



## Analysis of chemical trace contaminants in foods: performance and limits

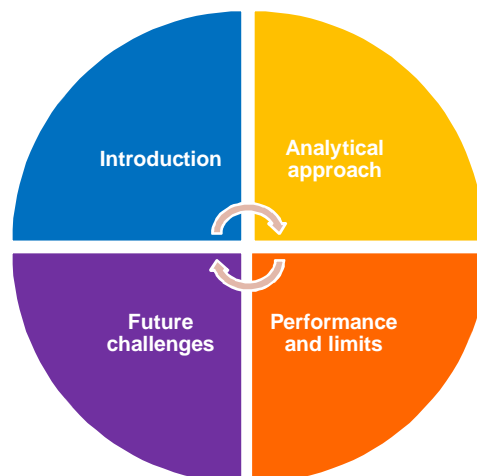
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Research Joint Unit GENIAL %génierie Procédés Aliments+ (INRA, AgroParisTech)



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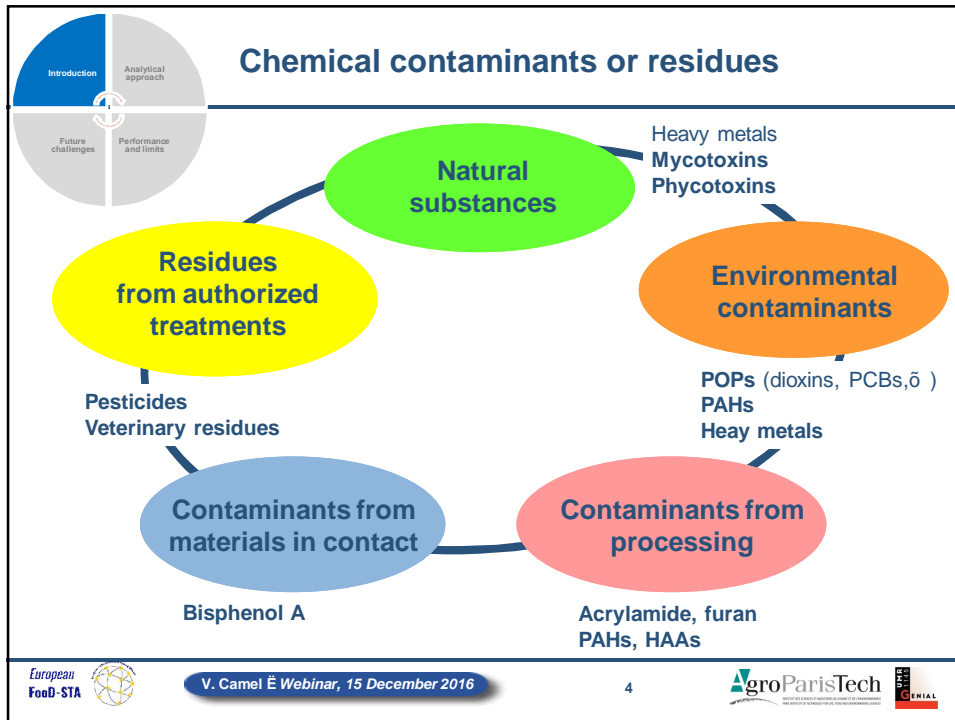
### Content of the course



## Chemical hazards in foods on covers!

The collage features several magazine covers with headlines related to food safety and chemical hazards:

- 60 millions de consommateurs (June 2015):** "Ces aliments qui nous empoisonnent" (These foods that poison us). Sub-headlines: "Les bons gestes dans la cuisine", "Perturbateurs endocriniens, pesticides, additifs..."
- 60 millions de consommateurs (December 2016):** "SAUMON Carton rouge pour le bio" (Salmon Red Card for organic). Sub-headlines: "Le meilleur rapport qualité-prix", "ARSENIC, MERCURE, PESTICIDES..."
- télérama (January 2011):** "Manger tue" (Eating kills).
- Sarkozy: le nous Observateur (March 2011):** "Attention à ce qu'il y a dans votre assiette!" (Attention to what's on your plate!).
- CHOISIR (October 2013):** "Des pesticides dans les vins..." (Pesticides in wines...). Sub-headline: "Nos analyses".
- CHOISIR (October 2016):** "Trop de pesticides dans les fruits" (Too many pesticides in fruits). Sub-headline: "Les dessous d'un scandale financier".



## European regulation on its way

<b>Pesticides :</b> <i>regulation 1107/2009/EC + 283/2013/EC &amp; 284/2013/EC</i>		<b>Maximal Residue Limits (MRLs)</b>
<b>Veterinary residues:</b> <i>regulation 2377/90/EC</i>		<b>Maximal Residue Limits (MRLs) + non-authorized substances</b>
<b>Processing contam.:</b> <i>regulation 1881/2006/EC (3-MCPD) + recommendations (acrylamide)</i>		<b>Maximum Levels (MLs) + « Guide » values</b>
<b>Mycotoxins:</b> <i>regulation 1881/2006/EC</i> <b>Maximum Levels (MLs)</b>	<b>Environmental contam.:</b> <i>regulation 1881/2006/EC + 420/2011/EC (Pb, Cd, Hg, Sn, dioxins, DL-PCBs, BaP) + 835/2011/EC (PAHs)</i>	<b>Maximum Levels (MLs)</b>
<b>Food contact materials:</b> <i>regulation 1935/2004/EC + 10/2001/EC &amp; 2016-1416/EC (plastics)</i>		<b>Specific Migration Limits (SMLs) (plastics)</b>

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## All operators are responsible for food safety

**Integrative approach:**  
 « From farm to fork »  
 « From stable to table »

```

      graph LR
        PP[Primary production] --> RM((Raw material))
        CF[Cattle feed] -.-> RM
        RM --> PM((Processed material))
        S1[Storage] --> PM
        PM --> PF((Packaged food))
        P[Processing] --> PM
        PK[Packaging] --> PF
        PF --> DF((Distributed food))
        D[Distribution] --> DF
        DF --> CF2((Consumed food))
        SC[Storage, cooking] --> CF2
      
```

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## Sampling and analysis: key issues!

**Samples**

- Monitoring plans
- Control plans

EU production  
 Importations  
 Exportations

EU recommendations for sampling / several contaminants

- Official routine labs
- National Reference Labs
- EU Reference Labs

**Validated methods**

**Analytical results**

**Risk assessment**

**RASFF**

**Regulation compliance**

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## Ex.: 2015 RASFF notifications

**Residues from authorized treatments**

- Natural substances
- Environmental contaminants
- Contaminants from materials in contact
- Contaminants from processing

*RASFF: Rapid Alert System for Food and Feed*

Hazard category	Undecided	Serious	Not serious
<b>Food contact materials</b>			
Adulteration/fraud	1		3
Composition		3	1
Foreign bodies			1
Heavy metals	30	13	26
Industrial contaminants	4	5	1
Labelling absent/incomplete/incorrect		1	
Migration	27	27	23
Not determined/other	1		1
Organoleptic aspects			3
Packaging defective/incorrect		1	
<b>Food</b>			
Adulteration/fraud	10	9	72
Allergens	11	125	1
Biocontaminants	1	43	
Biotoxins (other)	1	16	1
Chemical contamination (other)	4	2	2
Composition	29	56	20
Food additives and flavourings	15	28	97
Foreign bodies	6	48	52
Grain/hovel food	33	4	8
Heavy metals	7	130	2
Industrial contaminants	3	26	3
Labelling absent/incomplete/incorrect	4	9	12
Mycotoxins	3	472	1
Non-pathogenic microorganisms	4	2	41
Not determined/other	2	7	28
Organoleptic aspects	7		28
Packaging defective/incorrect	4	3	9
<b>Hazard category</b>			
Pathogenic microorganisms	67	536	34
Pesticide residues	188	133	77
Poor or insufficient controls	10	3	74
Radiation			26
Residues of veterinary medicinal products	12	28	16
<b>Feed</b>			
Adulteration/fraud	2		2
Composition		8	1
Foreign bodies		1	2
Heavy metals	1	2	8
Industrial contaminants	1	3	7
Mycotoxins	1	16	2
Non-pathogenic microorganisms		5	13
Pathogenic microorganisms	1	17	90
Pesticide residues	2		5
Poor or insufficient controls			1
Residues of veterinary medicinal products	1		3
TSEs			21

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**Food (and feed) matrices are highly complex**

Introduction Analytical approach  
Future challenges Performance and limits

**Food structure**

Heterogeneity? Variability?

Water content? Lipid content? Pigments? Others?

Free or bound contaminants?

Macromolecular compounds:  
- proteins  
- polysides

Fat matter

Minerals

Water

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**Å and contaminants present at low levels!**

Introduction Analytical approach  
Future challenges Performance and limits

Compound level (in mass fraction)

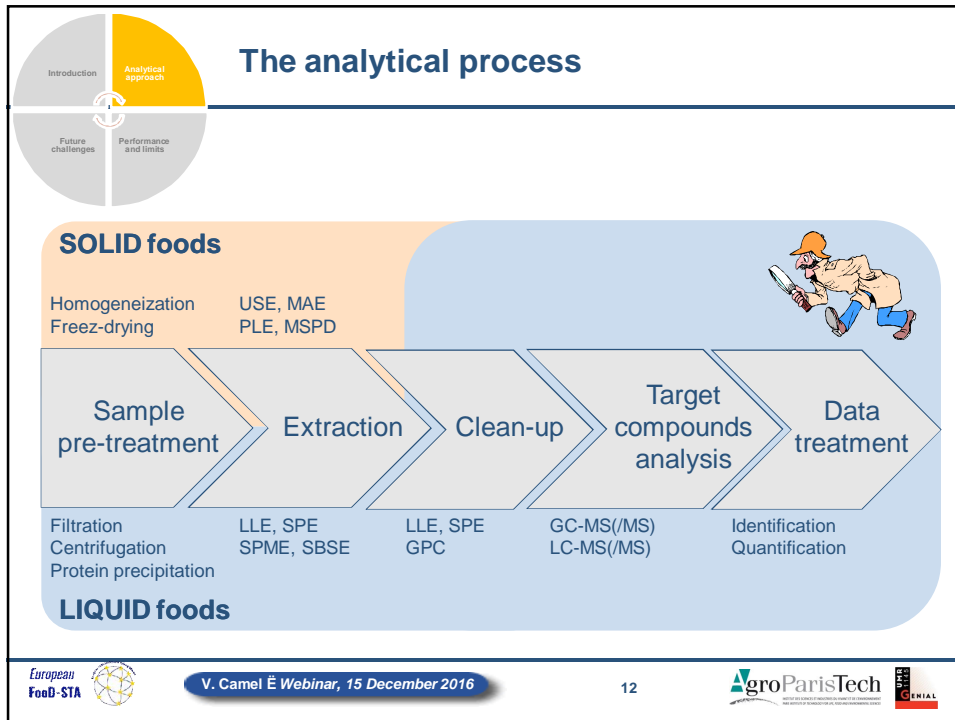
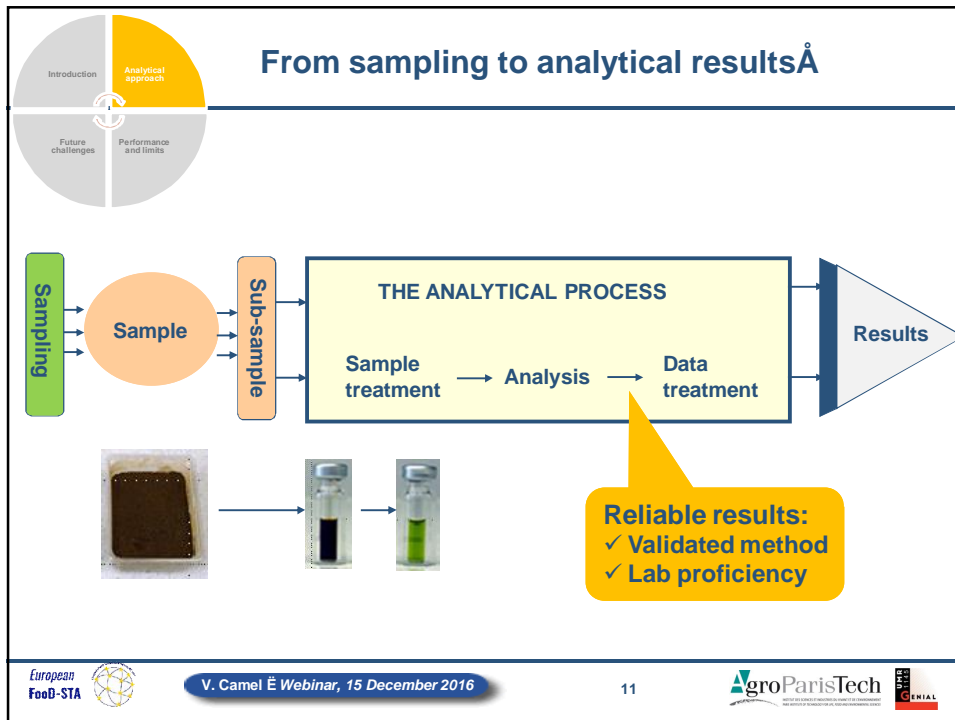
100%  
0.1%  
1 ppm  
1 ppb  
1 ppt

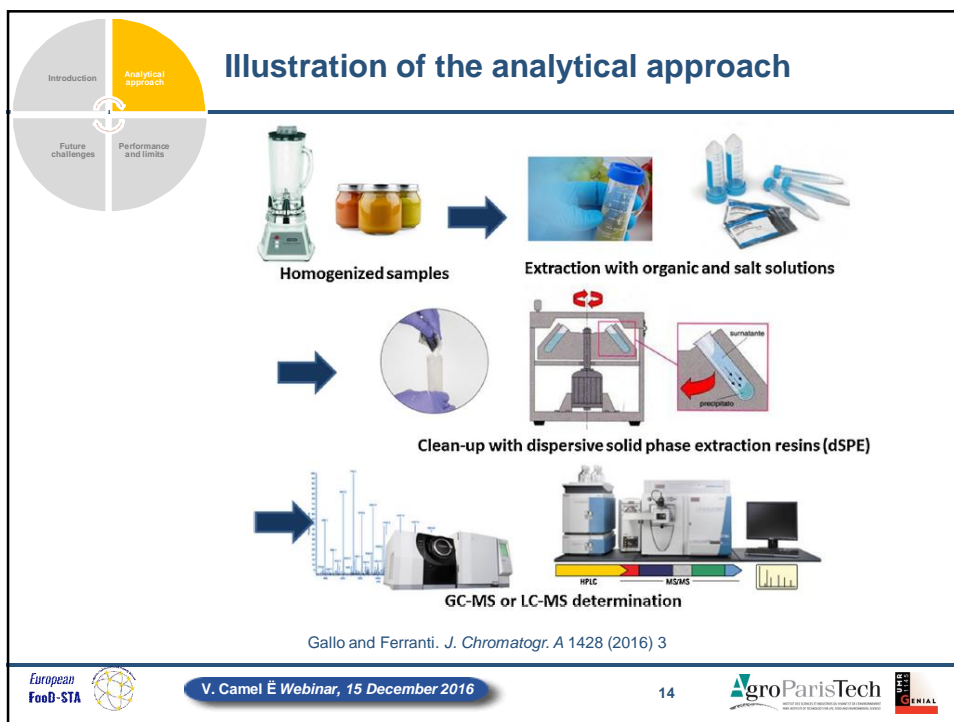
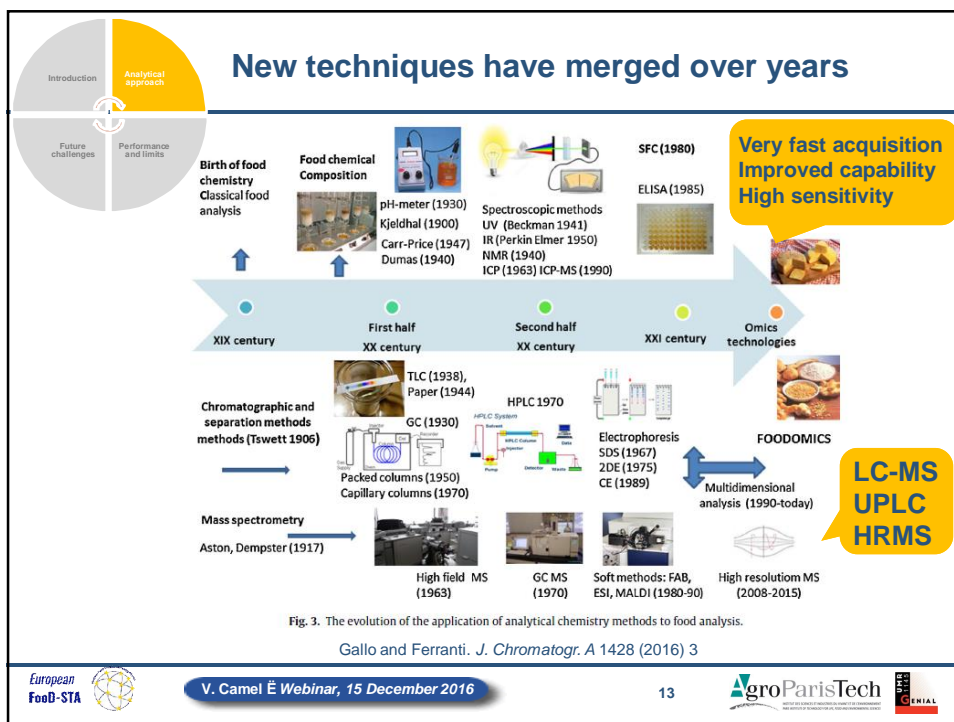
ppm : part per million (mg/L or mg/kg)  
ppb : part per billion (µg/L or µg/kg)  
ppt : part per trillion (ng/L or ng/kg)

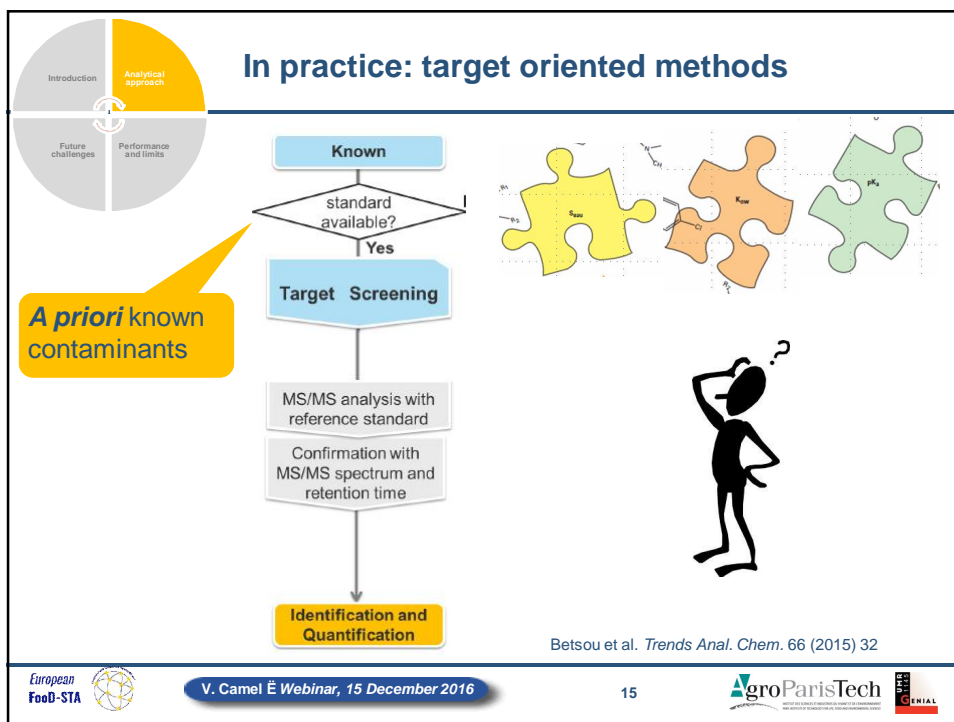
Major compounds  
Minor compounds  
Trace compounds  
Ultra-traces compounds  
Limits of analytical methods

Usual level expression

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## Food categories are also targeted

Vegetable and fruits, cereals and food of animal origin

Commodity groups	Typical commodity categories	Typical representative commodities	
1. High water content	Pome fruit	Apples, pears	
	Stone fruit	Apricots, cherries, peaches,	
	Other fruit	Bananas	
	Alliums	Onions, leeks	
	Fruiting vegetables/cucurbits	Tomatoes, peppers, cucumbers, melons	
	Brassica vegetables	Cauliflowers, Brussels-sprouts, cabbages, broccoli	
	Leafy vegetables and fresh herbs	Lettuce, spinach, basil	
	Stem and stalk vegetables	Celery, asparagus	
	Forage/fodder crops	Fresh alfalfa, fodder vetch, fresh sugar beets	
	Fresh legume vegetables	Fresh peas with pods, peas, mange tout, broad beans, runner beans, French beans	
2. High acid content and high water content <sup>10</sup>	Leaves of root and tuber vegetables	Sugar beet and fodder beet tops	
	Fresh Fungi	Champignons, chanterelles	
	Root and tuber vegetables or feed	Sugar beet and fodder beet roots, carrots, potatoes, sweet potatoes	
	Citrus fruit	Lemons, mandarins, tangerines, oranges	
	Small fruit and berries	Strawberries, blueberries, raspberries, black currants, red currants, white currants, grapes	
	Fruit pomace	Citrus fruits	
	3. High sugar and low water content <sup>11</sup>	Honey, dried fruit	Honey, raisins, dried apricots, dried plums, fruit jams
		Tree nuts	Walnuts, hazelnuts, chestnuts
	4a. High oil content and very low water content	Oil seeds	Oilseed rape, sunflower, cotton-seed, soybeans, peanuts, sesame etc.
		Pastes of tree nuts and oil seeds	Peanut butter, tahini, hazelnut paste
4b. High oil content and intermediate water content	Oily fruits and products	Olives, avocados and pastes thereof	
	5. High starch and/or protein content and low water and fat content	Dry legume vegetables/pulses	Field beans, dried broad beans, dried haricot beans (yellow, white/navy, brown, speckled), lentils
Cereal grain and products thereof		Wheat, rye, barley and oat grains; maize, rice wholemeal bread, white bread, crackers, breakfast cereals, pasta	
6. "Difficult or unique commodities" <sup>12</sup>	Cereal grain products thereof, incl. cereal based composite feed		

European Commission (2016)

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## Validation of target-oriented methods

1- Confirmation

Matrix effects?

**Target contaminant(s)**  
in real samples

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## Target analysis: 1- Compound confirmation

**Acquisition modes**

- Selected reaction monitoring (SRM) and/or
- MS/MS with data dependent acquisition
- High resolution mass spectrometry

**Peak detection and quantification**

- SRM transition chromatograms and/or
- Extracted ion chromatograms
- Searching compound databases
- Screening
- Quantification if standards analyzed

**Identification**

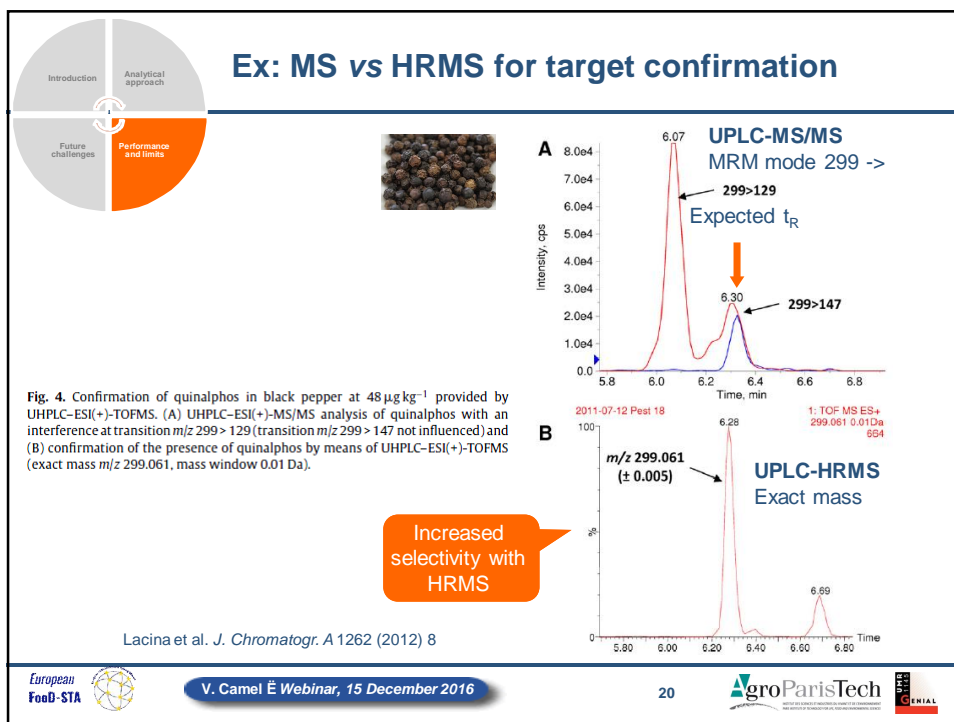
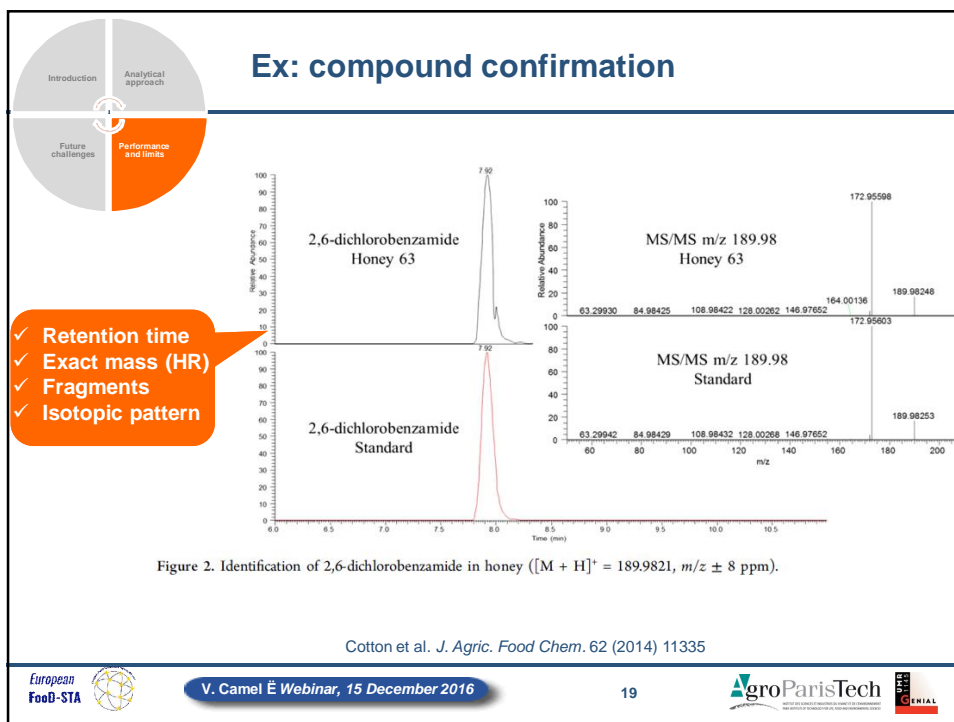
- Ion ratios and RT from standards
- MS/MS spectra and RT from library and/or standards
- Accurate mass, isotope pattern and RT from database and/or standards

✓ Check  $t_R$  stability  
✓ Selectivity and sensitivity

Hird et al. *Trends Anal. Chem.* 59 (2014) 59

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## Validation of target-oriented methods

Introduction

Analytical approach

Future challenges

Performance and limits

Expected  $t_R$

1- Confirmation

Target contaminant(s)  
in real samples

2- Quantification

LOQ (compliance with MRLs)  
Trueness  
Precision

Matrix effects?

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## Target analysis: 2- Quantification

Introduction

Analytical approach

Future challenges

Performance and limits

LOQ: level for S/N= 10

Performance criteria

- ✓ LOQ
- ✓ Recovery
- ✓ Trueness
- ✓ Precision

Reference value  $X$

Mean value  $Z$

Single result  $Z_i$

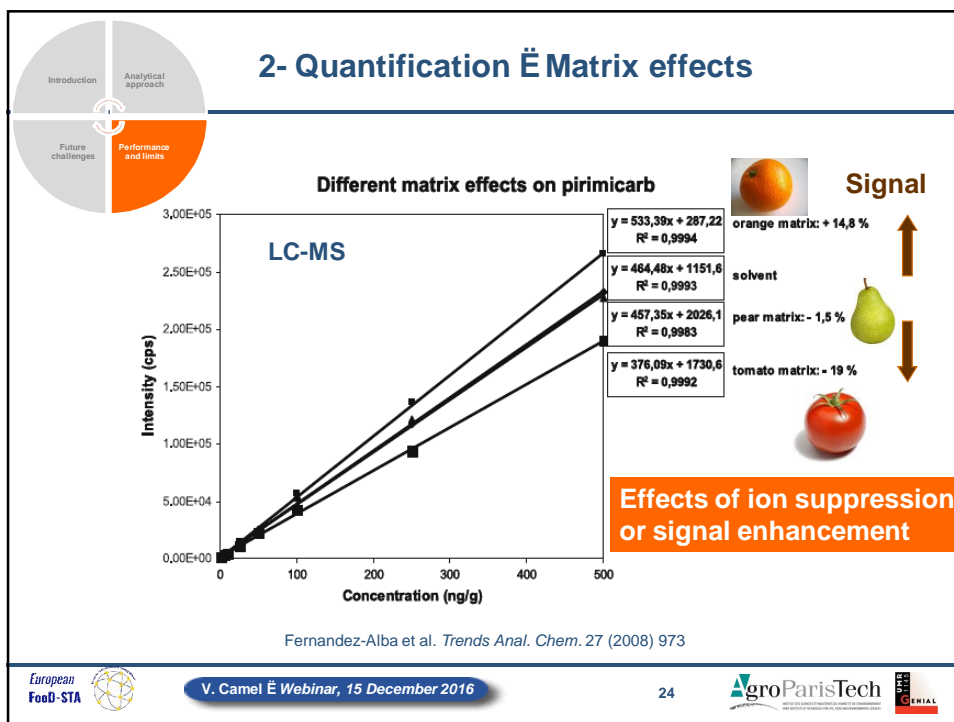
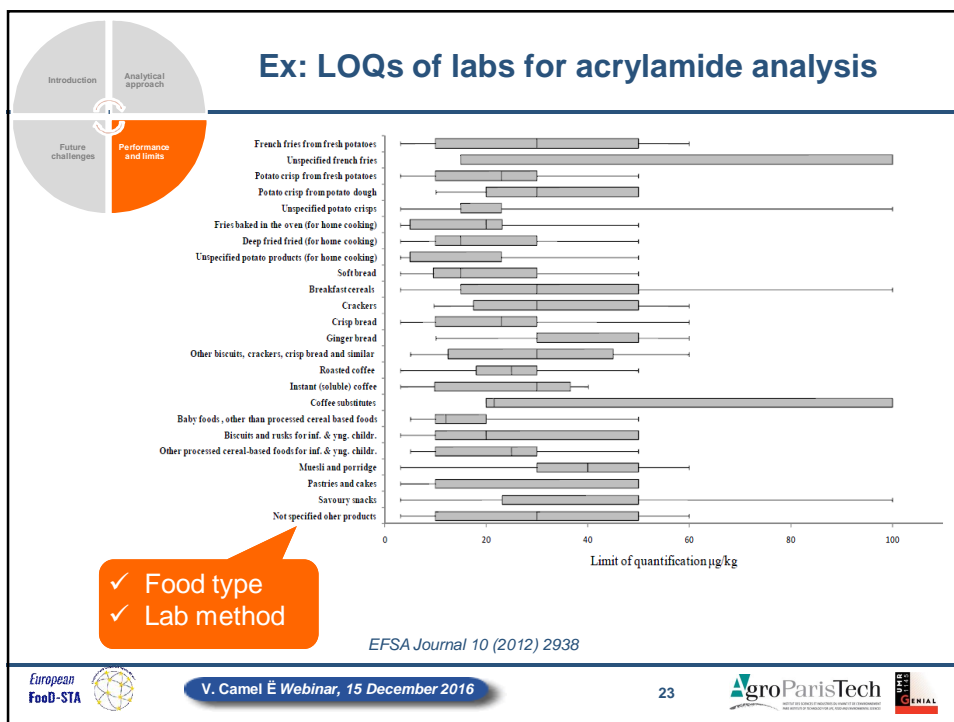
Bias

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## Strategies to limit matrix effects

Introduction

Analytical approach

Future challenges

Performance and limits

Concentration level: 100 µg kg<sup>-1</sup>  
EIC: m/z 253.0092

Ext. matrix match calibration

MS/MS or HRMS analysis

Dilute extract

Improve clean-up

Improve separation

Stable-isotope labelled int. std

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## Ex: HRMS analysis of target pesticides

Introduction

Analytical approach

Future challenges

Performance and limits

LC-TOF-MS Full scan

Expected t<sub>R</sub>

LOD : 0,04 .  
150 µg/kg

Extracted ion (exact mass)

Imazalil

287.0558

299.0526

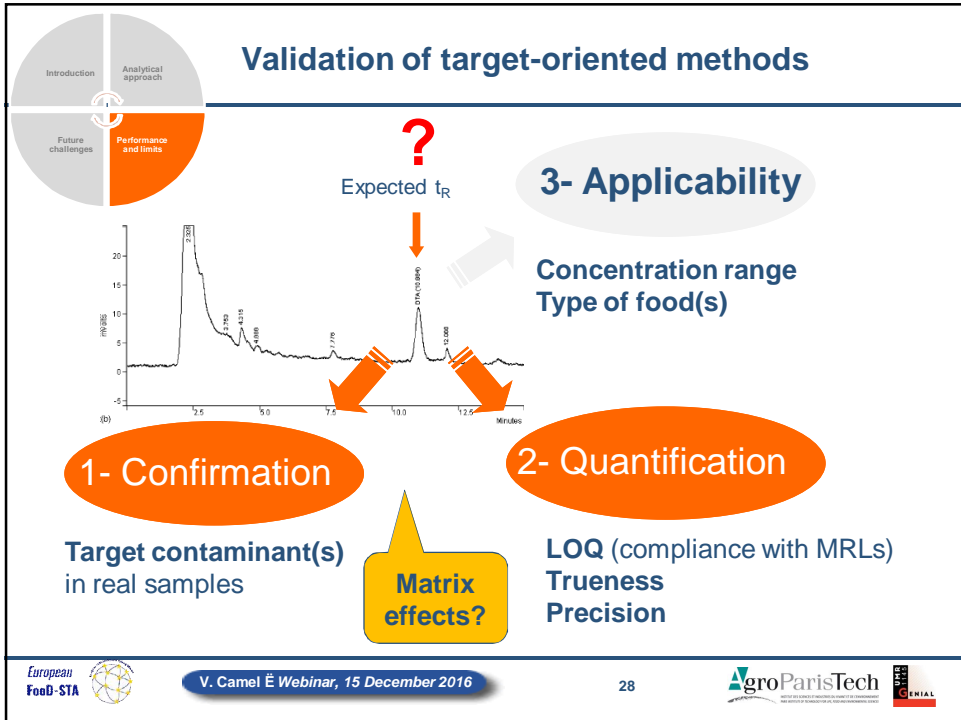
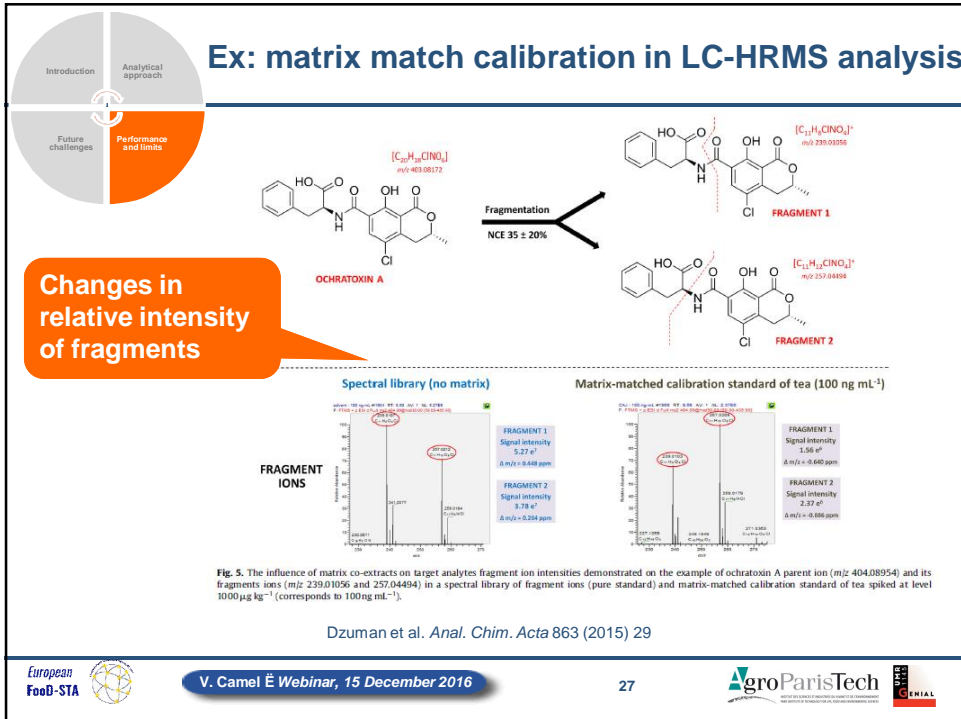
Ferrer et al. *J. Chromatogr. A* 1175 (2007) 24

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## Recent and future challenges

Simultaneous analysis of target multi-class contaminants?

Analysis of non target contaminants?

Identification of new contaminants?

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## Multi-residue / multi-class target analysis

LOQs < 10 µg/kg

vegetables

herbal tea

**EXTRACTION**  
(QuEChERS-based method)

**INSTRUMENTAL ANALYSIS**  
HPLC-HRMS/MS

**DATA EVALUATION**

323 pesticides  
55 mycotoxins  
11 plant toxins

Plant growth regulators ?      Most LOQs in range 1-10 µg/kg

Pesticides ?

Antibiotics ?

28 compounds

MeOH

Safe ?

HILIC  
MS/MS

Mycotoxins ?

Non selective extraction  
No clean-up  
Efficient separation  
MS/MS, HRMS

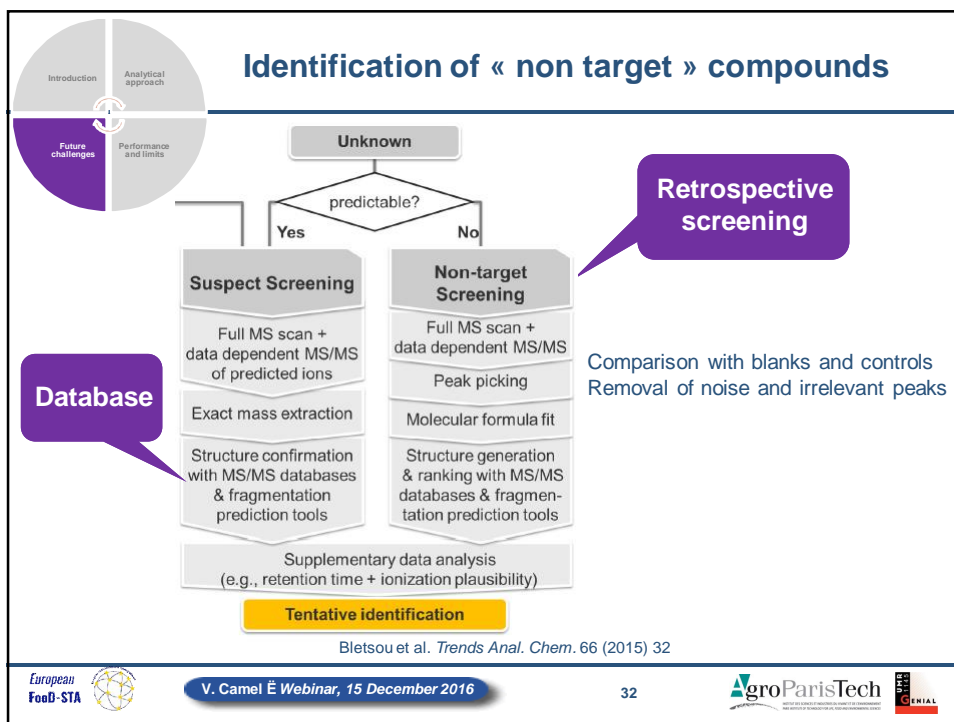
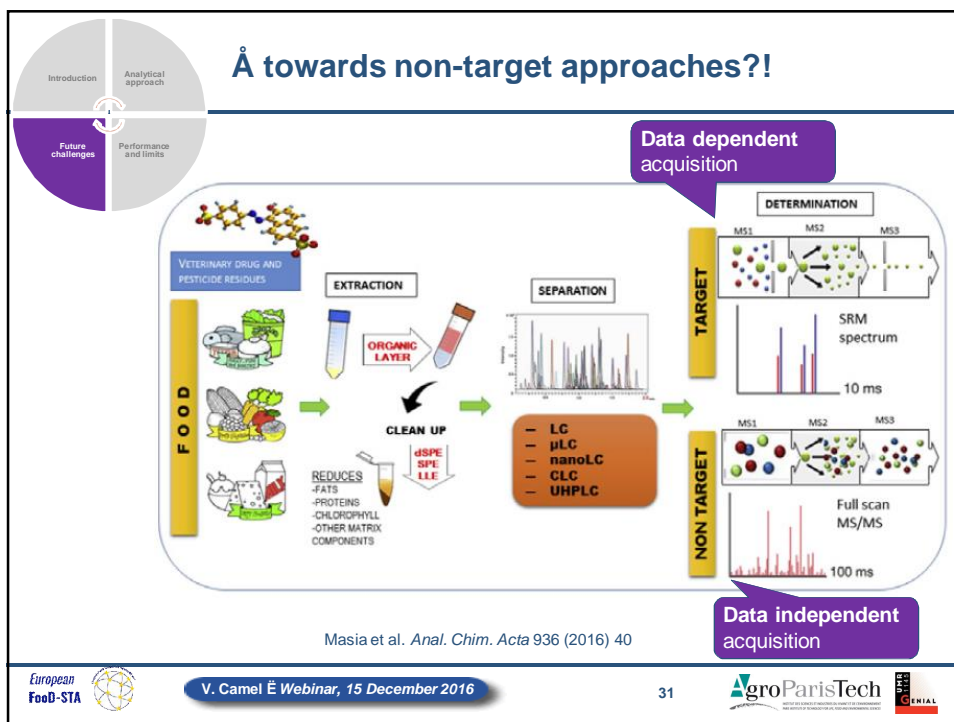
Dzuman et al. *Anal. Chim. Acta* 863 (2015) 29 . Danezis et al. . *Anal. Chim. Acta* 942 (2016) 121

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## Conclusion

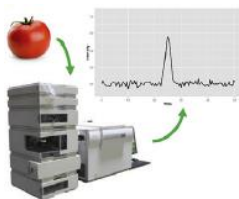
Past



Present



Future?



Evard et al. Anal. Chim. Acta 942 (2016) 40



## Thanks for your attention !

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