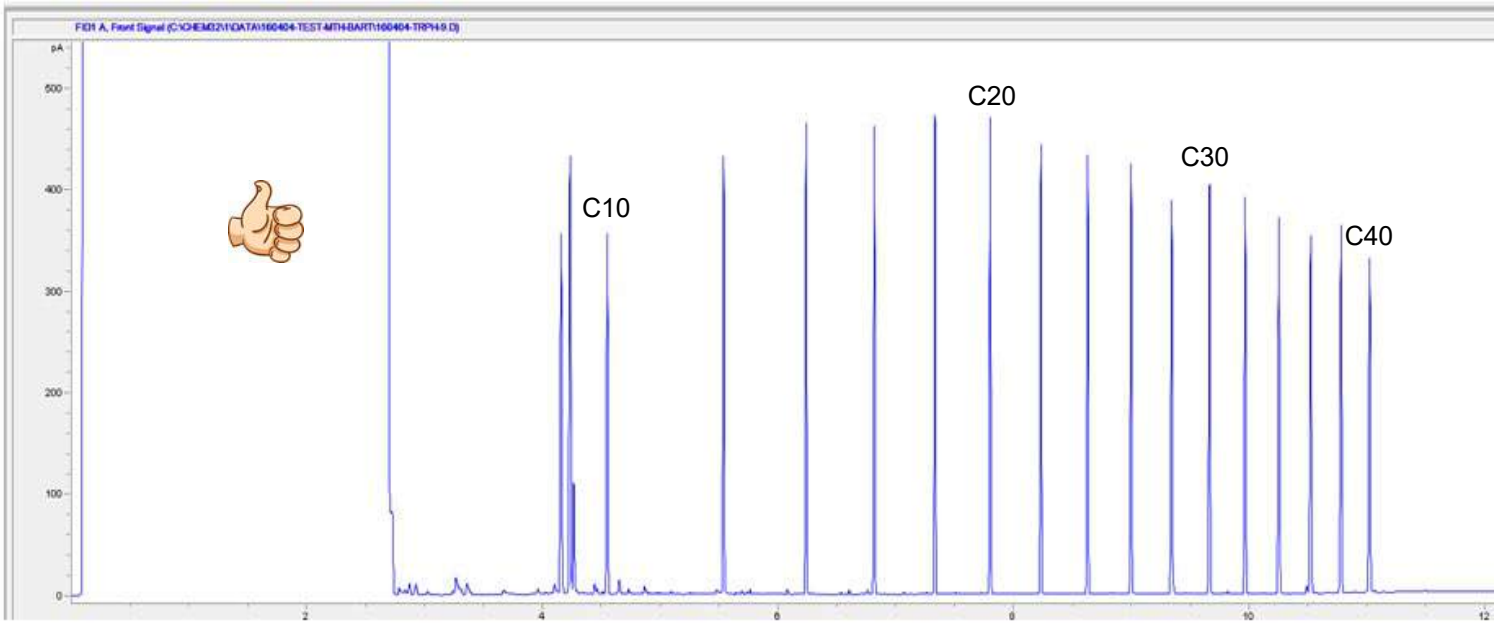




Difficulties encountered: discrimination of light hydrocarbons

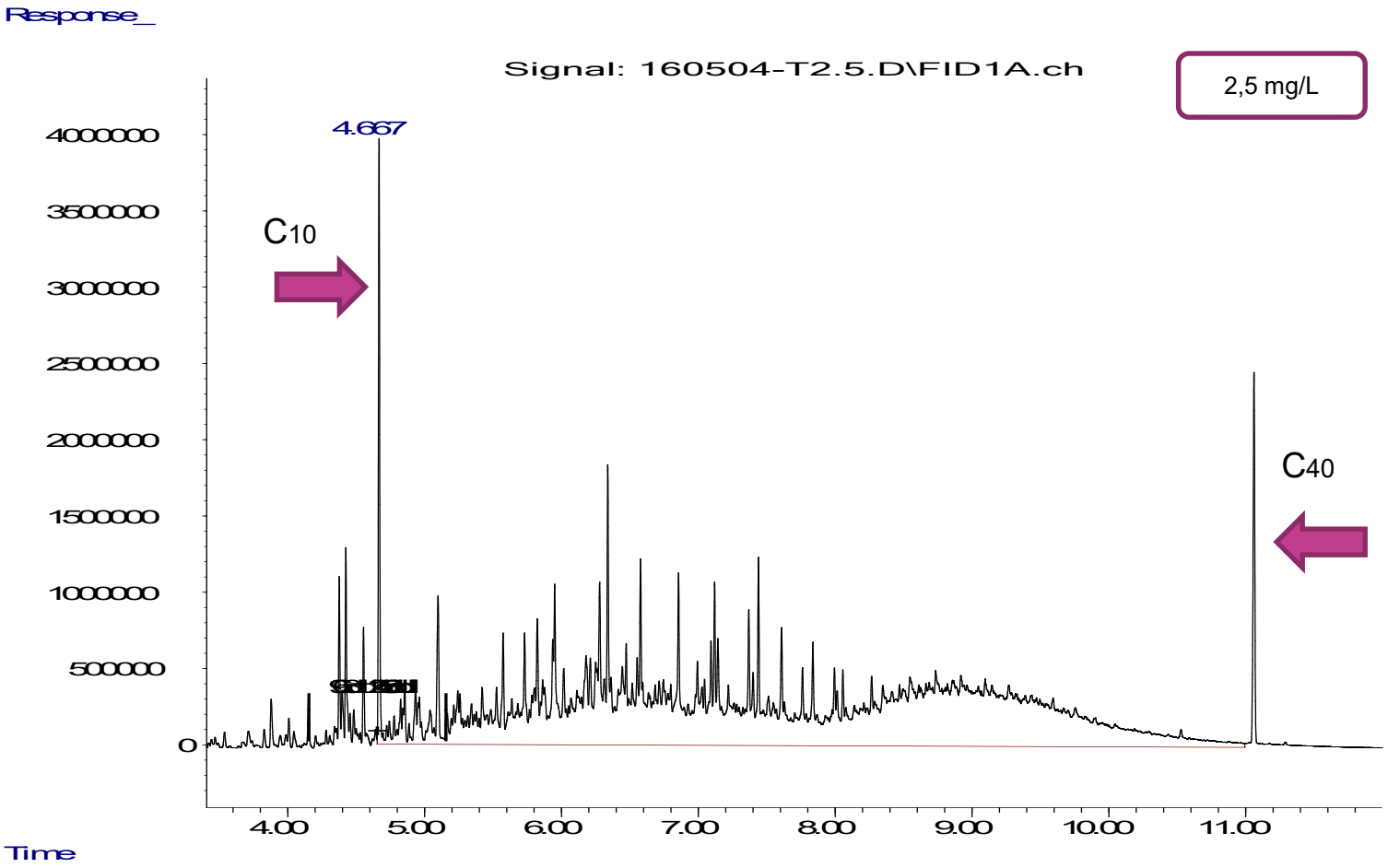
Conditions

CIS : 40°C during 1mn ➔350°C @12°C/s
PTV : -vent flow 75ml/mn
-vent pressure 8.2 psi
-vent time 0.02mn
-purge flow to split vent : 100ml/mn until 2mn
MPS : injection 50µL @ 2µL/s & **Liner *Bead Glass***

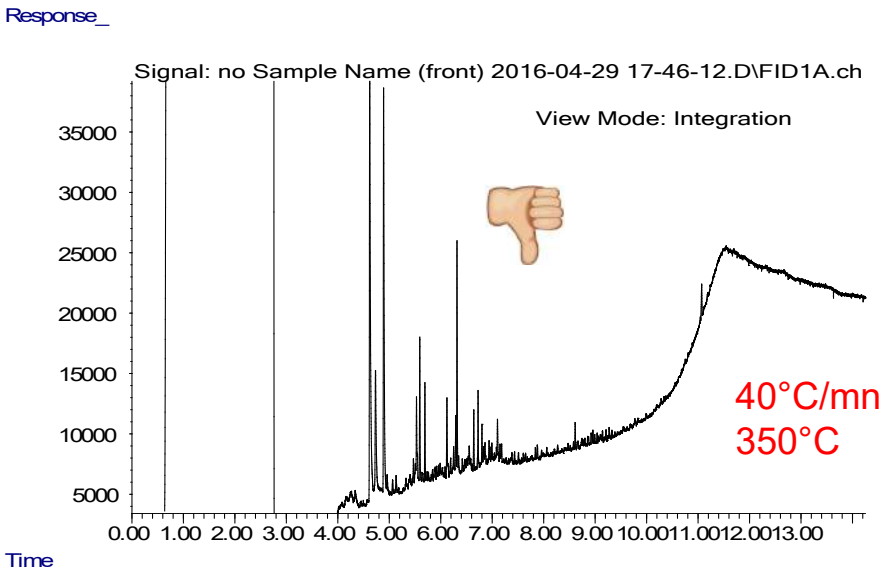


Difficulties encountered: baseline drift

INDEX = integration of area between C_{10} and C_{40}



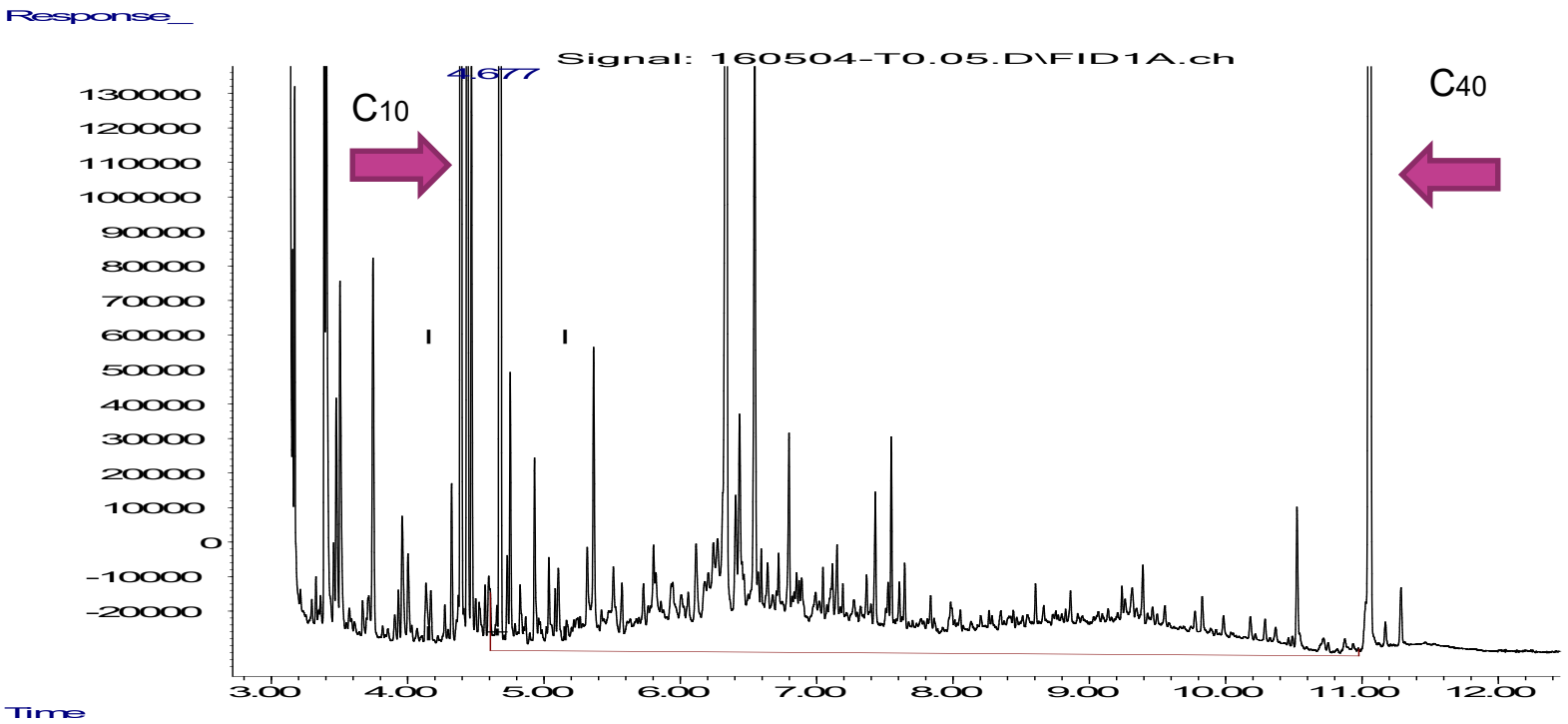
Difficulties encountered: baseline drift



Used of « baseline compensation » on Agilent GC-FID

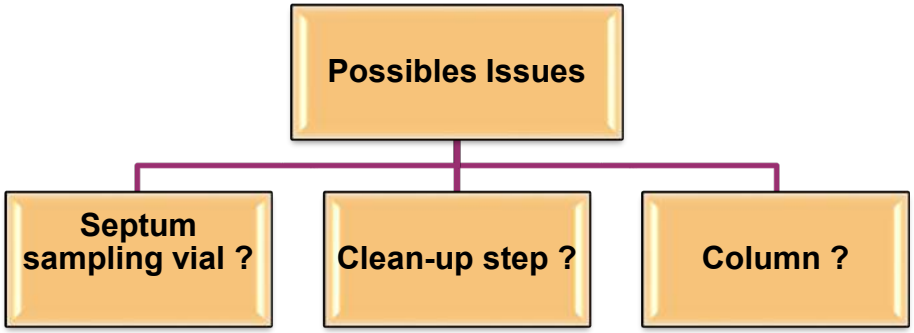
Difficulties encountered: baseline drift

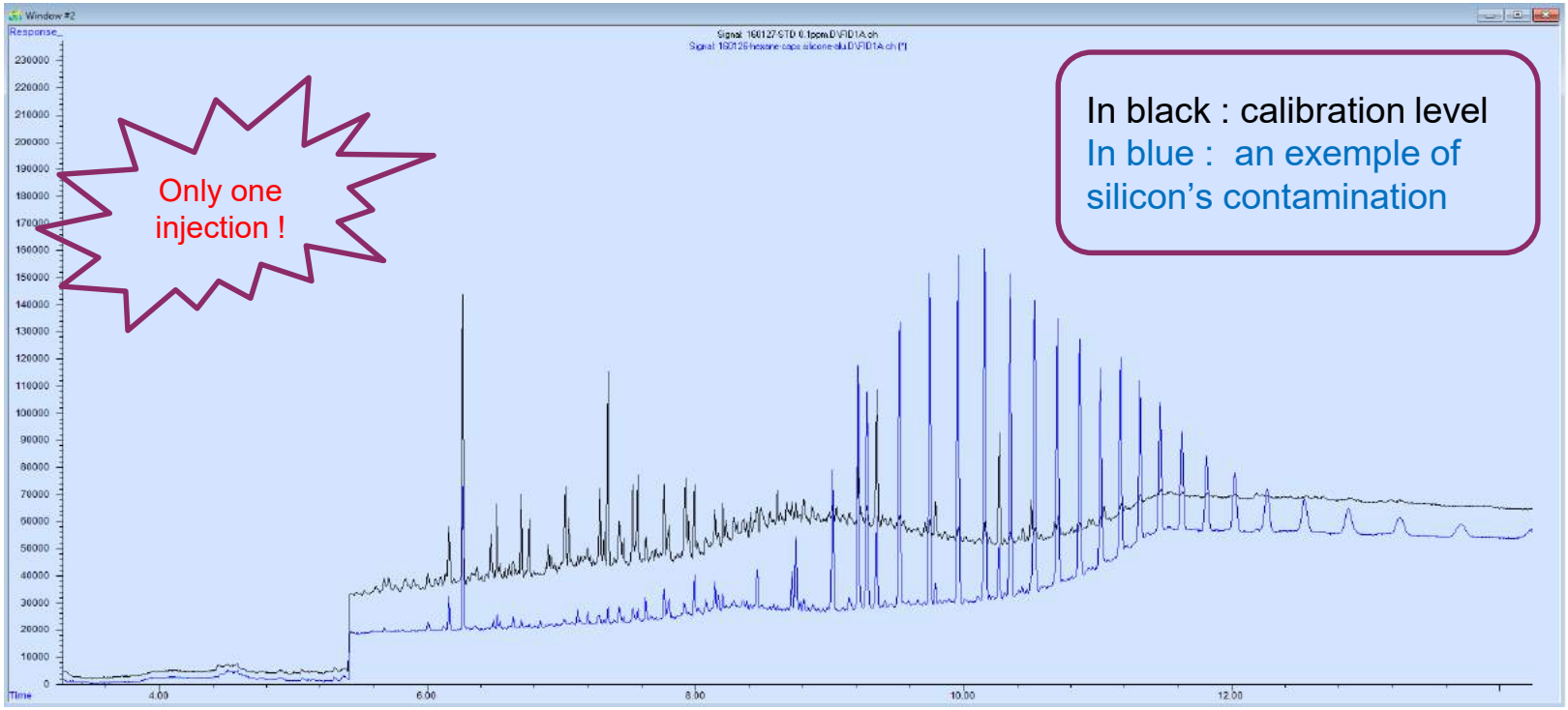
INDEX = integration of area between C_{10} and C_{40}



0,05 mg/L : 50 x less concentrated

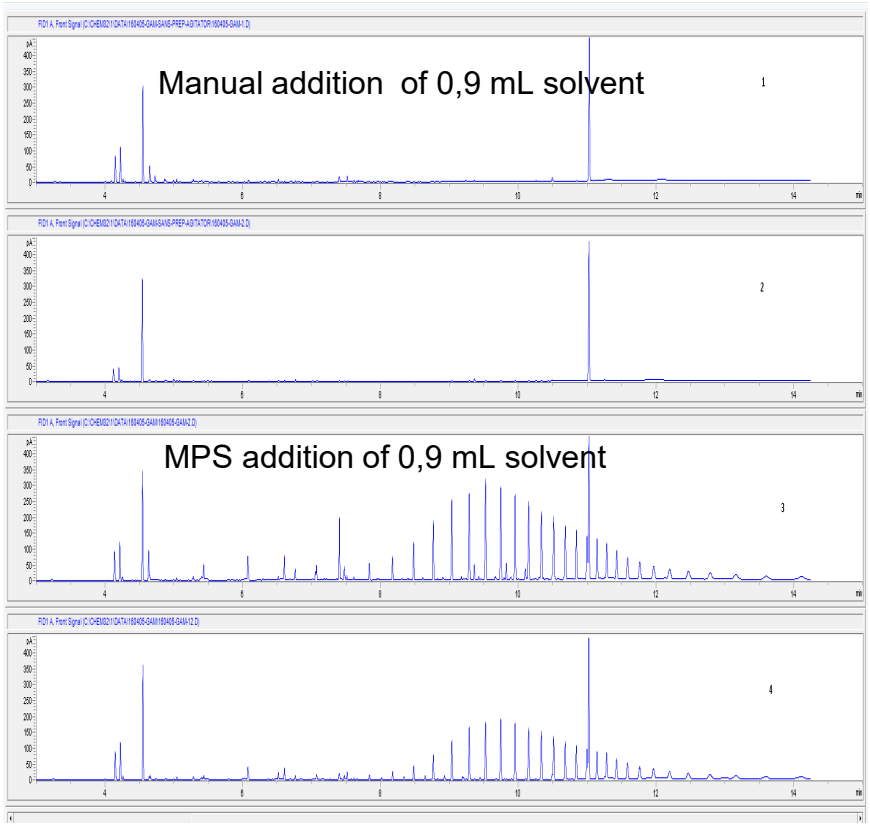
Difficulties encountered: silicone contamination

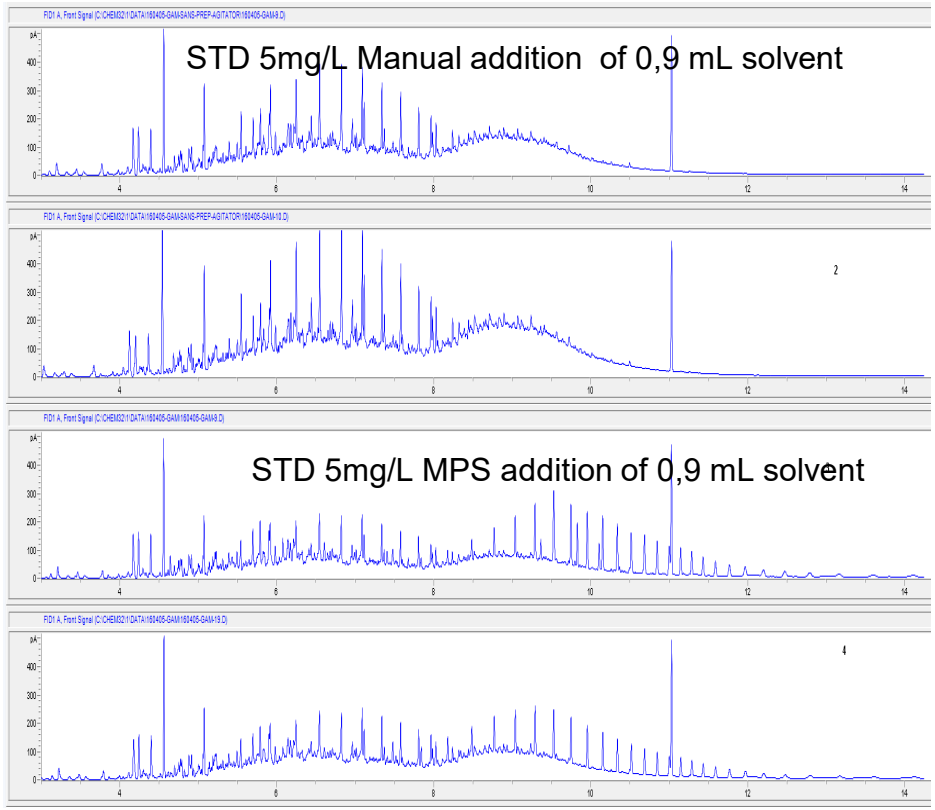




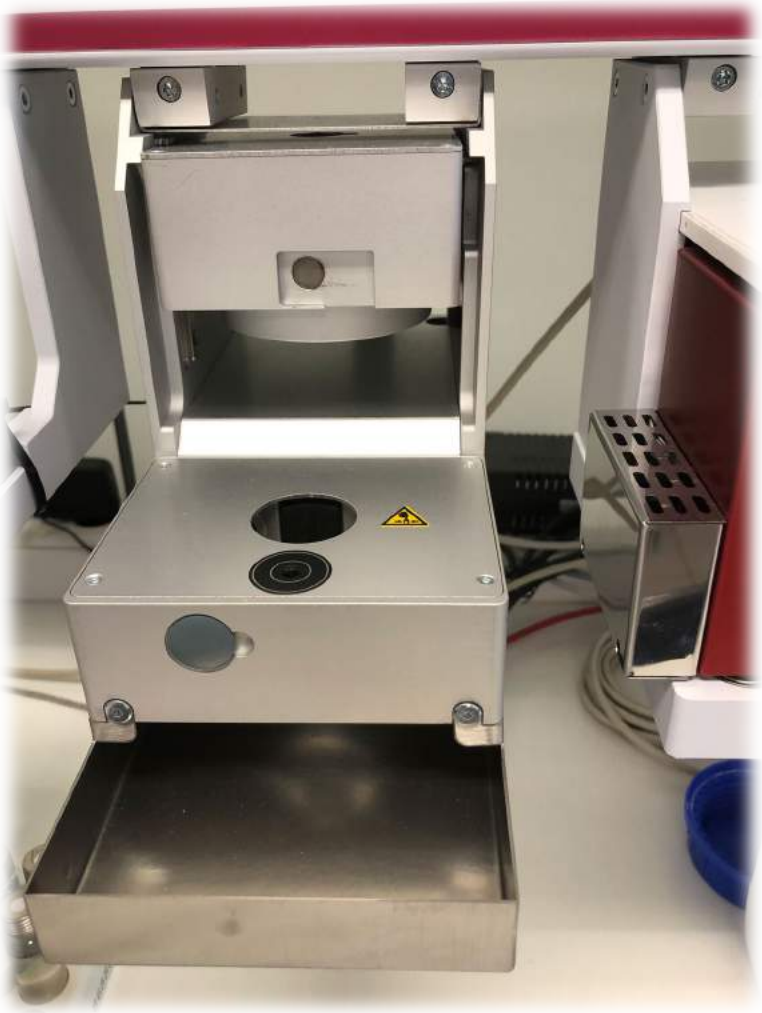
A problem but not least ...

The septum produces silicones during the addition of the extraction solvent (0.9 mL hexane) to the first step of automation





Capper / Decapper



RIC

GERSTEL

Intelligent Automation for GC/MS and LC/MS

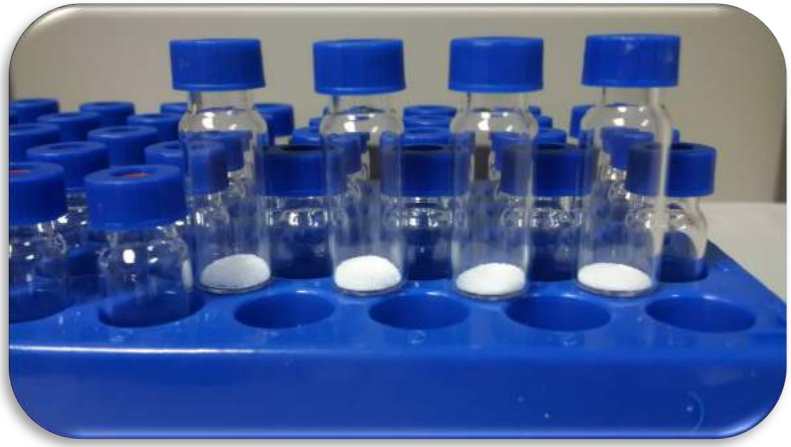
Silicone contamination during clean-up step

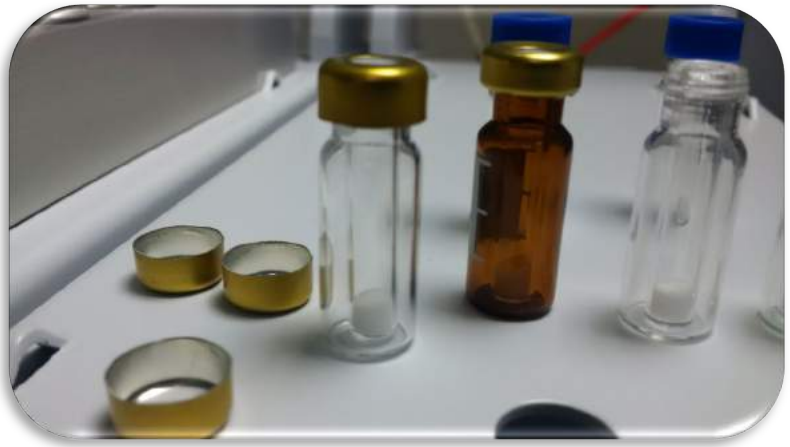
Aluminium !

- Agilent 100% PTFE (#5182-0871)
- Sigma Aldrich pastille PTFE (#27133)

Only one solution : DIY !

Silicone contamination during clean-up step



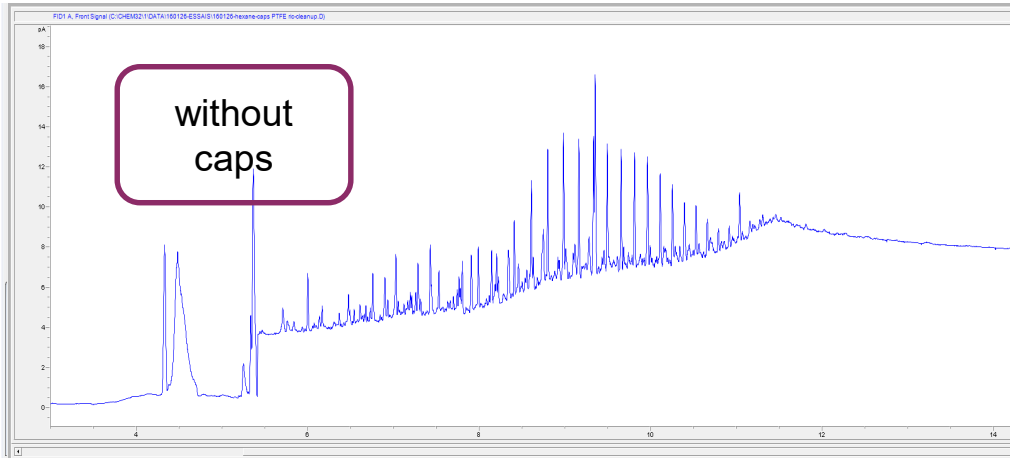


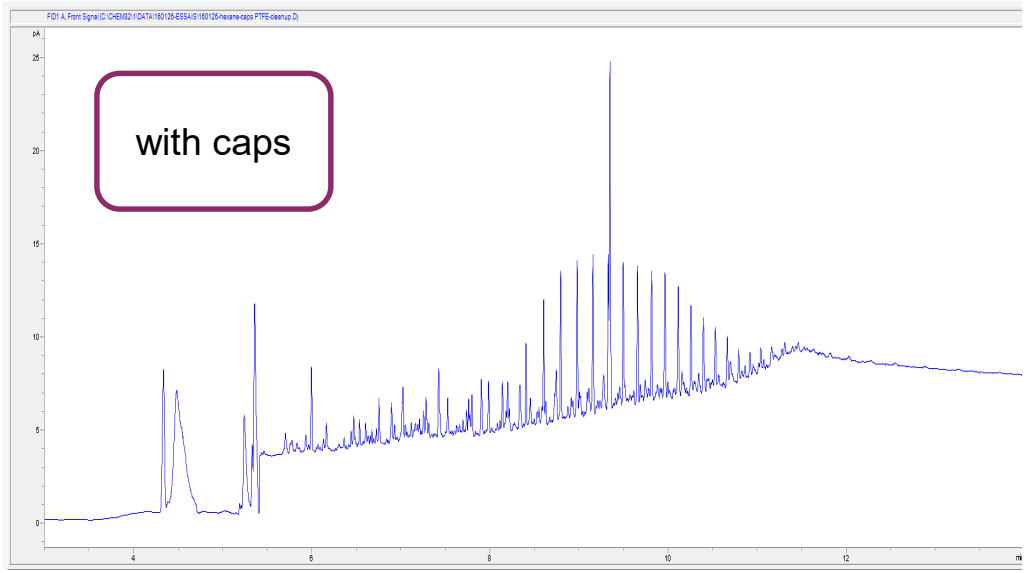
Restek: custom manufacture of a mixture: 30mg of Florisil® + 20mg sodium sulphate

Florisil®	
Retention of polar compounds	Organic and vegetal fat

Sulfate de sodium	
Drying Agent	Remove last trace of water in extract

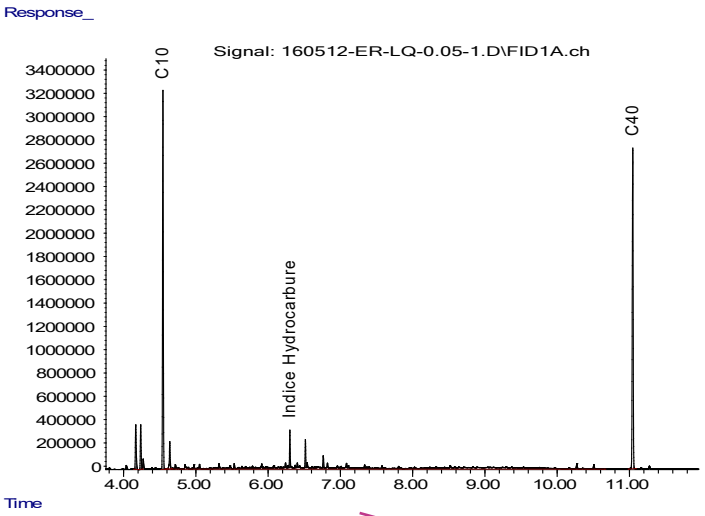
Silicone contamination during clean-up step



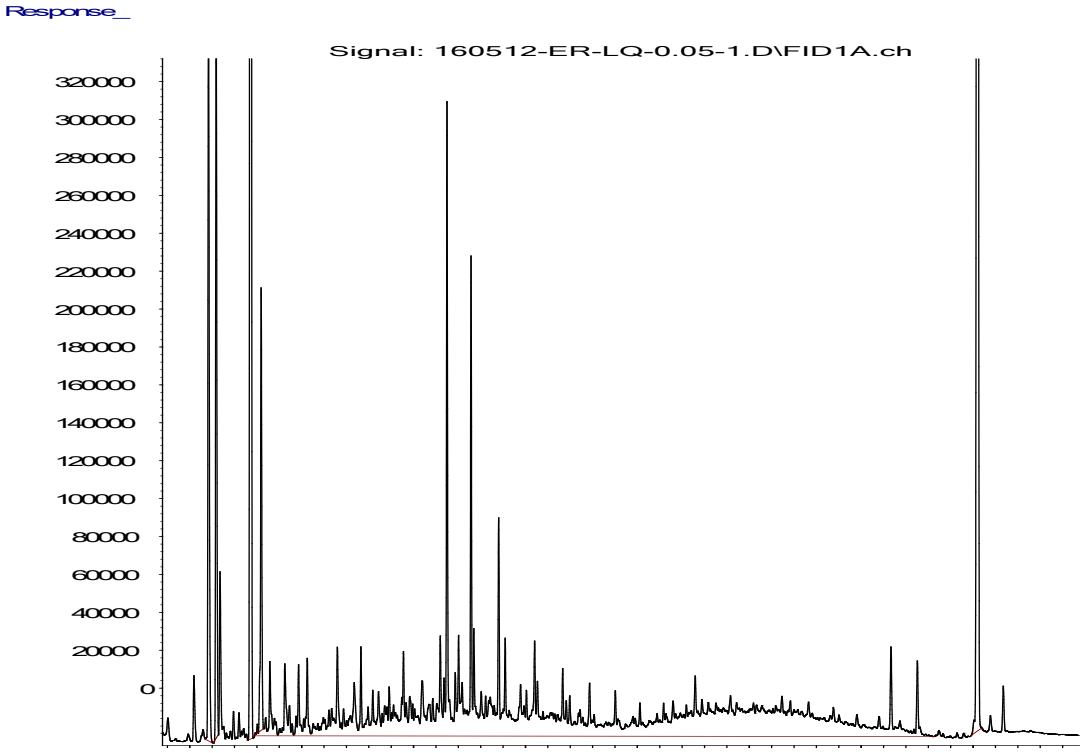


300µL d'hexane in contact with clean-up mixture

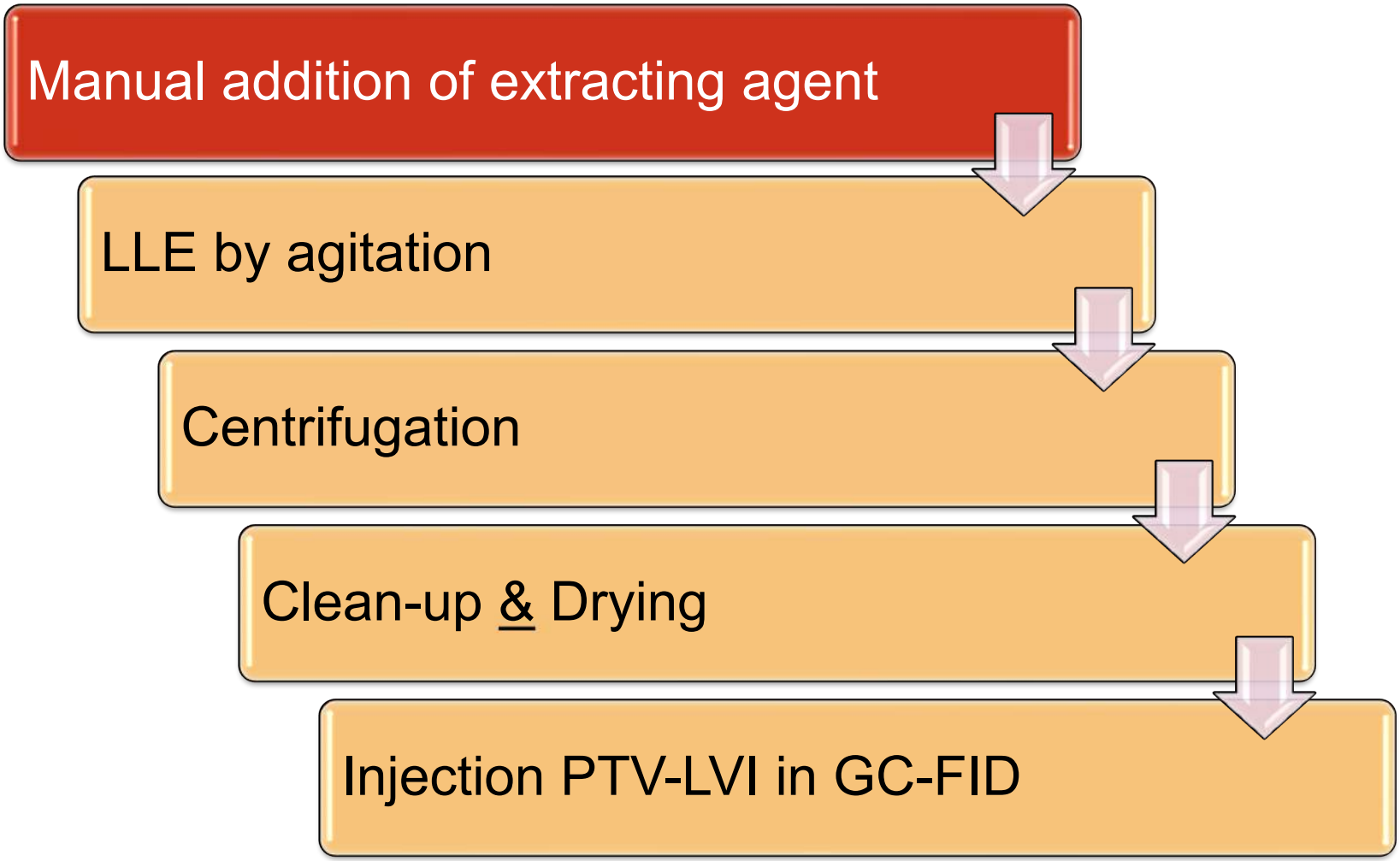
Silicone contamination : THE solution !



Mixt [Florisil® / Na2SO4] + reducer of 500µL have been placed in an oven at 250°C



Final experimental protocol



Summary

I. Presentation of traditional analytical method
   1. Definition according to standard NF EN 9377-2
   2. Protocol used in the laboratory

II. What interests to migrate to a Gerstel automated system ?
   1. Undeniable advantages
   2. Possible locks
   3. The different stages of miniaturization considered
   4. The final method

III. Problems encountered during development and how to fix it
   1. Discrimination of light hydrocarbons
   2. Various and varied contaminations

IV. Finalized method and validation
   1. Operating conditions
   2. NF T 90-210 standard

V. Conclusions and Outlooks

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Validation / Accreditation COFRAC (French committee of Accreditation)

ISO / IEC 17025 specifies "general requirements for the competence of testing and calibration laboratories"

It asks laboratories to validate their methods of analysis that they have developed when they are not standardized or outside the scope of this standard.
It also asks to assess the uncertainties of the results provided

PURPOSE: To show that the developed method is fit for the intended use ie according to the needs of the customer or the regulation

XPT-90 210 Standard is a tool for the validation of analitycal methods

Validation on 6 series

1 calibration range (CR)	2 spiked samples at LOQ	2 spiked samples at 20% CR	2 spiked samples at 80% CR	2 QC LOQ-20%-80%

Result calibration ranges (6 ranges)
Enter theoretical concentrations and recalculated concentrations

Calibration range study
Validate the calibration model

LOQ (real matrix, 2 samples x 6 tests)
Validates an LOQ and estimates the uncertainty of manipulation bias at LOQ

Recovery (real matrix, spiking at 20 and 80% of the range, 2 samples x 6 tests)
Validates yields and estimates the uncertainty of method bias at levels other than LOQ

Accuracy
Validate accuracy for an unrecognized method based on LOQ and recovery tests (20 and 80%)

Uncertainty
Estimate the uncertainties of the 3-level method (LOQ, 20% and 80% of the calibration range) through 2 QCs

Working range (concentration)

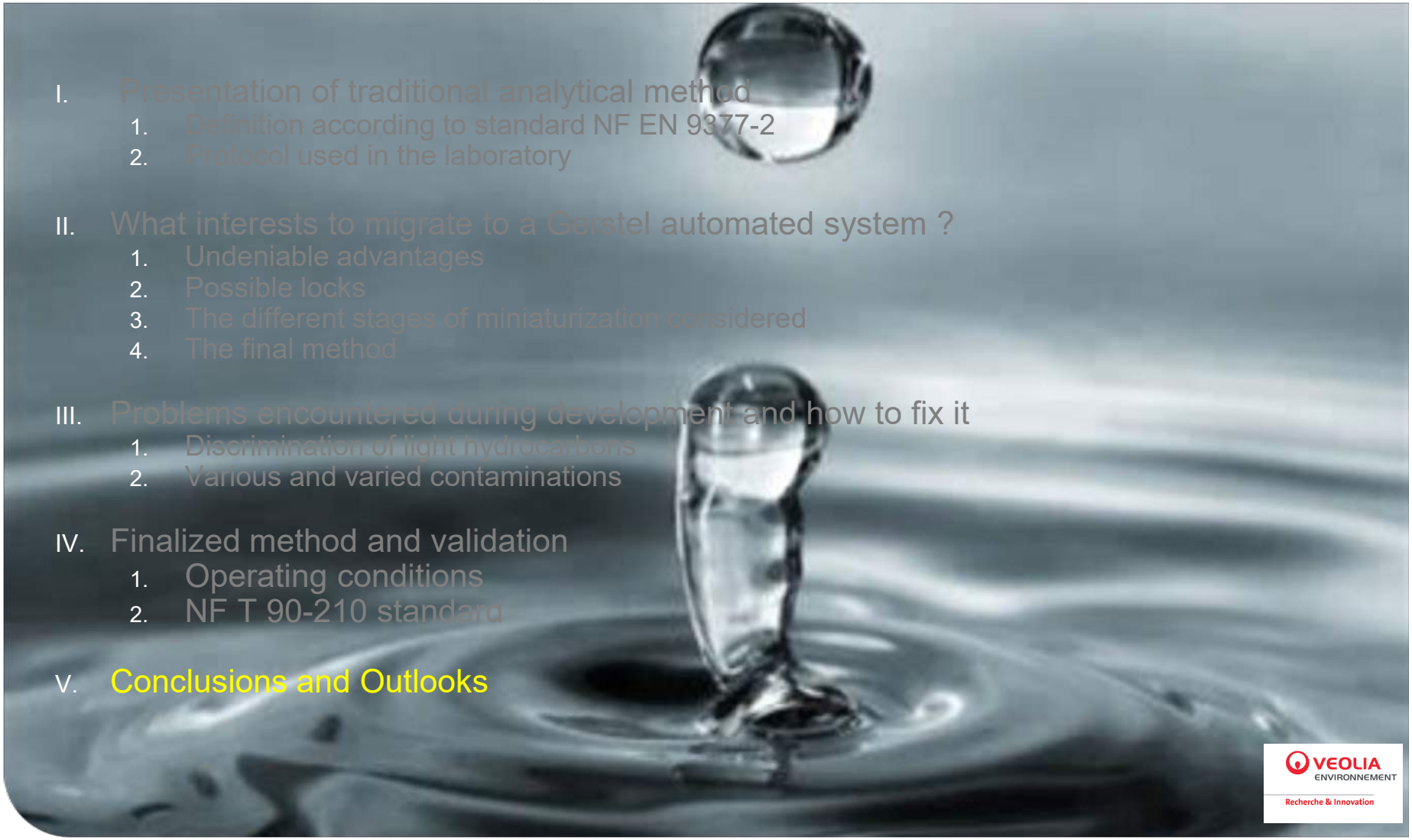
Validation was done on tap water (TW), raw river water (RRW), treated wastewater (TWW)

mg/L	NIV 1	NIV 2	NIV 3	NIV 4	NIV 5	NIV 6	NIV 7	NIV 8
TW	0,05	0,1	0,2	0,5	1	2,5	5	10
RRW	-	0,1	0,2	0,5	1	2,5	5	10
TWW	-	-	0,2	0,5	1	2,5	5	10

Only some validations was done (end of laboratory's activities)

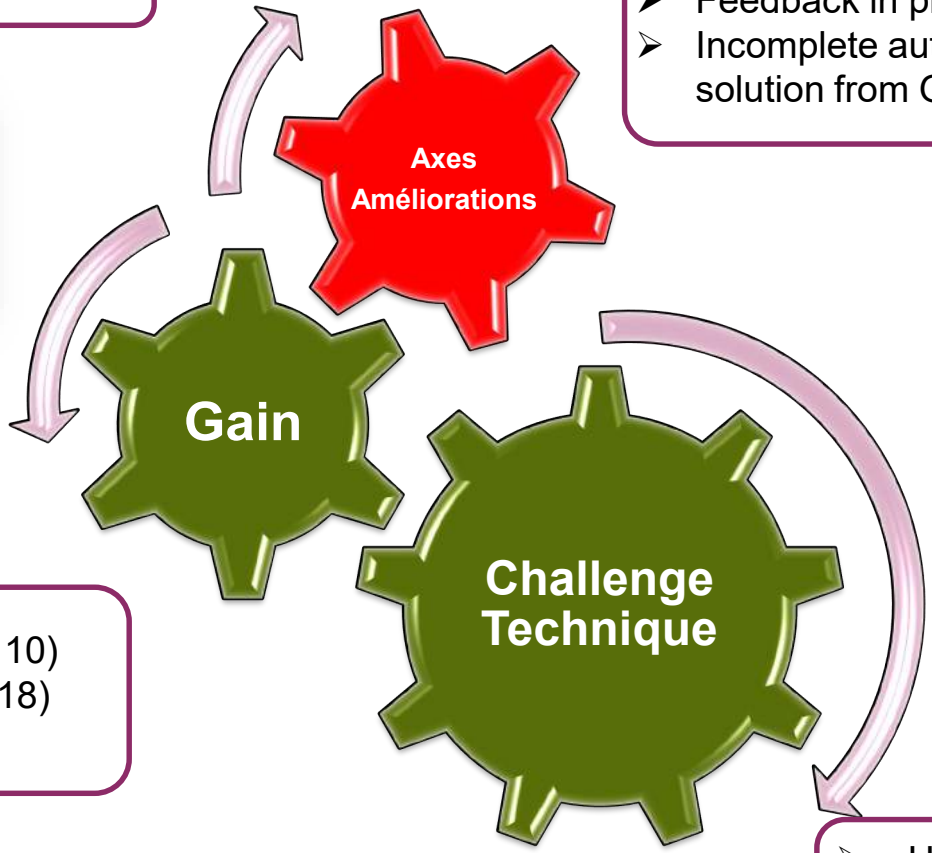
- ❑ 4 / 6 series for tap water matrix
- ❑ 2 / 6 series for raw river water
- ❑ 3 / 6 series for treated waste water

Summary



Conclusions and Outlooks

Automation …



- Feedback in production line
- Incomplete automation but new solution from Gerstel (decapper)

- Time saving (by 10)
- Saving cost (by 18)
- Security

- Holding LOQ
- Emulsion management
- Contaminations


Danke
Merci
Gracias
Thank you
Grazie
謝謝
Спасибо