

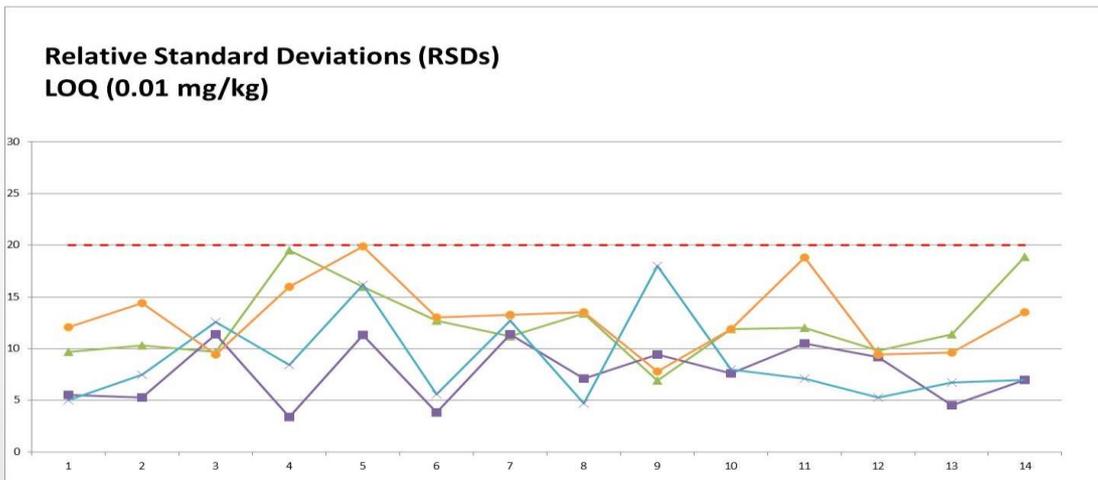
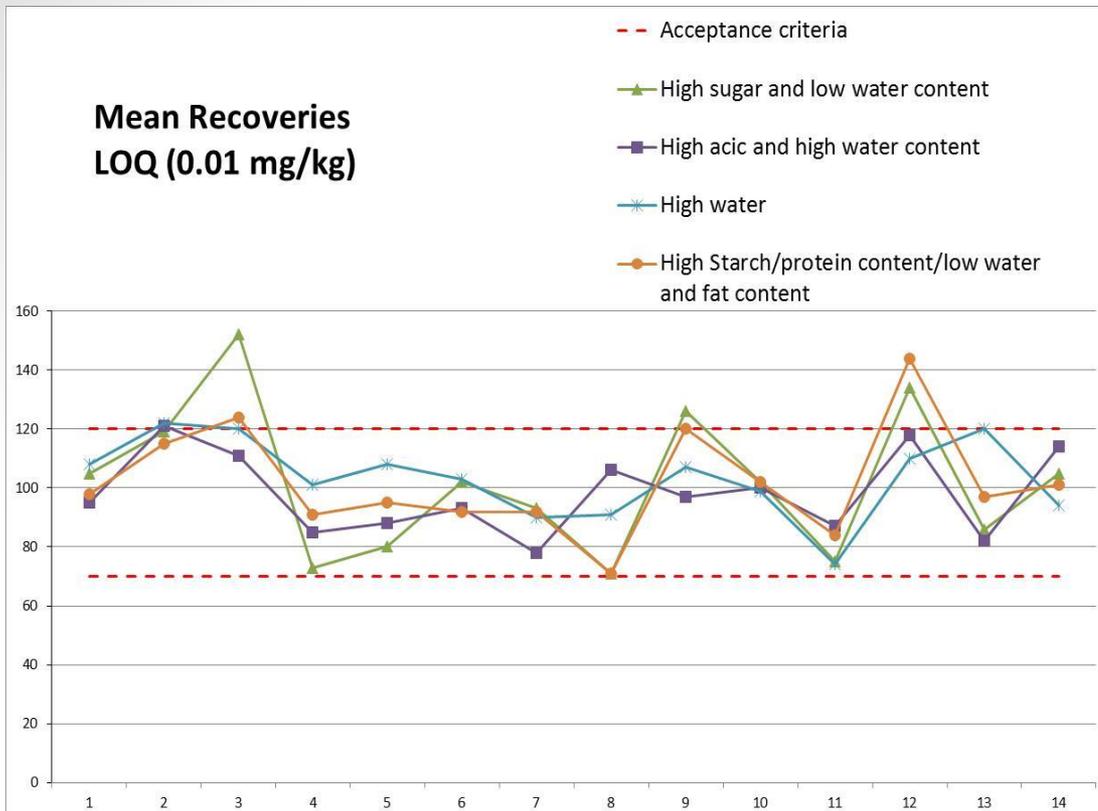


MRM Pesticides that are difficult to analyse or problematic, due to degradation during the extraction or due to other causes: Question?

**Italian official Laboratories and IT-NRL
Experiences**

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Pesticide Section – National Institute of Health (Istituto Superiore di Sanità)



Results from IT-NRL

- **Method EN 15662:2009**
- **GC/MS/MS**
(Agilent Technologies GC 7890 A equipped with a 7000 Triple Quad MS)
- **Single-level calibration**
- **Matrix matched calibration**
- **Internal standard**
- **Replicate experiments $n \geq 6$**
- **List of investigated compounds:**

Bifenthrin, Chlorpyrifos, Diazinon, Endosulfan alpha, Endosulfan beta, Endosulfan sulfate, gamma-HCH, Phosalone, Indoxacarb, Kresoxim-methyl, lambda-Cyhalothrin, Pirimiphos-methyl, Procymidone, tau-Fluvalinate

QuEChERS Multi Residue Method EN 15662:2009

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM
ICS 67.050

EN 15662
November 2008

English Version

Foods of plant origin - Determination of pesticide residues using
GC-MS and/or LC-MS/MS following acetonitrile
extraction/partitioning and clean-up by dispersive SPE -
QuEChERS-method

Commodity Groups

- ✓ High acid and high water content
- ✓ High water

- ✓ High sugar and low water content
- ✓ High starch/protein content/low water and fat content

Analytical Procedure – main differences

- Weighing: in the case of fruits and vegetables weigh 10



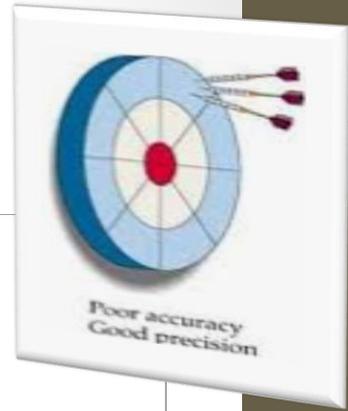
- Weighing: for dry sample materials like cereal products and honey weigh $5\text{g} \pm 0.05\text{g}$



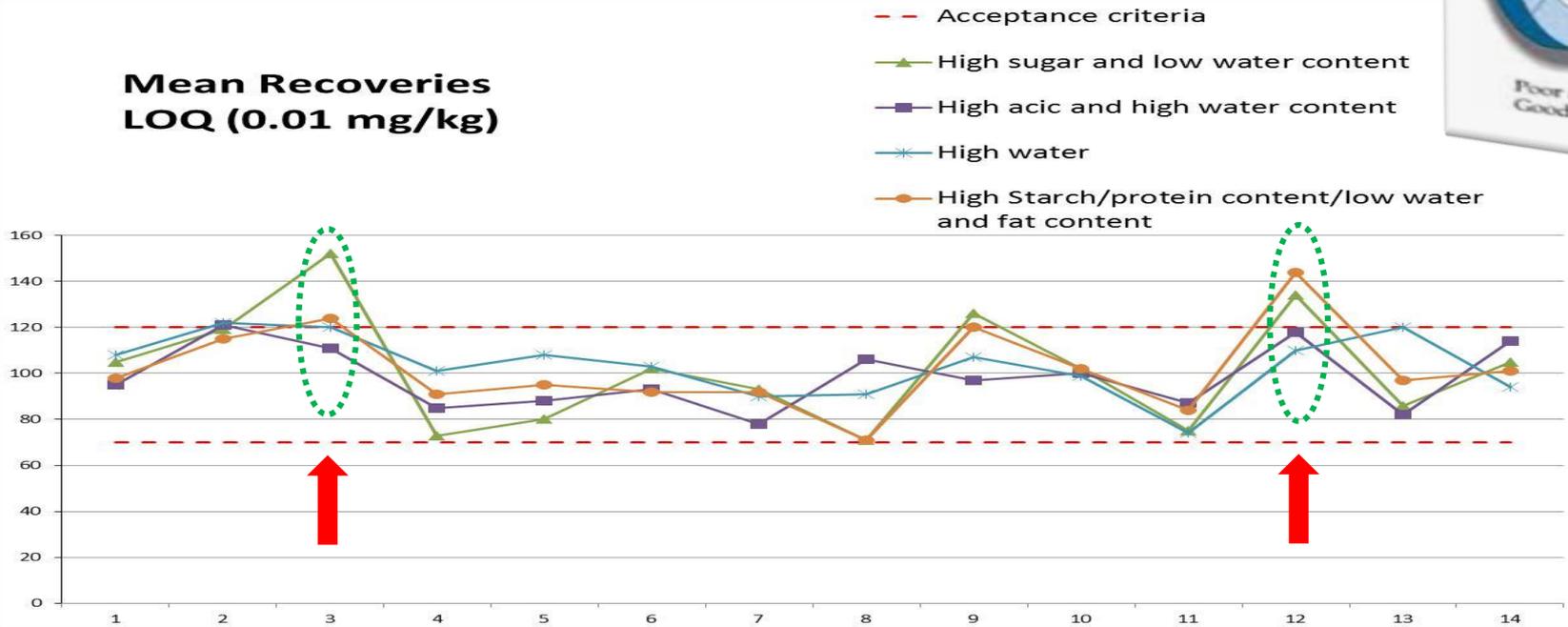
- Addition water
- Additional clean up: freezing + Dispersive SPE C18

Trueness \longrightarrow Case Studies

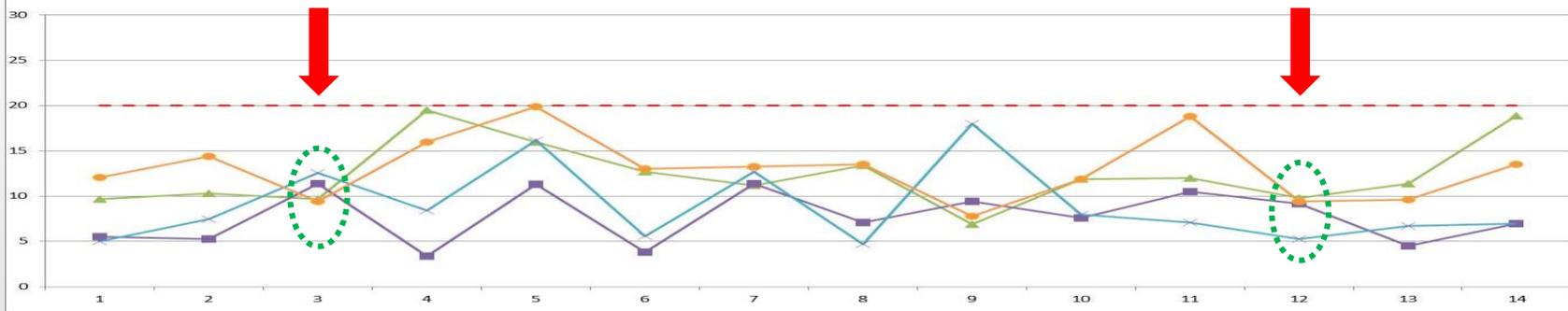
Diazinon and Pirimiphos-methyl



**Mean Recoveries
LOQ (0.01 mg/kg)**



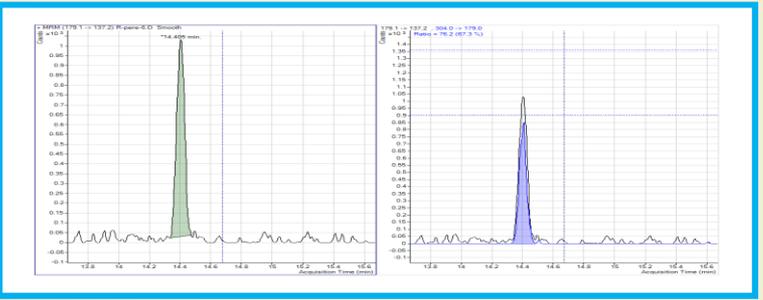
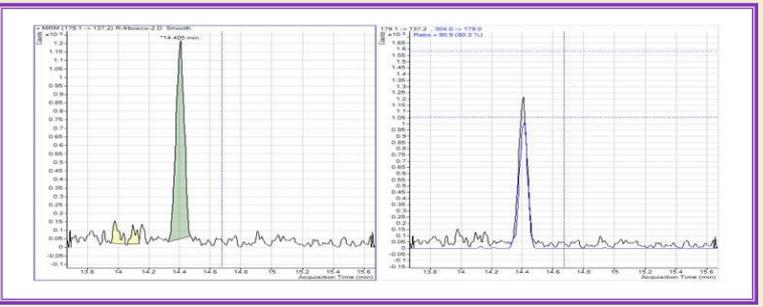
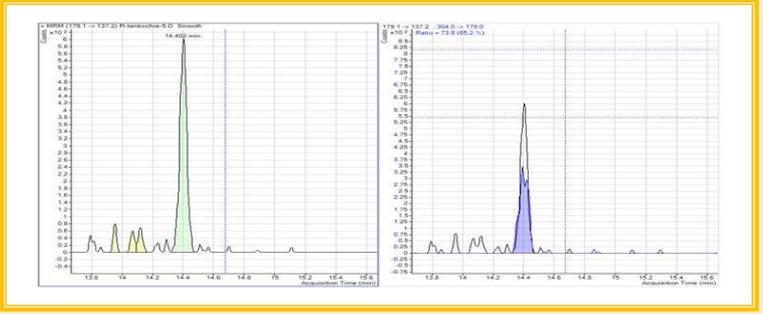
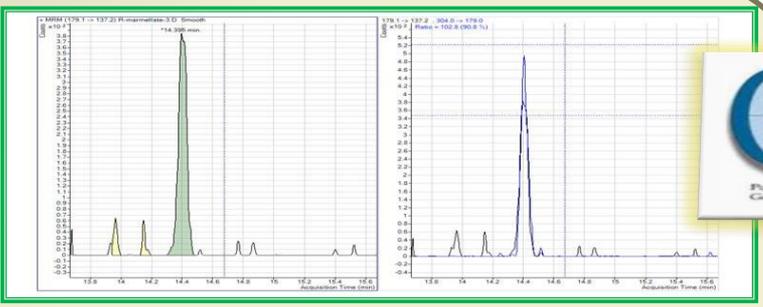
**Relative Standard Deviations (RSDs)
LOQ (0.01 mg/kg)**



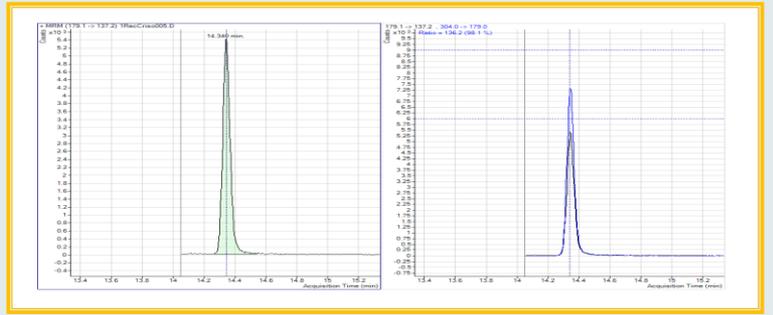
Case Study: Diazinon



- ▲ High sugar and low water content
- High acid and high water content
- ✕ High water
- High Starch/protein content/low water and fat content



LOQ: 0.01 mg/kg

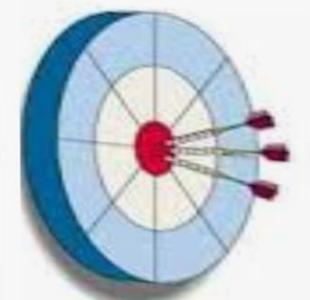


Cereals

Mean Recs: 100%

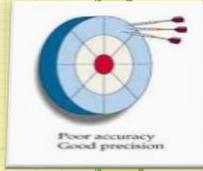
RSDs: 2,7%

Low Conc Level : 0.05 mg/kg

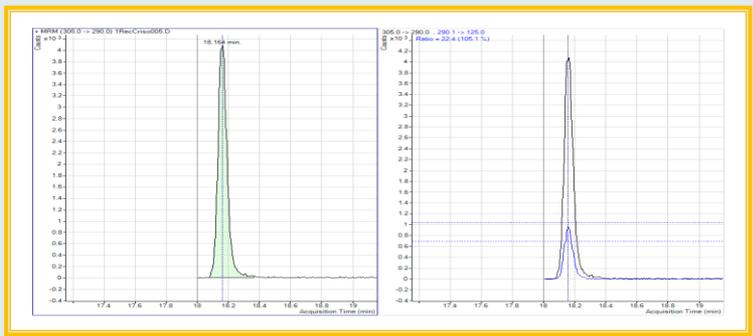
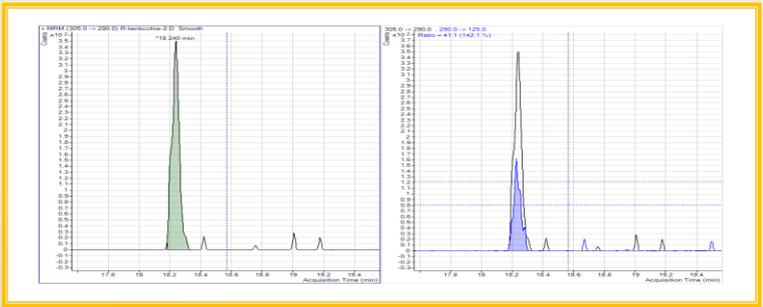
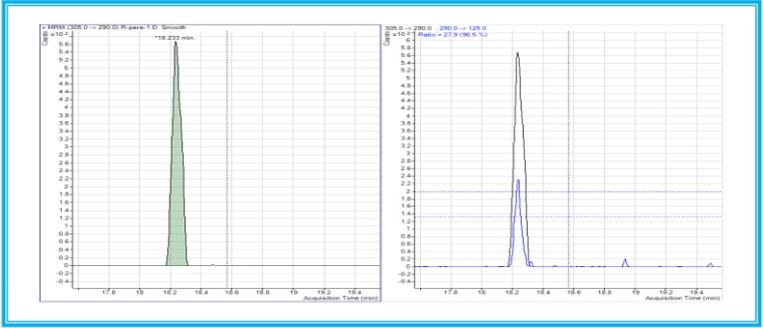
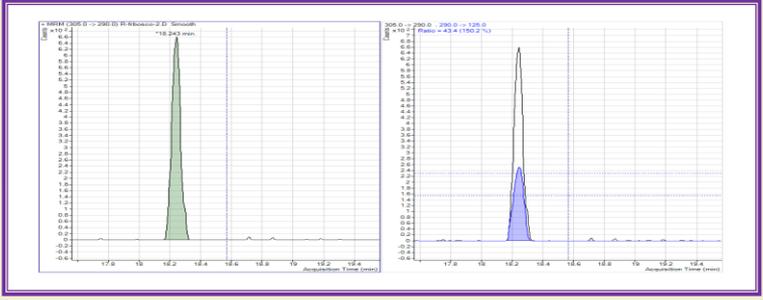
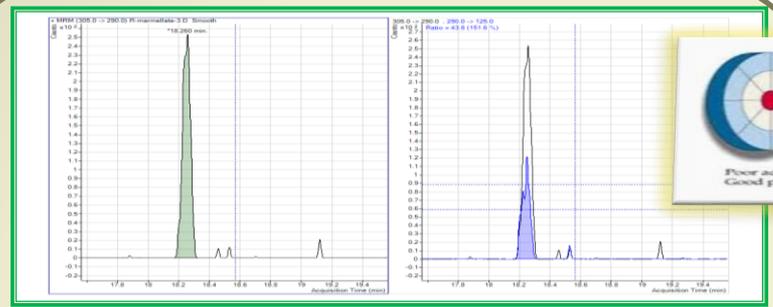


Good accuracy
Good precision

Case Study: Pirimiphos-methyl



- ▲ High sugar and low water content
- High acid and high water content
- ✕ High water
- High Starch/protein content/low water and fat content

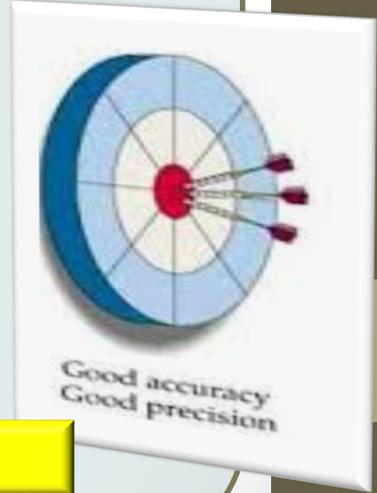


Cereals

Mean Recs: 108%

RSDs: 2,1%

Low Conc Level: 0.05 mg/kg



LOQ: 0.01 mg/kg

For Commodity Groups of high sugar and low water content , and high fat content and high starch/protein content at LOQ 0.01 mg/Kg it is necessary to stress the clean up of the Standard Method EN 15662

Question?

The clean up of the Standard Method could be improved

Could the procedure be revised?

Case study: Benfuracarb and Carbosulfan

Some laboratories have highlighted problems of poor accuracy and sensitivity for the Benfuracarb and Carbosulfan.

Not be capable of providing acceptable validation study.

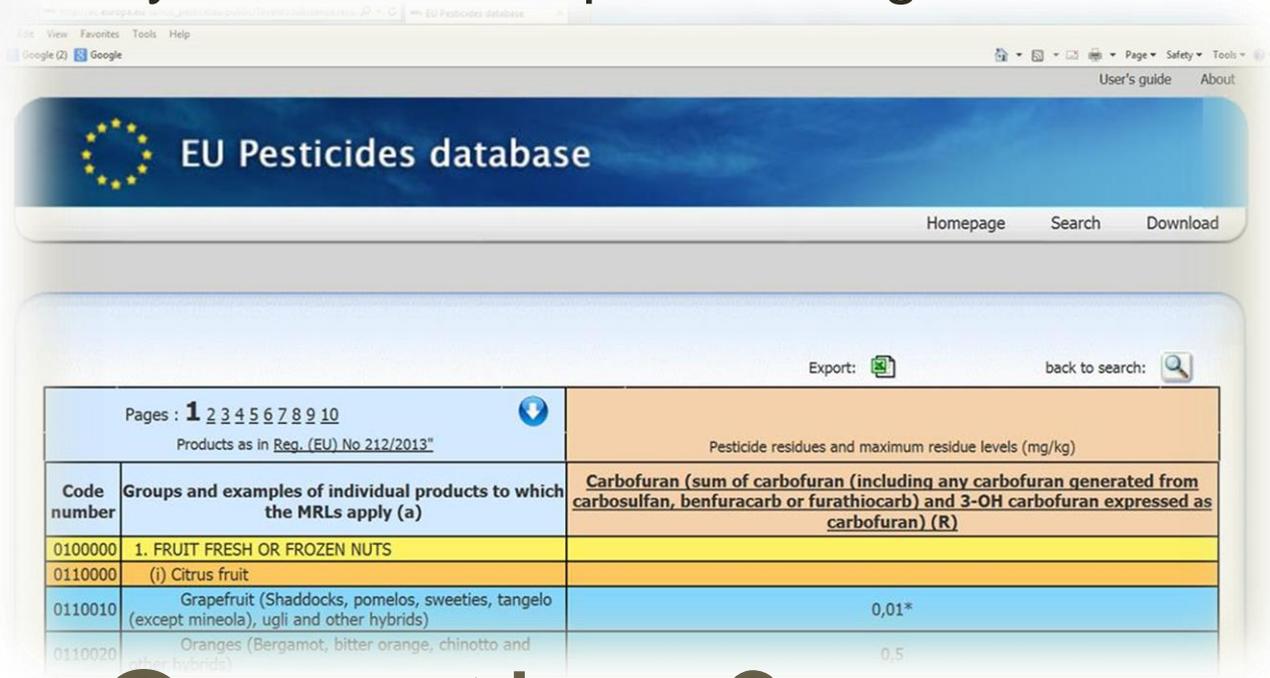
The image shows two overlapping screenshots of the EU Pesticides database. The top screenshot displays the search results for Benfuracarb, and the bottom screenshot displays the search results for Carbosulfan. Both screenshots show a table with columns for Code number, Groups and examples of individual products to which the MRLs apply (a), and Pesticide residues and maximum residue levels (mg/kg).

Pages : 1 2 3 4 5 6 7 8 9 10		Pesticide residues and maximum residue levels (mg/kg)	
Code number	Groups and examples of individual products to which the MRLs apply (a)	Benfuracarb	
0100000	1. FRUIT FRESH OR FROZEN NUTS		
0110000	(i) Citrus fruit	0,02*	
0110010	Grapefruit (Shaddocks, pomelos, sweeties, tangelo (except mineola), ugli and other hybrids)	0,02*	
0110020	Oranges (Bergamot, bitter orange, chinotto and other hybrids)	0,03*	

Pages : 1 2 3 4 5 6 7 8 9 10		Pesticide residues and maximum residue levels (mg/kg)	
Code number	Groups and examples of individual products to which the MRLs apply (a)	Carbosulfan	
0100000	1. FRUIT FRESH OR FROZEN NUTS		
0110000	(i) Citrus fruit		
0110010	Grapefruit (Shaddocks, pomelos, sweeties, tangelo (except mineola), ugli and other hybrids)	0,01*	
0110020	Oranges (Bergamot, bitter orange, chinotto and other hybrids)	0,1	
0110030	Lemons (Citron, lemon, Buddha's hand (Citrus medica var. sarcodactylis))	0,01*	

Case study: Benfuracarb and Carbosulfan

Maybe, these compounds degrade in Carbofuran (?)



The screenshot shows the EU Pesticides database interface. At the top, there is a navigation bar with 'Homepage', 'Search', and 'Download' links. Below this is a search area with an 'Export' button and a 'back to search' link. The main content is a table with the following structure:

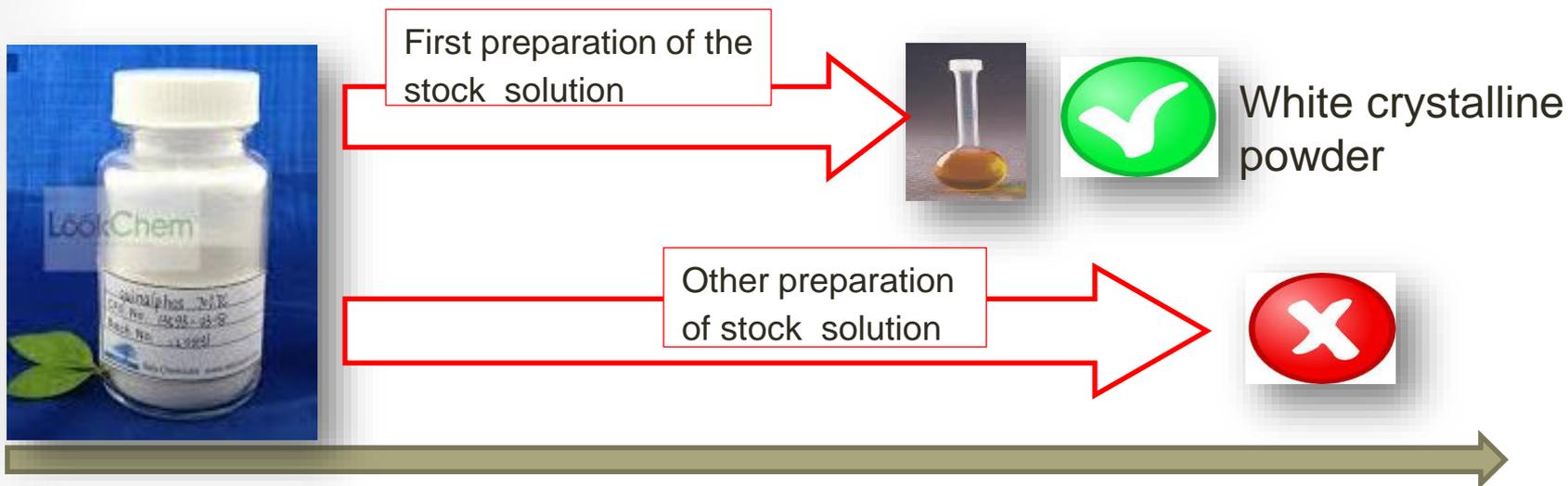
Pages : 1 2 3 4 5 6 7 8 9 10		Pesticide residues and maximum residue levels (mg/kg)	
Code number	Groups and examples of individual products to which the MRLs apply (a)	<u>Carbofuran (sum of carbofuran (including any carbofuran generated from carbosulfan, benfuracarb or furathiocarb) and 3-OH carbofuran expressed as carbofuran) (R)</u>	
0100000	1. FRUIT FRESH OR FROZEN NUTS		
0110000	(i) Citrus fruit		
0110010	Grapefruit (Shaddocks, pomelos, sweeties, tangelo (except mineola), ugli and other hybrids)		0,01*
0110020	Oranges (Bergamot, bitter orange, chinotto and other hybrids)		0,5

Question?

Could the Benfuracarb and Carbosulfan be included only in Carbofuran MRL residue definition?

Case study: Quinalphos

Some laboratories have highlighted changes in colour and physical state of the pure reference standard



Question?

Could pure reference standard degrade?

Thanks for your attention!!!