High throughput puff-by-puff quantification of smoke analysis

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Imperial Tobacco

Altadis

How to comply with the ever-increasing number of analyses ?

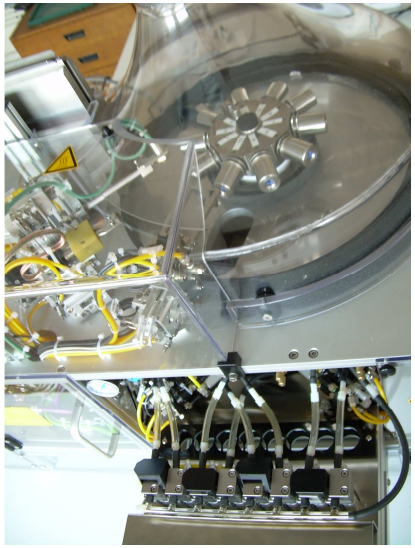
- Automatic puff-by-puff sampling system

  - ➔ Smoking Robot Vitrocell® VC 10 ® Chemcontrol
  - ➔ Carbonyls- Whole smoke
    - Example : Formaldehyde & FV

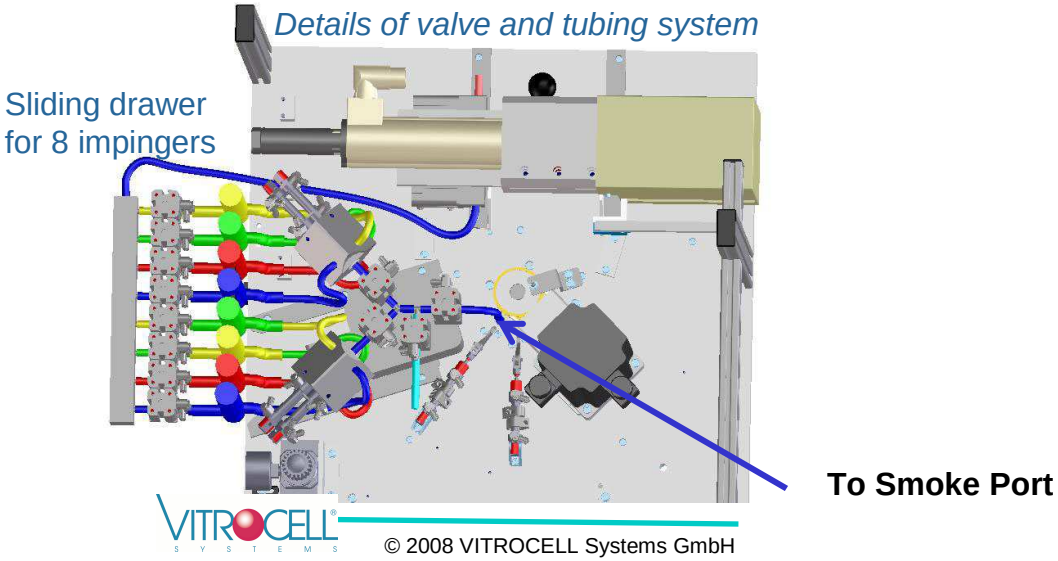
- On line puff-by-puff quantification system

  - ➔ Two phases :
    - Analytical step using the GC MACH® System
    - Connection to the smoking machine
  - ➔ Volatile compounds- Gas phase smoke

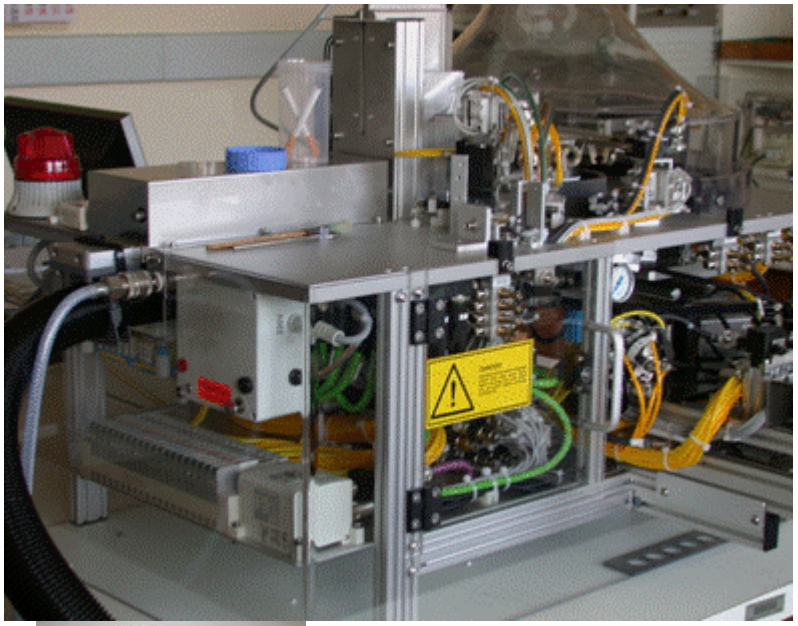
Device n°1 : Geometric design



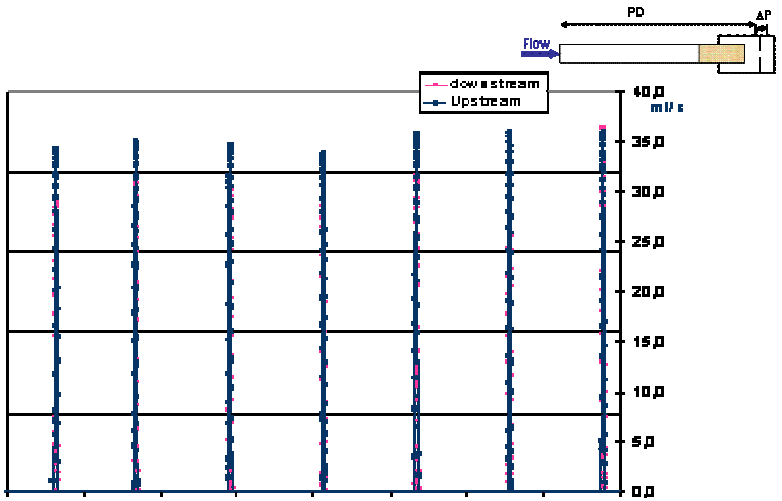
- specification targets : automatism & flexibility
  - Flexibility: smoking run
    ISO- Canadian Intense…in-house regime
  - Versatile use: *whole smoke, gas phase..*
  - Automatic sampling points *(for puffs # 1 … 8)*
  - Automatic purging gas



Geometric control



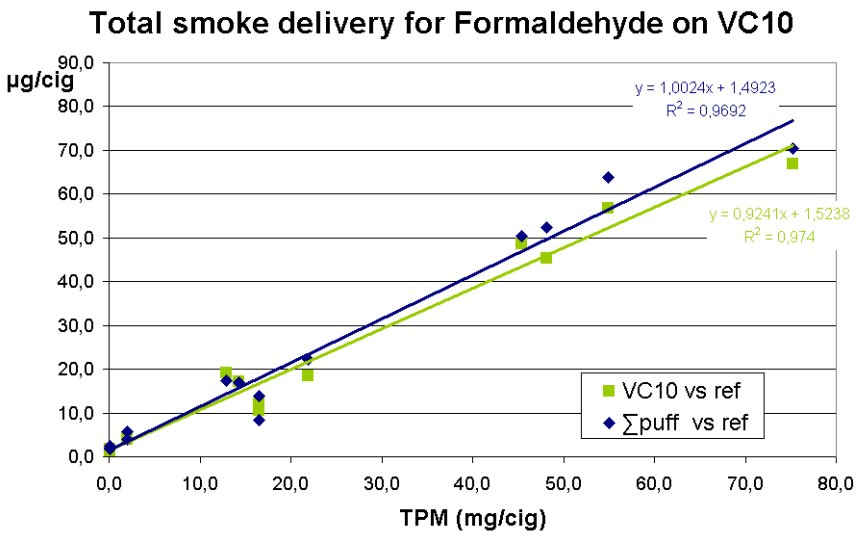
- flow and volume check on SPA\M
  - ➔ 2R4F – lit cigarette
  - ➔ Upstream & downstream

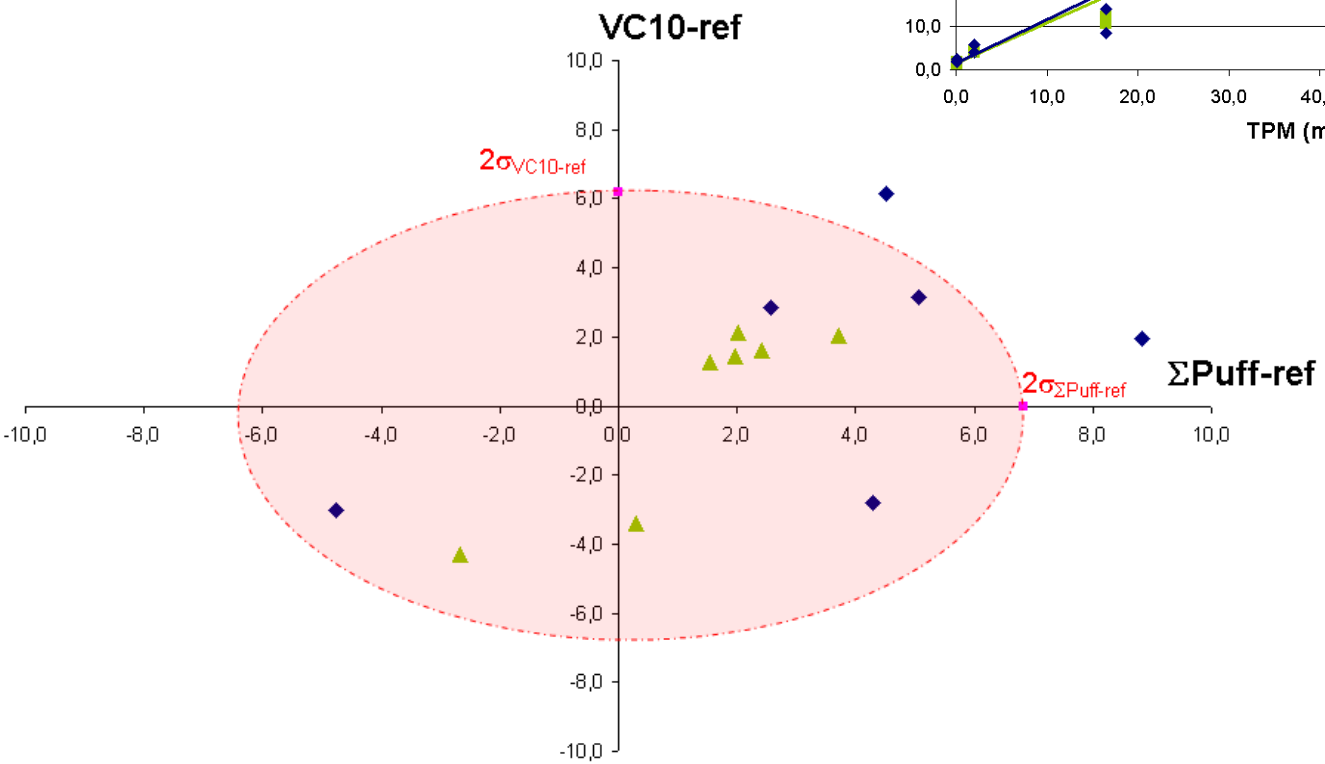


- Volume - repeatability error < 3.1% (n=7 puffs)
  - ➔ Always performed with 100 mL cylinder to avoid cylinder exchange

Data consistency

VC10	total yield
∑Puff	addition of all individual puff-by-puff data
ref	classical rotary RM20CSR or linear SM540 machine yield





Sensitivity request

- LOQ

(signal/noise ratio 9:1 or standard deviation*9)

	LOQ (µg/puff)
Formaldehyde	0,013
Acetaldehyde	0,009
Acetone	0,016
Acroleine	0,004
Propionaldehyde	0,006
Crotonaldehyde	0,009
Butanone	0,009
Butyraldehyde	0,027

High sensitivity required to study Ultra Low tar products

- Variability of monitor

(VC10 total yield)

2R4F	Average (µg/cig)	CoV (%)
Formaldehyde	12,0	14,0
Acetaldehyde	569,8	5,4
Acetone	205,0	7,2
Acroleine	43,4	7,9
Propionaldehyde	32,0	8,8
Crotonaldehyde	8,5	18,9
Butanone	53,1	3,9
Butyraldehyde	29,8	9,7

Limiting factors

- The smoking machine
  - ➔ Requires a meticulous control of the leaks

- HPLC determination
  - ➔ Currently carried out on conventional HPLC system
  - ➔ Pötter team :
    analyse time < 5 min. with ultrafast HPLC

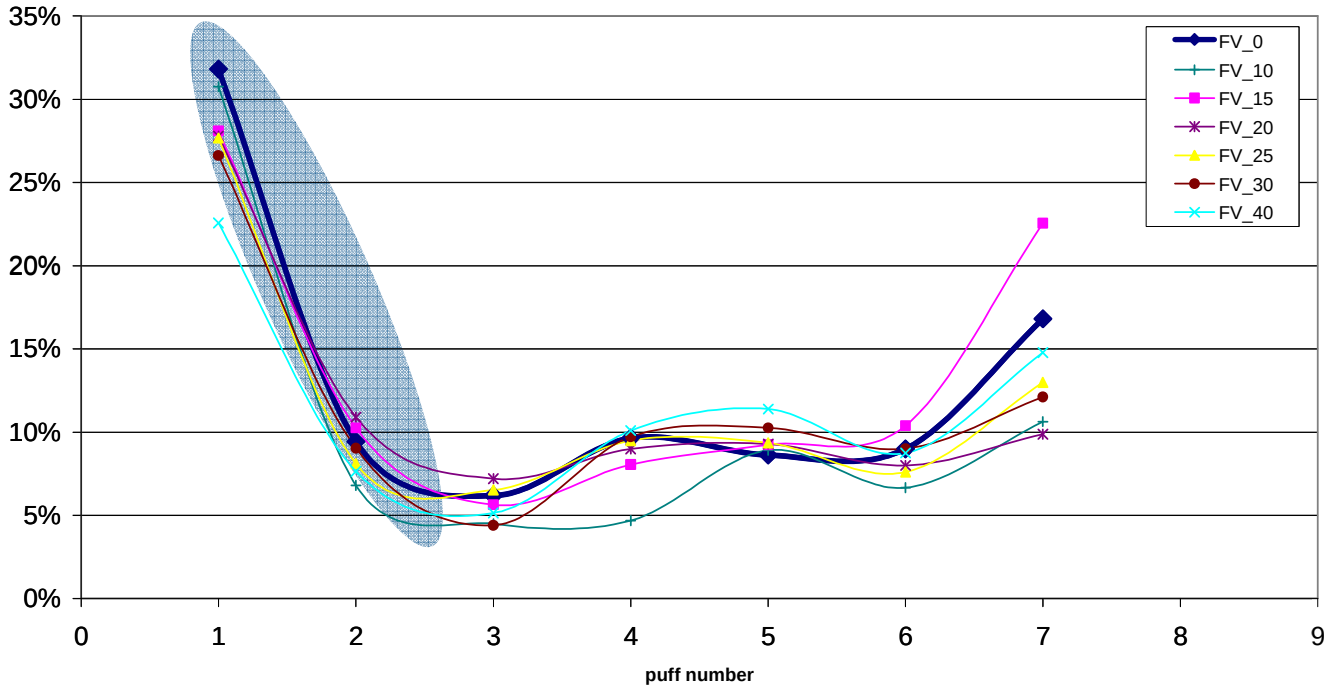
    W. Pötter, S. Lamotte, H. Engelhardt and U. Karst
    J. Chrom. A, 786 (*1997*) 47-45.

Application : profile shape *vs* filter ventilation

	FV (%)	TAR (mg/cig)	PUFF	CO (mg/cig)
CIG_FV0_REF_	0.4	12.17	7.15	15.6
CIG_FV10_	11.1	11.24	7.2	14.1
CIG_FV15_	16	10.76	7.45	13.2
CIG_FV20_	20.9	10.22	7.4	12.3
CIG_FV25_	26.2	10.01	7.75	11.4
CIG_FV30_	31.1	9.28	7.7	10.5
CIG_FV40_	40.1	8.8	7.95	9.8

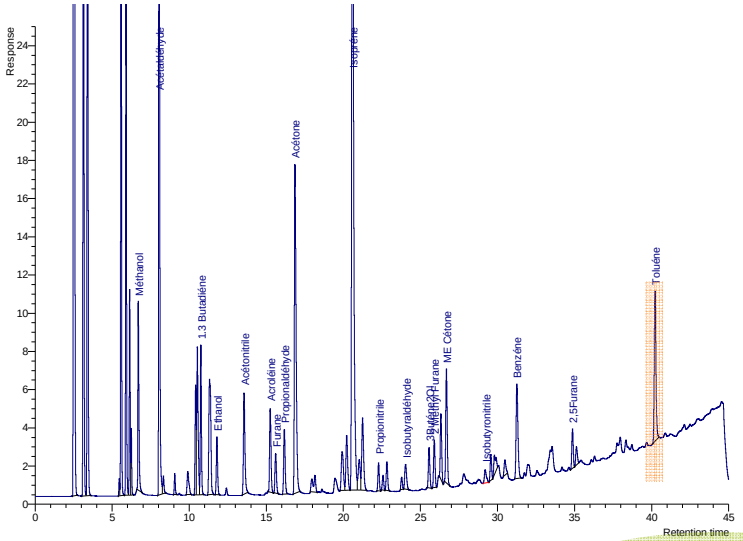
NTM, blend constants
acetate filter

Percent Formaldehyde delivery per puff

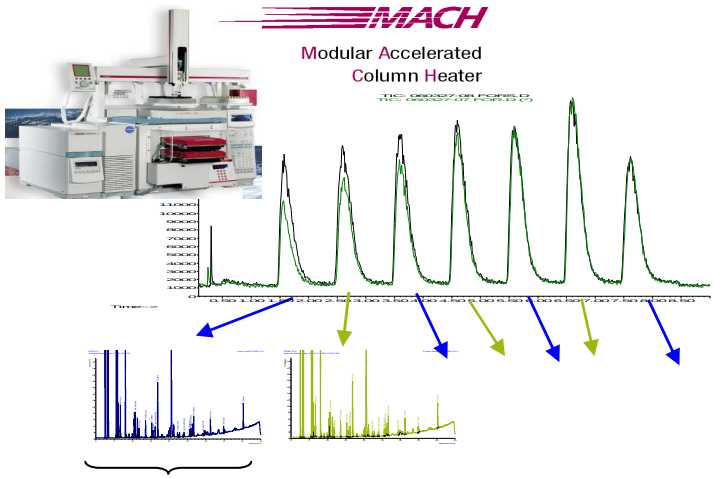


Device n°2 : Analytical improvement

Mainstream gas phase profile (gas bag method)



run time : 45 min



Run time < 1 min

- analytical targets :
  - Develop a fast GC-MS method to monitor gas phase compounds in Tobacco Smoke.
  - Target Analysis time < 1 min
  - Target Solutes: acetonitrile – acrolein – isoprene – benzene – toluene
  - PUFF analysis: 6-10 consecutive runs of 1 minute each

MACH technology is based on Low Thermal Mass Technology.

Fast heating and fast cooling = Short analysis cycles and high throughput.

Separation capabilities

Method 1

- 10 m x 150 µm ID x 1.2 µm DB-1
- 40℃ – 0.5 min – 50℃/min – 65℃ – 100℃/min – 200℃ – 1 min (3.35 min)
- GC: 200℃ iso (5 min)
- He (carrier gas)
- Split 1/50
- MS in scan mode

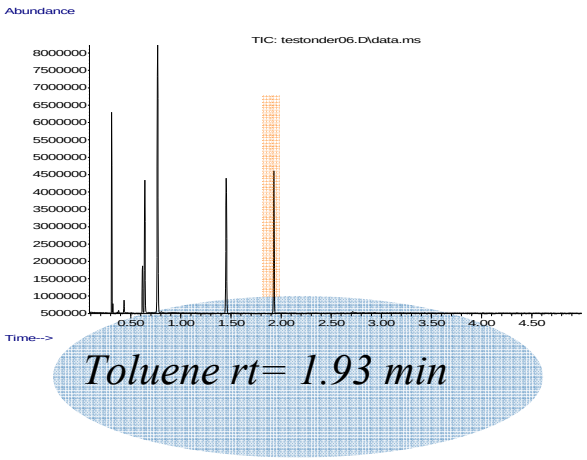
Method 2

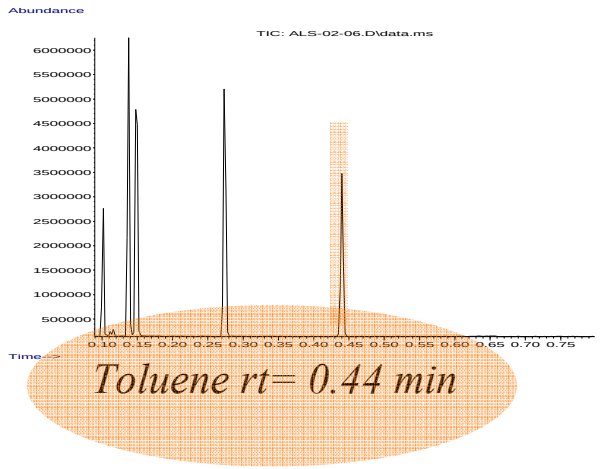
- 3 m x 100 µm ID x 0.4 µm DB-1MS
- 50℃ – 0.2 min – 100℃/min – 90℃ (0.60 min)
- GC: 150℃ iso (0.7 min)
- Split 1/50
- MS in scan mode

Heater 250 ℃ // Pressure 328 kPa
Total Flow On 60.195 mL/min
Septum Purge Flow On 3 mL/min
Split Flow 56.074 mL/min
Injection Pulse Pressure 68.948 kPa Until 0.75 min

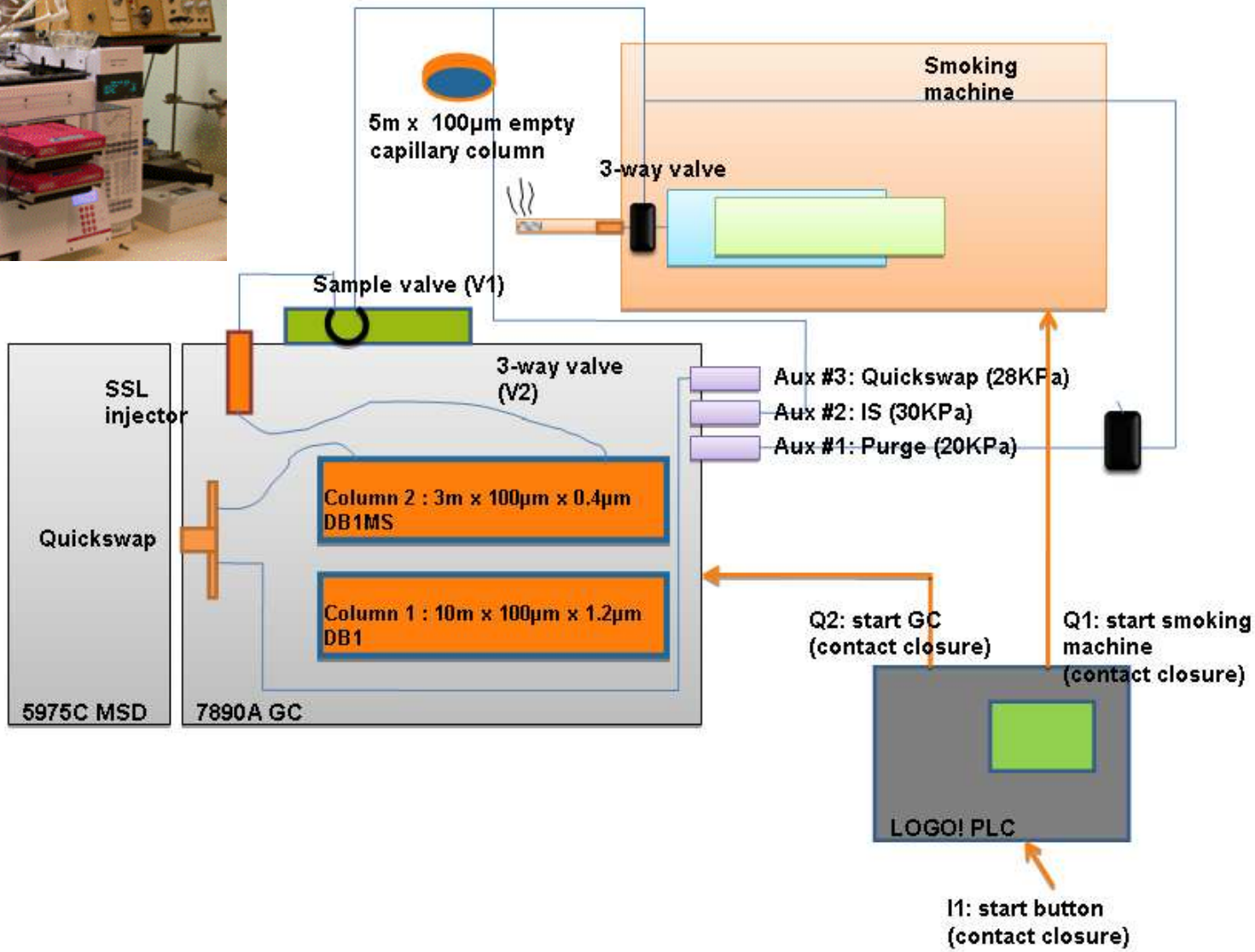
Separation of (CO2) – acetonitrile – acrolein – isoprene – benzene – toluene in 2 min.

Loss in resolution for acetonitrile, acrolein isoprene, benzene, toluene < 0.5 min



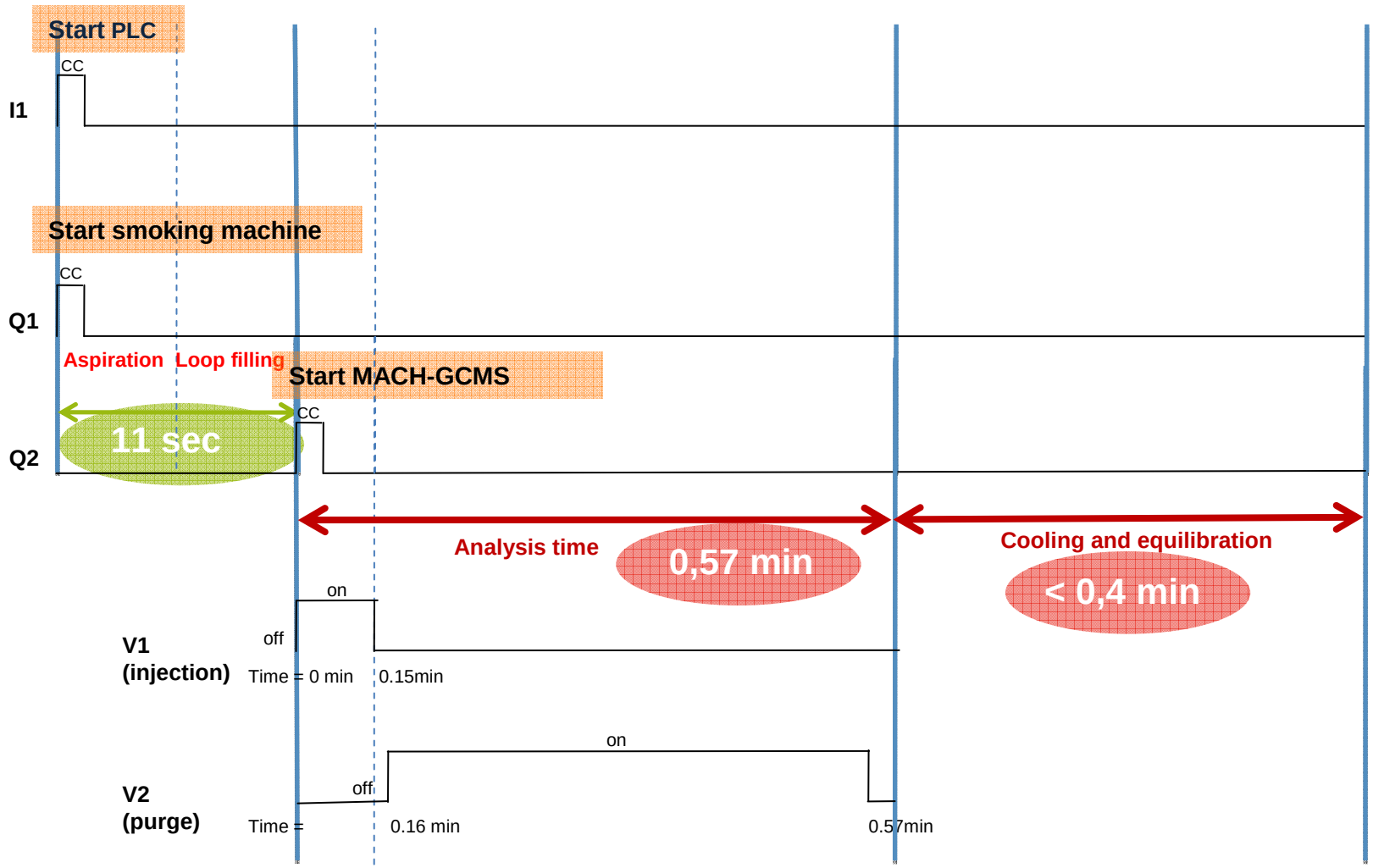


Experimental set-up



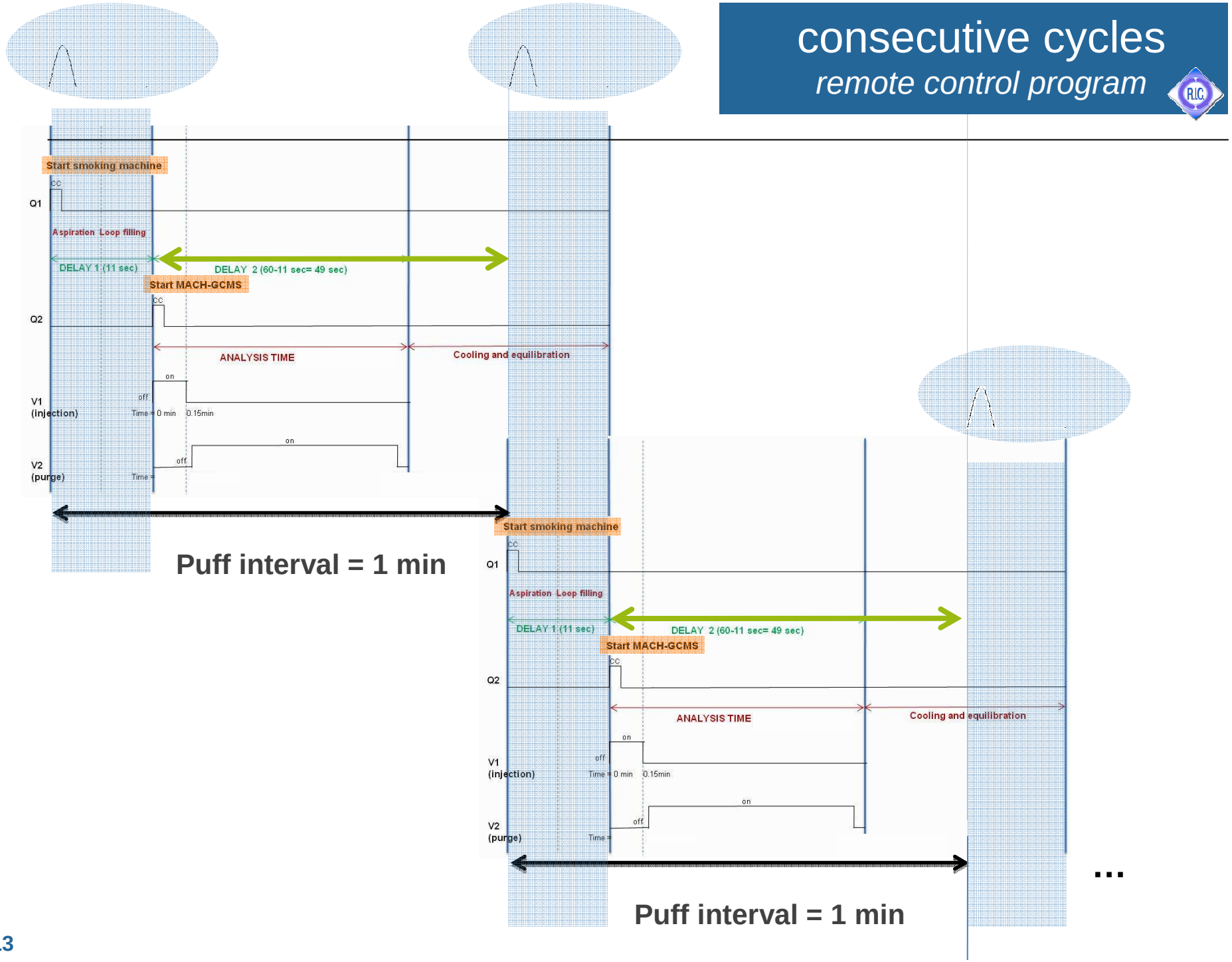
One cycle

remote control program



consecutive cycles

remote control program



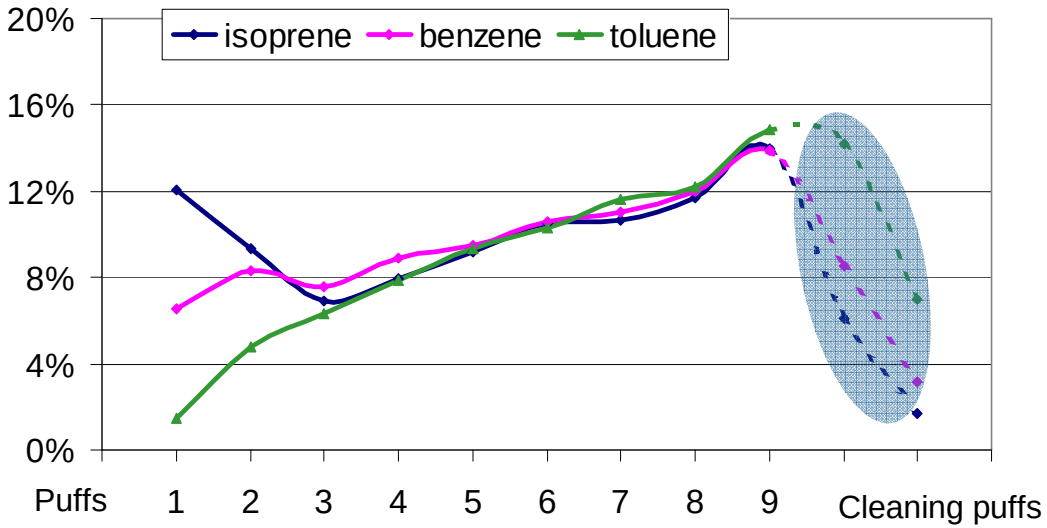
First results

- What calibration standard to use for establishing a basis for testing and quantification?
  - ➔ external calibration (static dilution)
  - ➔ compendium Method TO-15

- 3R4F profile : percentage of delivery per puff

SIM acquisition
dwell time : 15 ms

Isoprene m/z 53, 67, 68
Benzene m/z 77,78
Toluene m/z 91, 92



Drawbacks

- Old smoking machine = old problems
  - ➔ chemically inert surface : Siltek®/Sulfinert® treated tubing

- Only one cigarette smoked
  - ➔ cigarette imperfections could add analytical variability

Sum up

One way to comply with the ever-increasing number of controls required is to adopt faster techniques

- Automatic puff-by-puff sampling system
  - ➔ Flexible VC 10® Smoking Robot
  - ➔ Study design with a limited number of cigarettes
  - ➔ Reliable for Carbonyls quantification

- On line puff-by-puff quantification system
  - ➔ Interface to be improved
  - ➔ MACH® : quick GC cycle-time < one minute achieved

This flexibility enables us to be more imaginative for our future tests.

Acknowledgements

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