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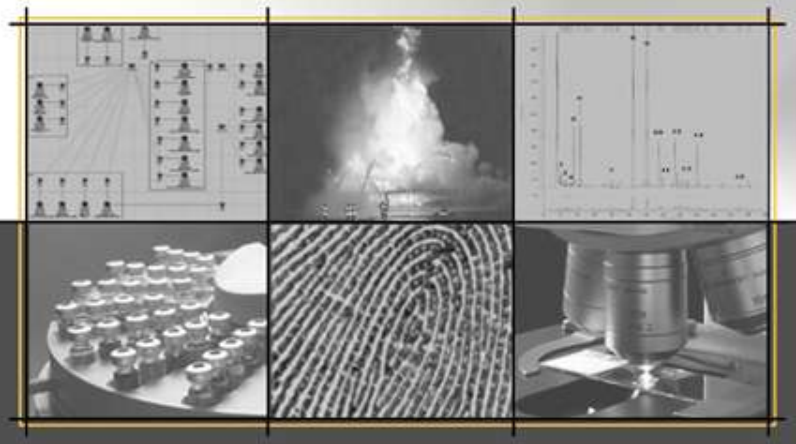
The Potential of Pyrolysis-GC/MS for the Analysis of Tire Treads and Tire Traces.



Trace Evidence Symposium
August 8-11, 2011
Kansas City, Mo.

ESC école des sciences criminelles
UNIL | Université de Lausanne

Context

- **Accident scene investigation:**
  - Multiple collisions

    The attribution of the different traces to each vehicle involved is a precious help for the reconstruction of each trajectory.

- **Any crime scene where a tire trace is observed and collected:**
  - A chemical comparison between the trace and the tires of the suspected vehicle could link the vehicle to the crime scene.

Aim of the research

Link the tire trace to its source

H_0: The recovered trace comes from the suspected tread.
H_1: The recovered trace comes from another source.

Work plan

- Method optimisation:

  Choice of the analytical parameters to produce low intravariability on the same tire.

- Method application:

  Application on a limited set of different tires. Evaluation of the intravariability and intervariability.

- Apply and test the method on tires traces.

- Increase the number of tires.

Experimental Design

- Find the important factors of the analytical method and their effects on the response surface
- Identify the possible interactions between these factors
- Interpret the results correctly while optimizing efforts and time

Method optimisation

Find the analytical parameters that give the smallest intravariability for a same sample.

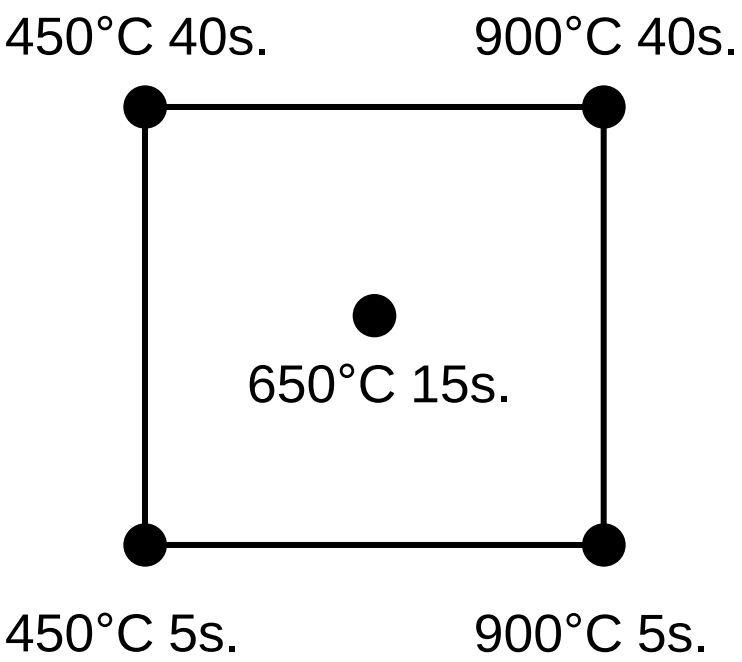
Pyrolysis factors : Temperature & Time

Response factor : Variability

Samples : Two tires from different brands

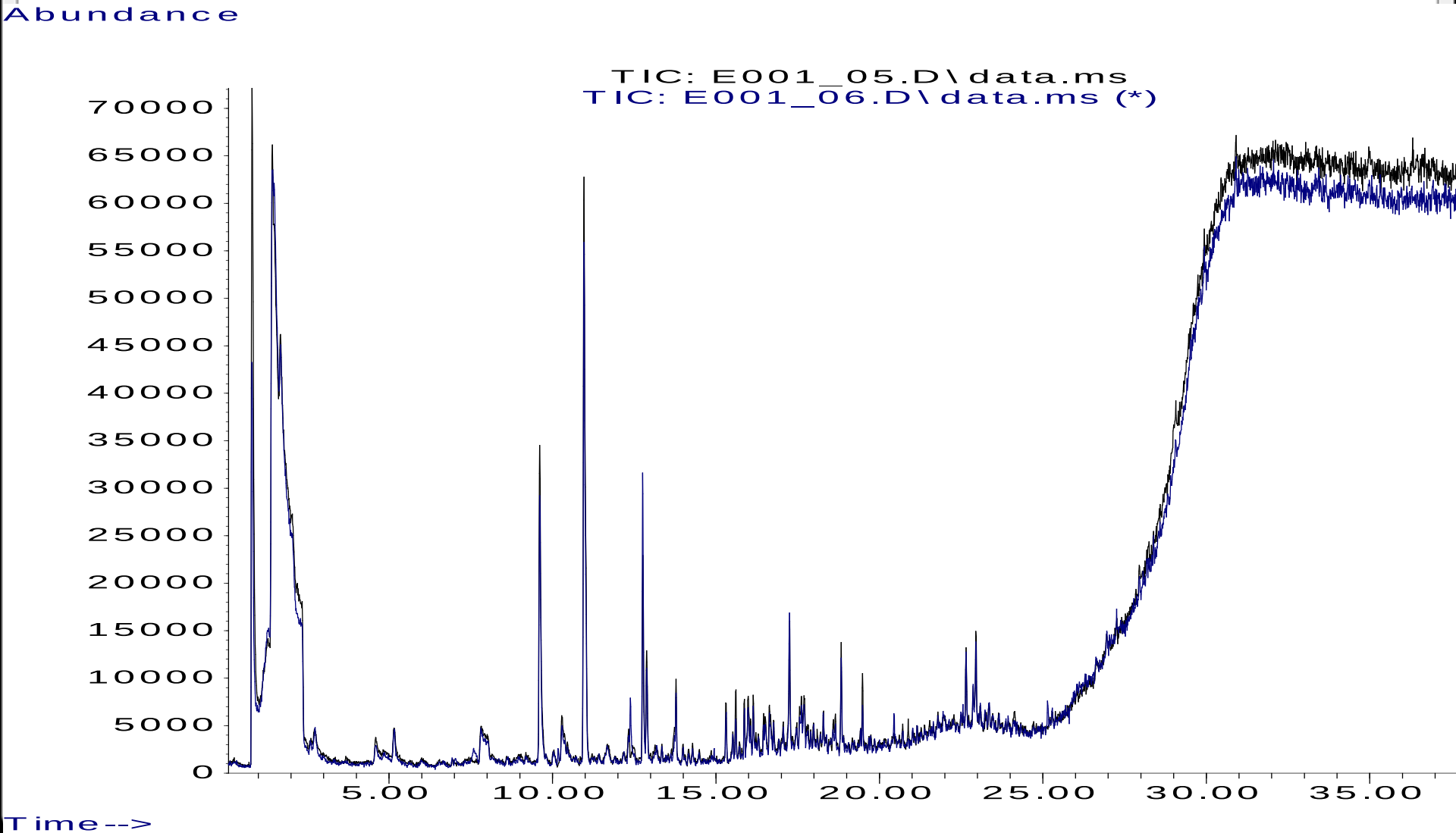
Experimental design

Pyrolysis conditions :



First cycle results

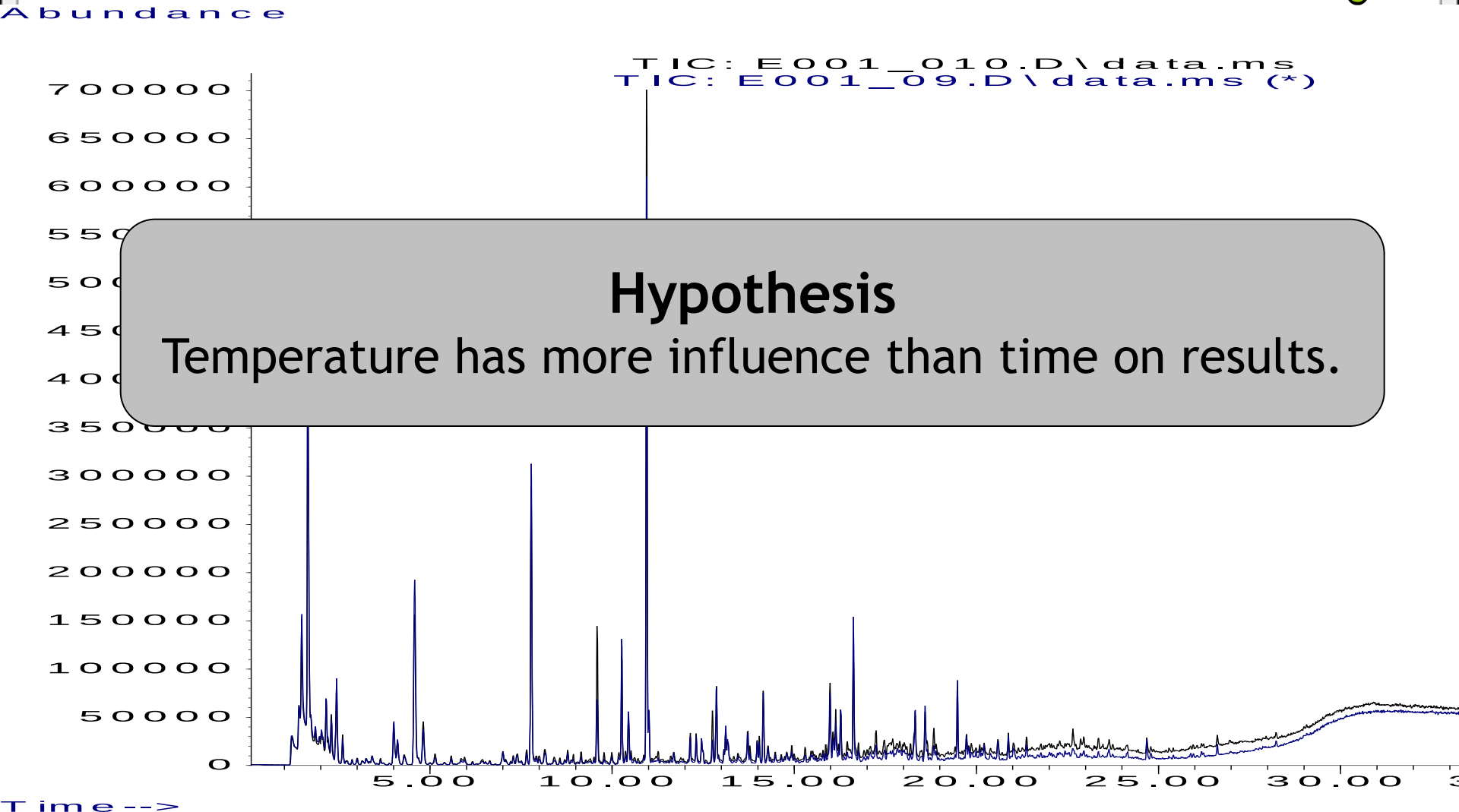
~~At 450°C~~ few compounds, low intensity, difficult peak discrimination



First cycle results

650°C
900°C

Greater number of compounds, good intensity and better peak discrimination



Hypothesis

Temperature has more influence than time on results.

Variability Study

- Visual comparison (superimposition)
- Peak integration (>80 peaks)
- The Total Variance and the RSD (Relative Standard Deviation) are chosen as response factors. The number of RSD >5% has been compared for the different points of the design.

Variability Study

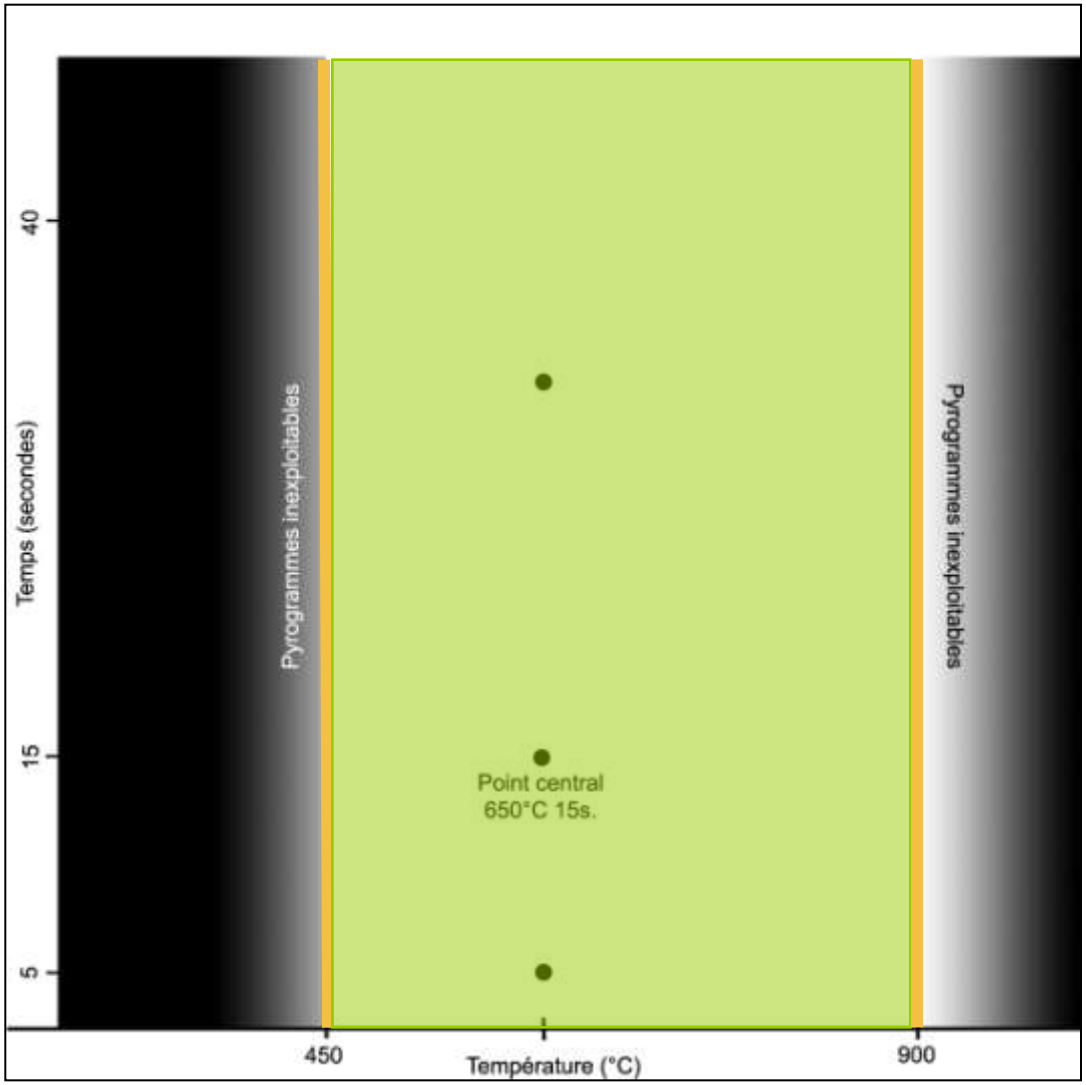
Sample 1

Design point	Total Variance	RSD > 5%
450°C 5 and 40s.	*Unusable chromatograms*	
650°C 15s.	~0.00199	0
900°C 5s.	~0.01235	40
900°C 40s.	~0.01550	41

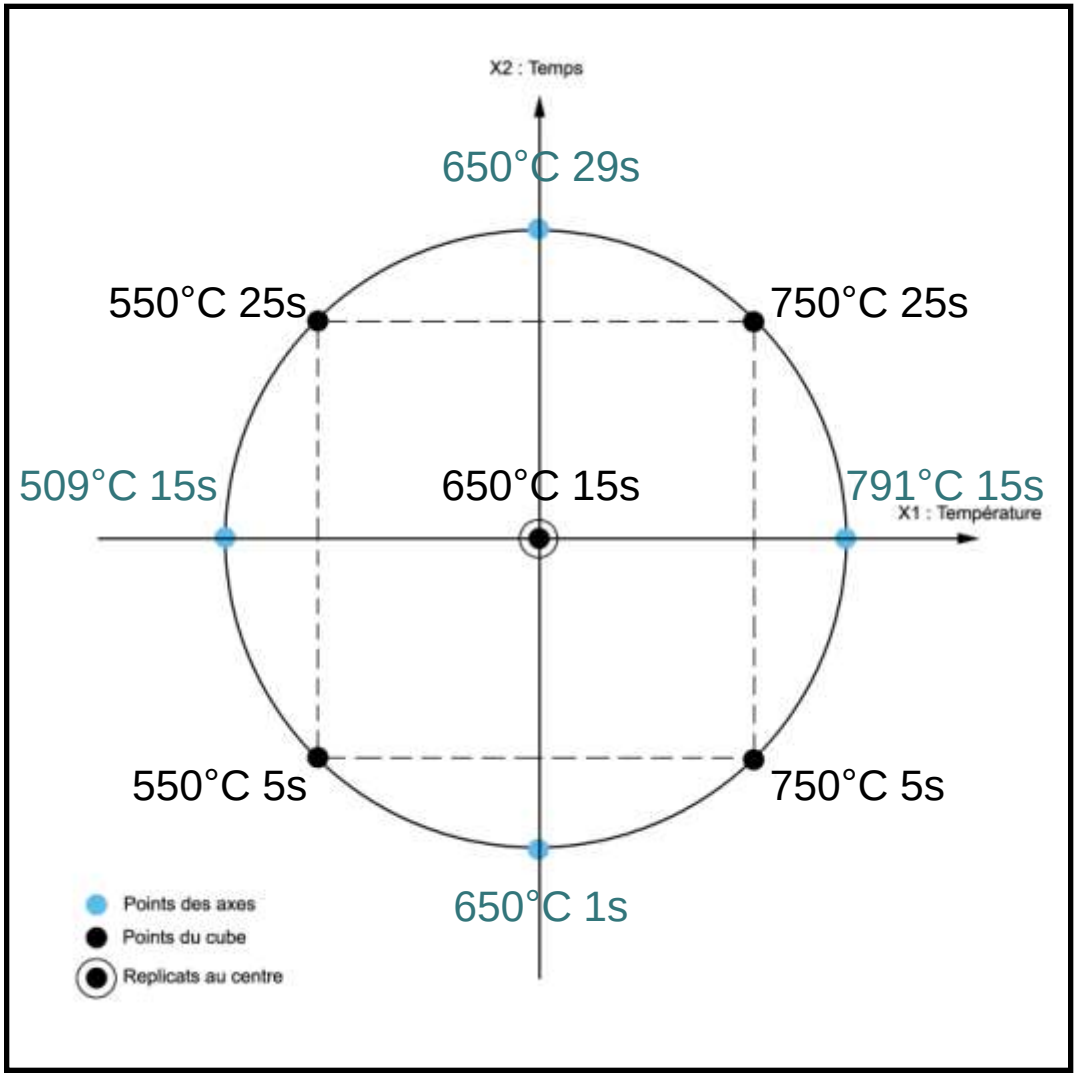
Sample 2

Design point	Total Variance	RSD > 5%
450°C 5 and 40s.	*Unusable chromatograms*	
650°C 15s.	~0.00243	1
900°C 5s.	~0.00574	11
900°C 40s.	~0.01268	20

Response surface reduction



Central Composite Design



Conclusion

Experimental design allowed to model the response surface and find a local optimum with relative few runs.

Parameters of the analytical method used further on in this study
650°C 15s

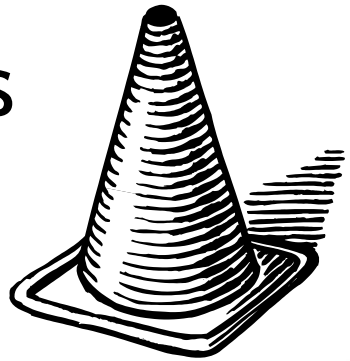
Collaboration

UNIL | Université de Lausanne
Institut de police scientifique

> TCS : Number one in Switzerland in the field of assistance and road rescue (including legal insurance and road security).

Tests :

- On the racetrack:
  - Emergency brakings were performed to produce tires traces
  - Detection and sampling of these traces
  - Sampling of the tires treads
- Back to the laboratory:
  - Py-GC/MS : tires treads and traces



Tires selected for the tests

Brand	Model	Size	DOT-Nr.	Made in
Continental	PremiumContact 2	205/55 R 16	0709	Portugal
Bridgestone Turanza	ER300	205/55 R 16	1608	Poland
Goodyear	OptiGrip	205/55 R 16	3708	Germany
Dunlop	SP Fastresponse	205/55 R 16	1808	Germany
Fulda Carat	Exellero	205/55 R 16	2408	Germany
Semperit	Speed-Life	205/55 R 16	1808	France
Matador	Ultra Sport Hectorra 2	205/55 R 16	1708	Slovakia
Avon	ZV5	205/55 R 16	0508	England
Mabor	Sport-Jet 2 2)	205/55 R 16	2108	Portugal
Goodyear	Efficient Grip	205/55 R 16	0809	France

Test - Procedure

1. Cleaning

2. Driving - braking

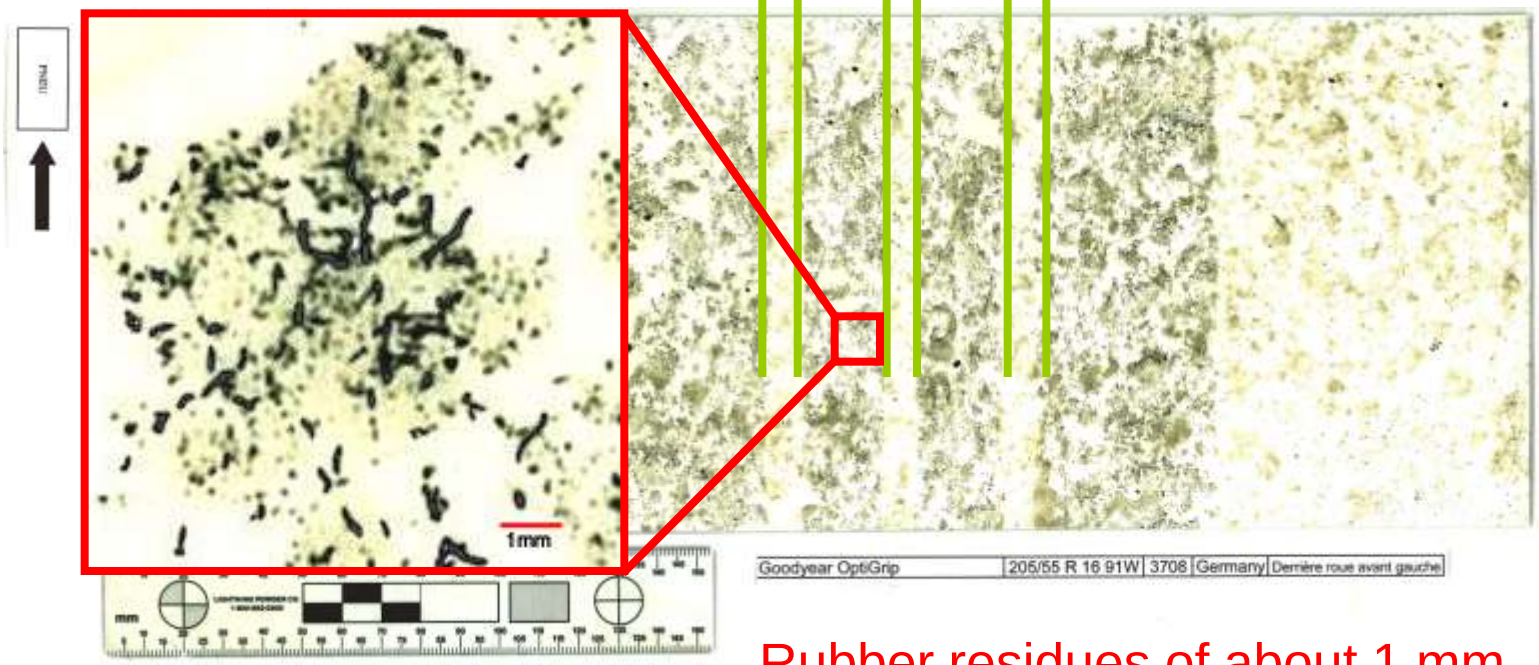
3. Sampling

Test - Procedure

4. Tire changing

5. Tire sampling

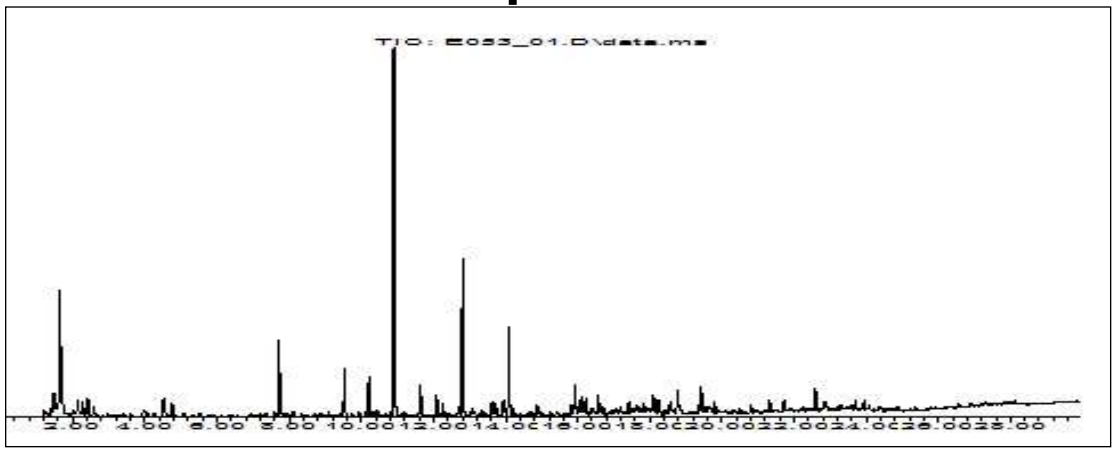
6. Labelling

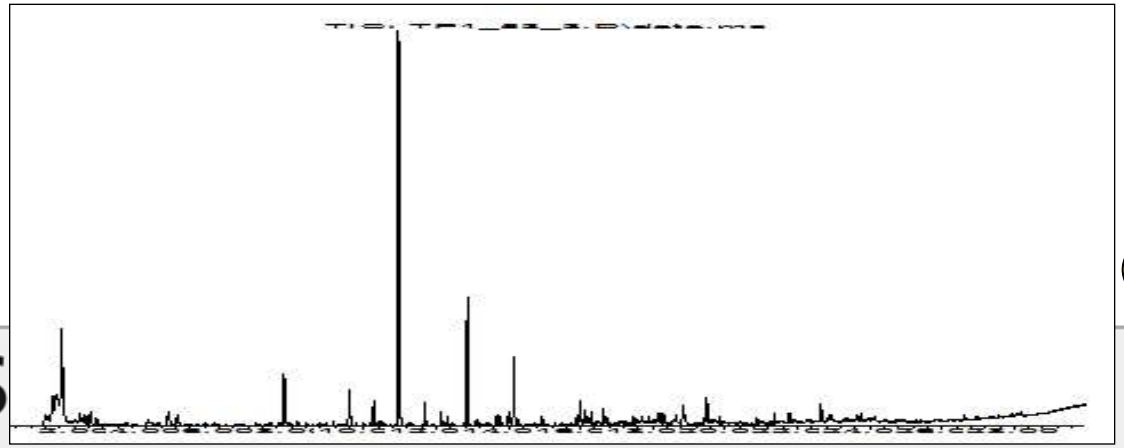


Rubber residues of about 1 mm.

Analysis

The rubber residues (traces) and the tire treads were analysed by Pyrolysis-GC/MS in order to compare their : “chemical-profiles”





Tire tread

Comparison

Tire trace

Testing : tire tread homogeneity

For each tire : several samples

Samples

Tires:

Brand and model	#Samples	#Analysis	DOT-Nr.	Made in
Continental PremiumContact 2	5	13	0709	Portugal
Bridgestone Turanza ER300	4	11	1608	Poland
Goodyear OptiGrip	2	7	3708	Germany
Dunlop SP Fastresponse	4	11	1808	Germany
Fulda Carat Exellero	6	15	2408	Germany
Semperit Speed-Life	5	13	1808	France
Matador Ultra Sport Hectorra 2	5	13	1708	Slovakia
Avon ZV5	6	15	0508	England
Mabor Sport-Jet 2	5	13	2108	Portugal
Goodyear Efficient Grip	4	11	0809	France
	Total	**122**		

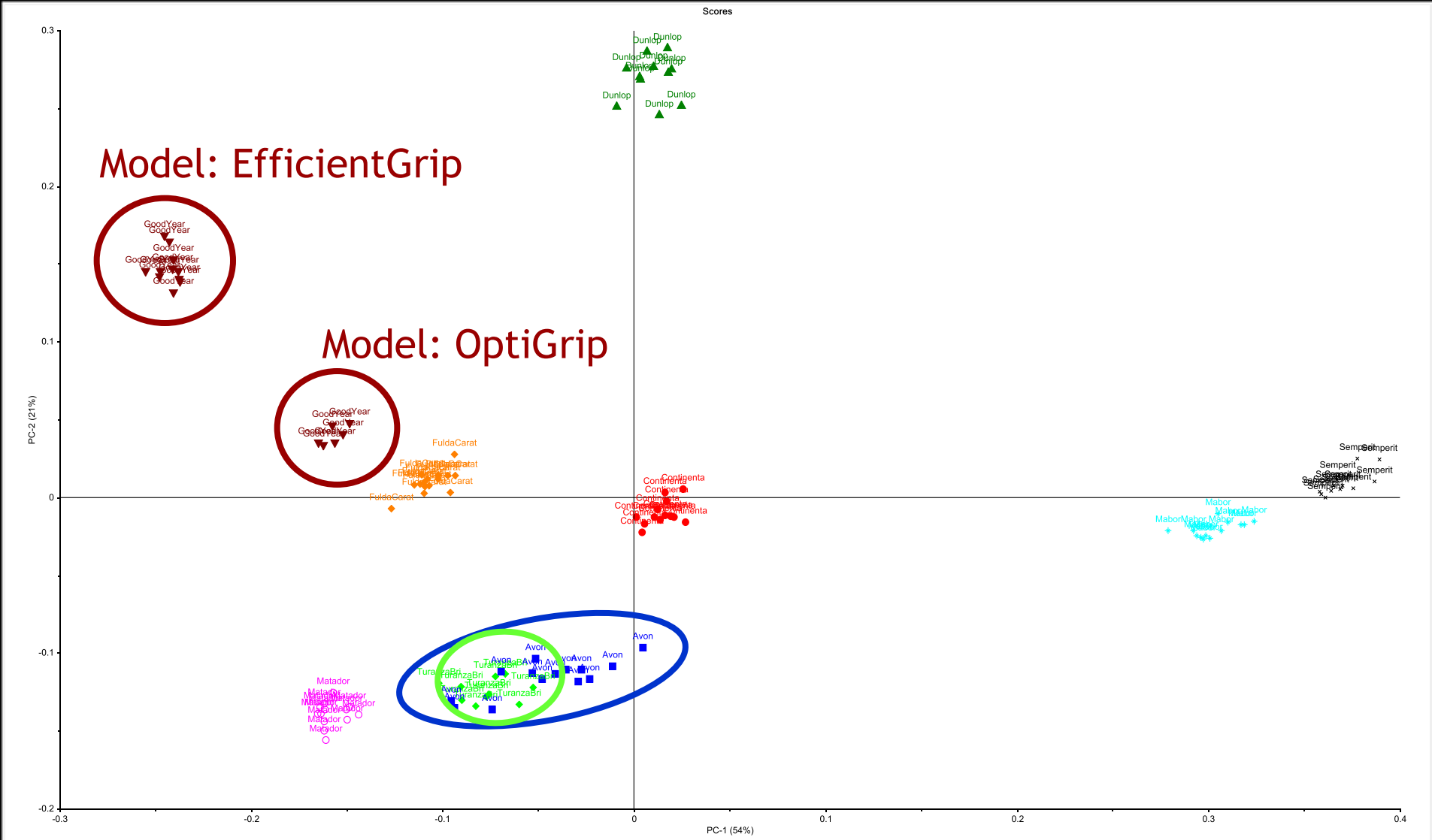
Traces → 3 particles analysed (separately)

Chromatogram analysis

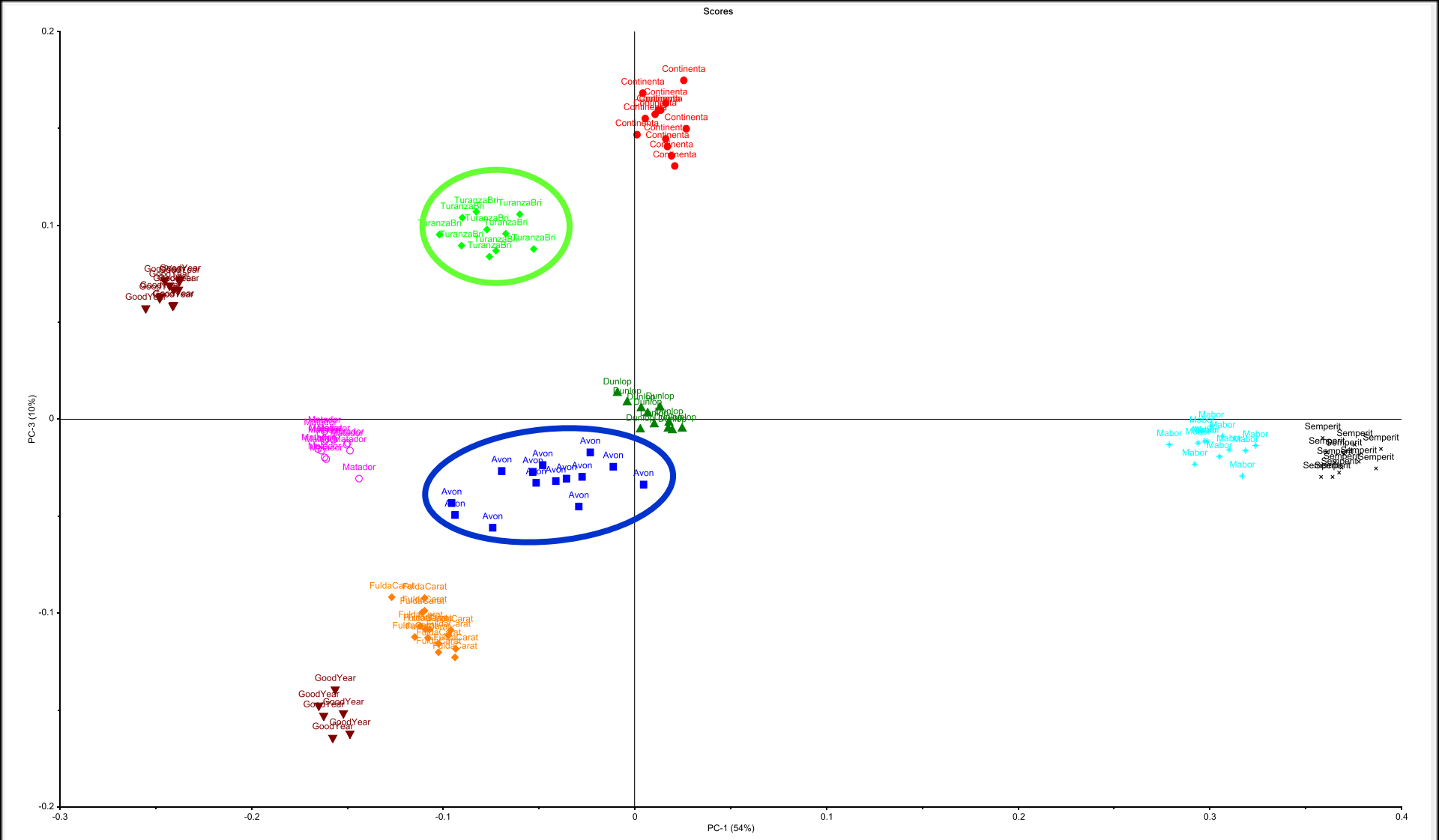
Tires and traces (~150 analyses) **:**

- Integration of the peaks :
  - based on : retention time and MS spectra
  - more than 80 peaks
- Pre-treatments
- Exploratory statistics (to visualize the data):
  - Principal Components Analysis (PCA)
  - Clustering

PCA : PC1-PC2 Brands



PCA : PC1-PC3 Brands



All the traces are grouped in the same cluster as its corresponding tire
Ward's method using Squared
Relative distance
0
1
2
3
4

Conclusion:

- For the ten tires tested :
  - The replicates from the same tire are grouped randomly in the same cluster:

    The samples are homogeneous and the method is repeatable.

    The intravariability for each tire is low.

  - All the tires are grouped in different clusters

    The intervariability between the different tires is greater than the intravariability.

Conclusion

- For the traces analysed :
  - The three analyses from one trace are grouped in the same cluster :

    The trace samples are homogeneous and the method is repeatable.

    The intravariability for each trace is low.
  - Each trace is grouped in the same cluster as the corresponding tire:

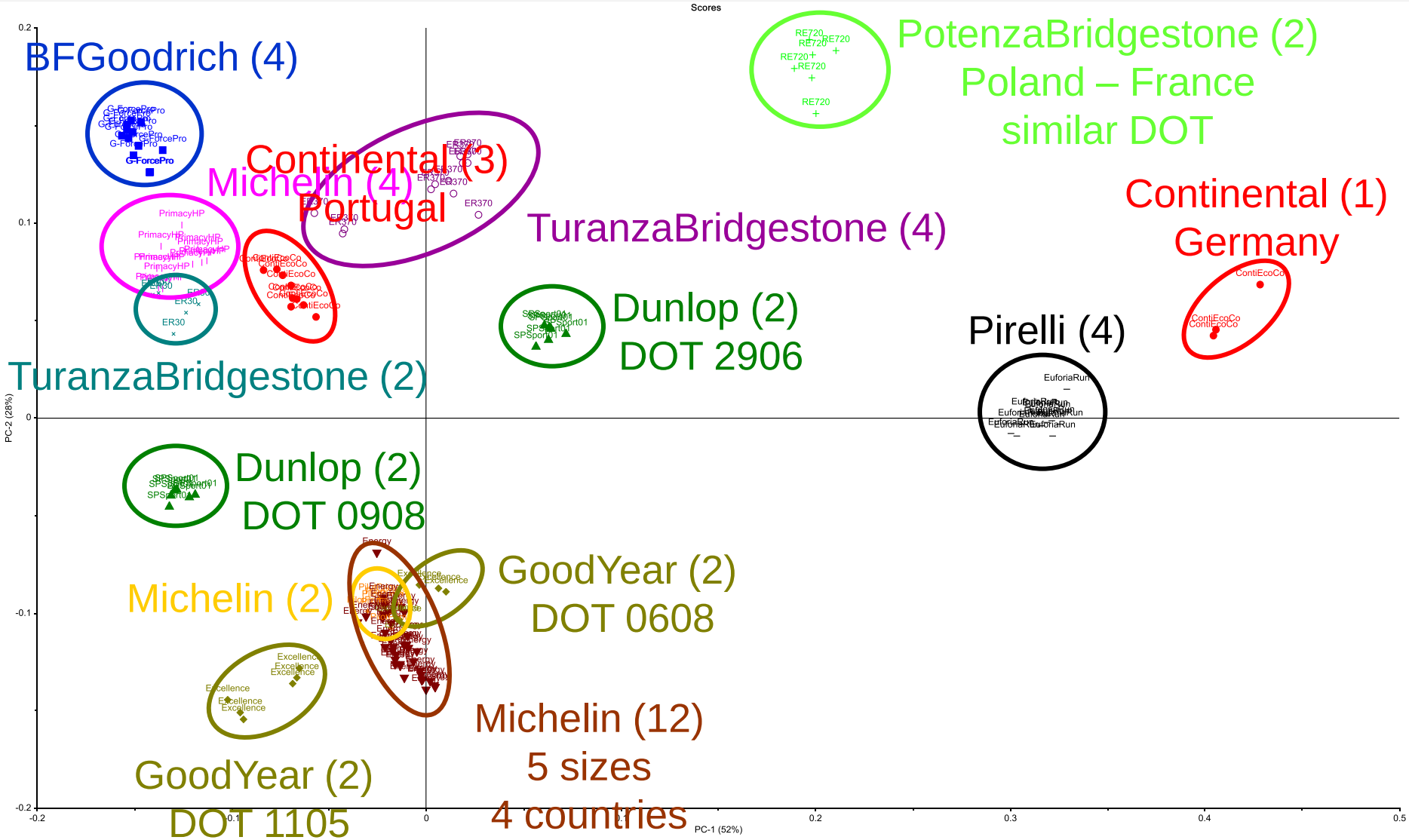
    The $\text{intravariability}_{\text{trace-its tire}}$ is lower than the $\text{intervariability}_{\text{trace-another tire}}$

More tires

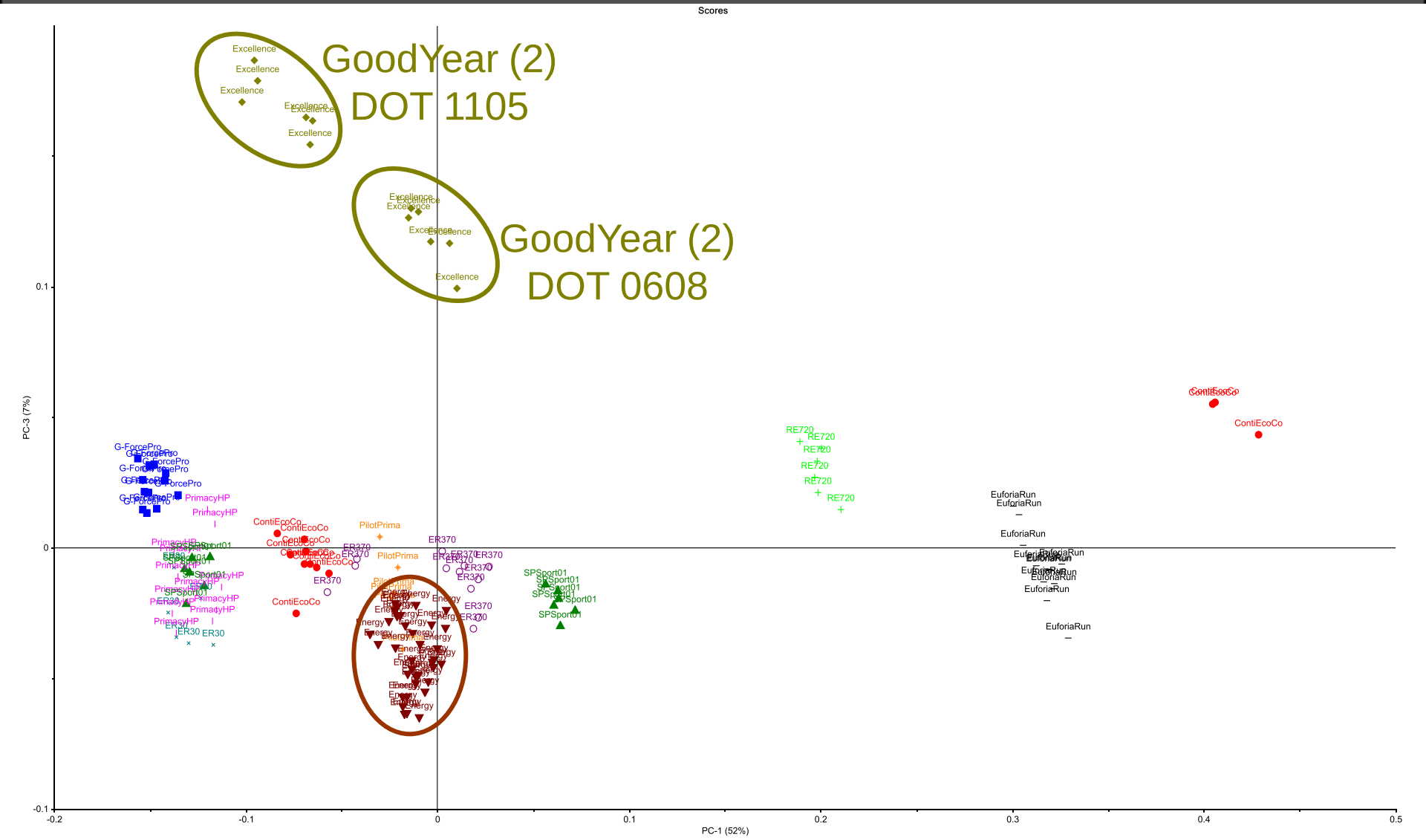
46 tires : split in 11 categories (brand and model)

Brand	Model	# Tires	Caracteristics (made in, DOT, size, etc.)
BF Goodrich	G-ForceProfiler	4	4 tires = same caracteristics
Continental	ContiEcoContactEP	4	3 tires made in Portugal - 1 made in Germany
Dunlop	SpSport01	4	2 tires DOT=2906 - 2 tires DOT=0908
GoodYear	Excellence	4	2 tires DOT=1105 - 2 tires DOT=0608 195/50R15 205/55R16
Michelin	Energy	12	5 sizes, 4 countries, DOT 1004-4707
Michelin	Pilot Primacy	2	2 tires = same caracteristics
Michelin	Primacy HP	4	4 tires = same caracteristics
Pirelli	EuforiaRun	4	4 tires = same caracteristics
PotenzaBridgestone	RE720	2	1 tire made in Poland - 1 tire made in France
TuranzaBridgestone	ER30	2	2 tires = same caracteristics
TuranzaBridgestone	ER370	4	4 tires = same caracteristics
	TOTAL	46	

PCA : PC1-PC2


Scores
PC-2 (28%)
PC-1 (52%)
0.2
0.1
0
-0.1
-0.2
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
BFGoodrich (4)
Michelin (4)
Continental (3)
Portugal
TuranzaBridgestone (4)
PotenzaBridgestone (2)
Poland – France
similar DOT
Continental (1)
Germany
Dunlop (2)
DOT 2906
Pirelli (4)
TuranzaBridgestone (2)
Dunlop (2)
DOT 0908
Michelin (2)
GoodYear (2)
DOT 0608
GoodYear (2)
DOT 1105
Michelin (12)
5 sizes
4 countries
DOT 1004-4707

PCA : PC1-PC3


Scores
GoodYear (2)
DOT 1105
GoodYear (2)
DOT 0608
Excellence
G-ForcePro
PrimacyHP
ContiEcoCo
PilotPrima
ER370
ER30
SPSport01
RE720
EuforiaRun
Energy
PC-3 (7%)
PC-1 (52%)
0.1
0
-0.1
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5

Conclusion

- Py-GC/MS:

  → Good potential for the analysis and discrimination of tire traces and treads.

  → High power of discrimination based on :

  - Brand and model
  - BUT also : DOT, size, made in

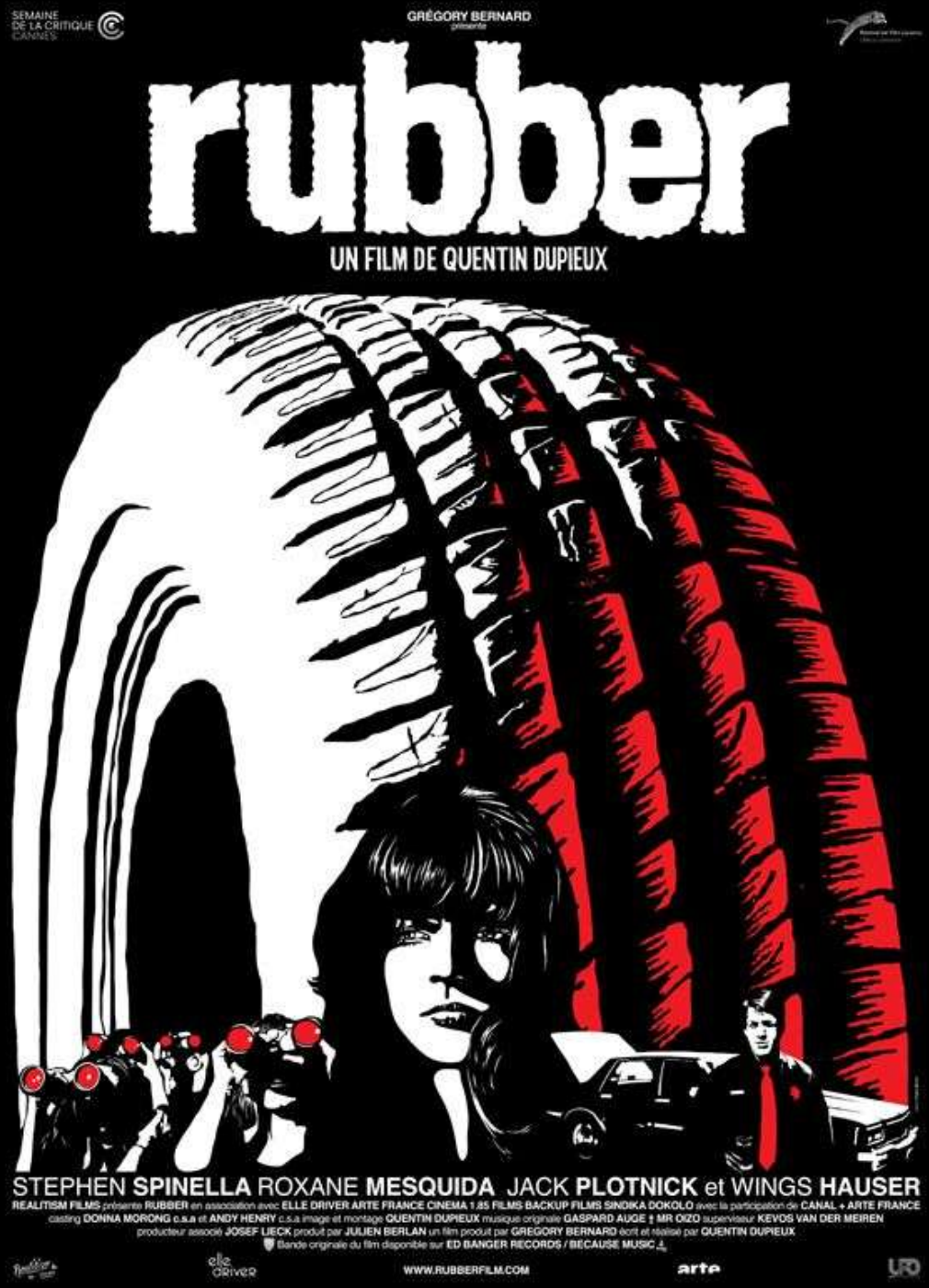
  → Difficulty in building a database (large number of tires and regular updates)

Future

> Extend the model to more tires

> Blind tests and application to real cases

> Special thanks to the TCS team :



THANK YOU

FOR

YOUR

ATTENTION