EUPT-SRM19 (Grape-Matrix) and News from SRM

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Selection of Commodity & Pesticides to be spiked

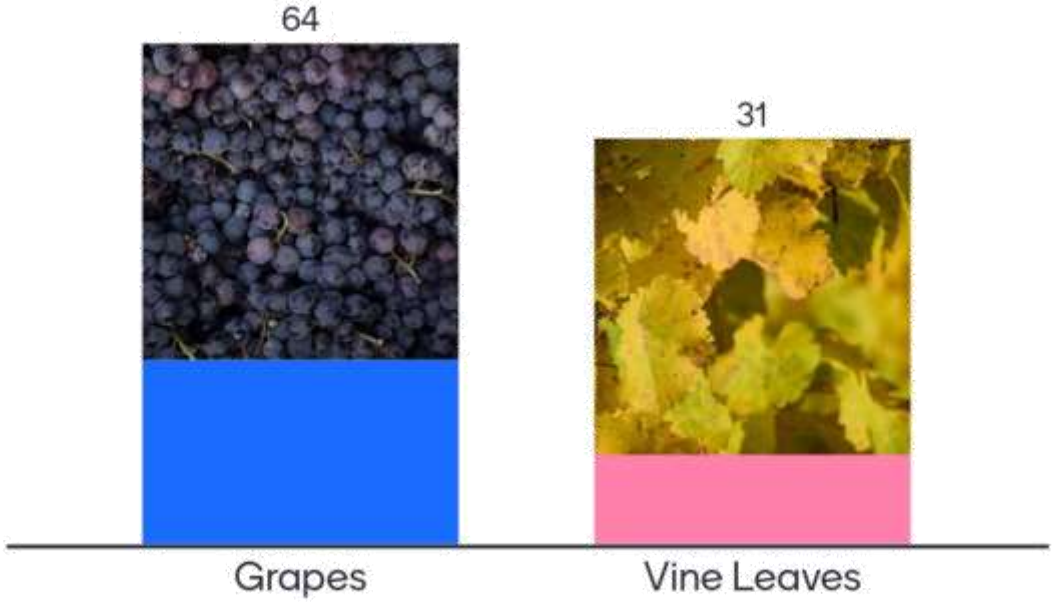
COMMODITY & DATE Selection

AdvG-Meeting (Jun 2023)

- **Tentative matrices:** Grapes or Vine Leaves
- **Tentative timing:** 1st EUPT in 2024-season (shipment early Feb. 24)

EURL-Workshop (Oct 2023)

- **Survey:** *"Which matrix do you propose for the EUPT-SRM19 (2023)?"*



EUPT-SRM19 Organisation

Announcement/Invitation: 10th Nov. 2023

Registration: 15th Dec. 2023 – 7th Jan. 2024 — 23 days

Sample Shipment: 5th Feb. 2023 — 11 weeks

38 days

Results Submission: 12th Feb.* – 12th Mar. 2023

(*Webtool Opening)

Submission of missing Info: 13th – 21st Mar. 2023 — 7 working d

Preliminary Report: 19th Apr. 2024 — 4 weeks

Collection of info on underperformance: Apr.-Jun. 2024

EURL-SRM

EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

CALENDAR for the EUPT – SRM19

Matrix: Grape Homogenate

(update on 20/11/2023)

Activity	Dates
Announcement of the EUPT-SRM19 opening of the EUPT-SRM19 Website with links to all relevant documents	10 Nov. 2023
Registration Period for EUPT-SRM19 via "EURL-DataPool" Labs classified as "OBLIGED" to participate in the EUPT-SRM19 MUST enter the EUPT-Registration Form within the EURL-DataPool and either register OR give explanations for non-participation	15 Dec. 2023 – 7 Jan. 2024*
Dispatch of EUPT-SRM19-Specific Protocol	by 18 Jan. 2024
Shipment of EUPT-SRM19 Test Item	5 Feb. 2024
Confirming Sample Receipt and Acceptance via "EUPT-SRM19 Result Submission Webtool"	From 6 Feb. 2024 onwards
Submission of Results (Pesticide scope, Results, Method Info) via "EUPT-SRM19 Result Submission Webtool"	12 Feb. –12 March 23 h (11 p.m.) CET
Submission of Additional/Missing Information e.g. Method info on tentatively false negative results via "EUPT-SRM19 Result Submission Webtool"	13 – 21 March 2024
Dispatch of Preliminary Report containing results as well as preliminary assigned values and z-scores only	Within 3 weeks after the submission deadline
Collection of reasons for underperformance and missing information on methods	April & May 2024
Dispatch of Final Report	Dec. 2024

*Please make sure to register for the EUPT from 15 December 2023 to the deadline 7 January 2024 via EURL-DataPool. Any wish for registration after this deadline or not using the registration website cannot be considered.

REMARK:
Please note that the dates given above may be subject to minor changes. In case of changes significantly affecting the participants or their results, the participants will be informed via e-mail. However, please still check periodically our website for possible updates in case the email does not get through to you.
Contact: eurl-srm@cvuas.bwl.de

The EUPT-SRM Team

Selection of Commodity & Pesticides to be spiked

ANALYTE Selection for TARGET LIST - Factors considered for includion

a) EU Monitoring Documents (MACP-Reg. & WD for NCPs):

- MACP-Regulation (MACP) ➔ ***COMPULSORY***
  - ***Spiked****: Avermectin B1a, Clopyralid, Copper, Dithianon, DTCs, Folpet/PI, MPP, NAGlu, …*
  - ***Non-spiked:*** 2,4-D, Captan/THPI, Chlormequat, Emamectin B1a, Ethephon, Glufosinate …
- Working Document for National Control Programs (WD) ➔ ***OPTIONAL / EXTRA***
  - ***Spiked****: Meptyldinocap, 2,4-DNOP* ; ***EXTRA****: Gamma Cyhalothrin (Chiral Chr/phy), DFA*
  - ***Non-spiked:*** Amitrole, MCPA, Triclopyr, Trimesium

b) Suggestions/Voting by EUPT-Scientific Committee

c) Relevance to matrix *(Not to fruits in general this time, as grapes are sprayed with a very wide range of compounds)*

d) Capacities and Capabilities of Participants (and of EURL-SRM): Keep no. of methods moderate

EURL-SRM

SRM19 TARGET PESTICIDES List

Compulsory Compounds

Compounds	Listed in	MRRL
2,4-D (free acid)	MACP-Reg. (grapes explicitly named)	**0.01**
Avermectin B1a	MACP-Reg.	**0.01**
Captan	MACP-Reg.	**0.01**
Captan (sum)	MACP-Reg.	**0.03**
THPI	MACP-Reg.	**0.01**
Chlormequat-chloride	MACP-Reg. (grapes explicitly named)	**0.01**
Clopyralid	MACP-Reg. (grapes explicitly named)	**0.01**
Copper	MACP-Reg.	**0.2**
Dithianon	MACP-Reg. (grapes explicitly named)	**0.01**
Dithiocarbamates as CS_2	MACP-Reg.	**0.01**
Emamectin B1a	MACP-Reg.	**0.01**
Ethephon	MACP-Reg. (grapes explicitly named)	**0.01**
Folpet	MACP-Reg.	**0.01**
Folpet (sum)	MACP-Reg.	**0.03**
Phthalimide	MACP-Reg.	**0.01**
Glufosinate	MACP-Reg.	**0.01**
MPP (aka MPPA)	MACP-Reg.	**0.01**
N-Acetyl Glufosinate	MACP-Reg.	**0.01**

Optional Compounds

Compounds	Listed in	MRRL
Amitrole	WD (grapes explicitly named)	**0.01**
MCPA (free acid)	WD (grapes explicitly named)	**0.01**
Meptyldinocap	WD (grapes explicitly named)	**0.02**
Meptyldinocap (sum following hydrolysis)	WD (grapes explicitly named)	**0.01**
Meptyldinocap (sum calculated)	WD (grapes explicitly named)	**0.01**
2,4 DNOP	WD (grapes explicitly named)	**0.01**
Triclopyr (free acid)	WD (grapes explicitly named)	**0.01**
Trimethylsulfonium cation	WD (grapes explicitly named)	**0.01**

Extra Compounds

Compounds	Listed in	MRRL
Difluoroacetic acid (DFA)	WD (grapes explicitly named)	**0.02**
Gamma-Cyhalothrin	WD (grapes explicitly named)	**0.01**

EURL-SRM

PESTICIDES INCURRED AND SPIKED

OVERVIEW: COMPOUNDS APPLIED IN LAB AND INCURRED ONES

		residues incurred	compounds spiked in the lab	Compound form used for spiking in the lab
Avermectin B1a	MANDATORY	-	✓	Avermectin B1a + B1b
Clopyralid	MANDATORY	-	✓	Clopyralid
Copper	MANDATORY	-	✓	Copper sulfate pentahydrate
Dithianon	MANDATORY	-	✓	Dithianon
Dithiocarbamates as CS2	MANDATORY	-	✓	Metiram (CELAFLOR)
Ethephon	MANDATORY	-	✓	Ethephon
Folpet	MANDATORY	-	✓	Folpet
Folpet metabolite Phthalimide	MANDATORY	traces	✓	Folpet metabolite Phthalimide
Glufosinate metabolite MPP (aka MPPA)	MANDATORY	-	✓	MPP (aka MPPA)
Glufosinate metabolite N-Acetyl Glufosinate	MANDATORY	-	✓	N-Acetyl Glufosinate
Meptyldinocap	OPTIONAL	-	✓	Meptyldinocap
Meptyldinocap metabolite 2,4 DNOP	OPTIONAL	-	✓	2,4 DNOP
Difluoroacetic acid (DFA)	OPTIONAL	-	✓	Difluoroacetic acid (DFA)
Gamma Cyhalothrin	OPTIONAL	-	✓	Gamma Cyhalothrin + Lambda Cyhalothrin

Preparation of PT-Item

100 kg grapes frozen but left to partly defrost

Thermomix milling (<0°C) (liquid due to high sugar)

Filled into a tank and cooled down to -4°C

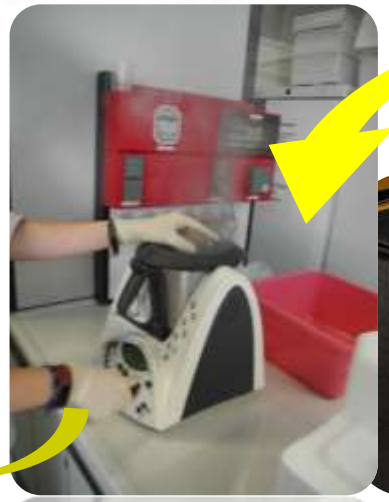
Spiked and homogenized (Silverson stirrer)

Liquid homogenate (at 4°C) filled into bags

Express delivery (with dry ice)

Bottling and sealing

Snow-like material



Milling with dry ice

Bags placed in freezer

Preparation of PT-Item

Spiked Homogenate portions in freezer

Milling w. dry ice

Despite cooling at -18°C for several days, homogenate in the bags remained lethery soft

- Probably due to the **high sugar content.**

Homogenate **initially snow-like**

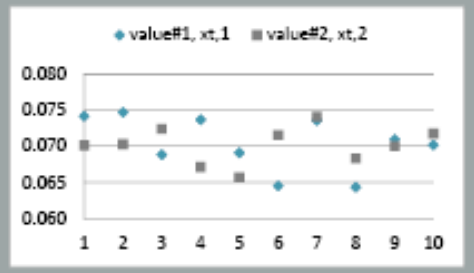
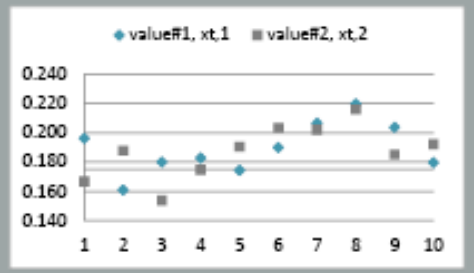
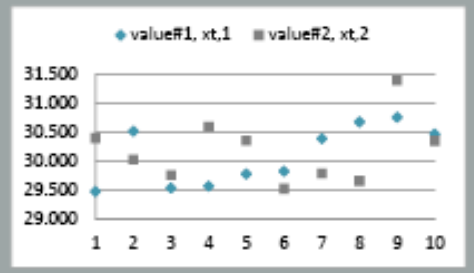
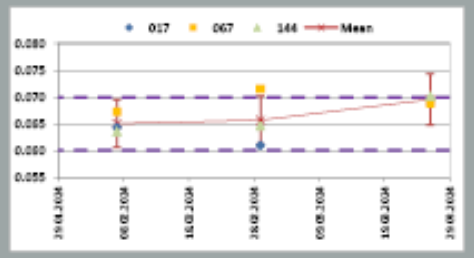
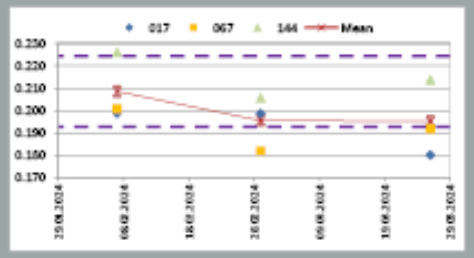
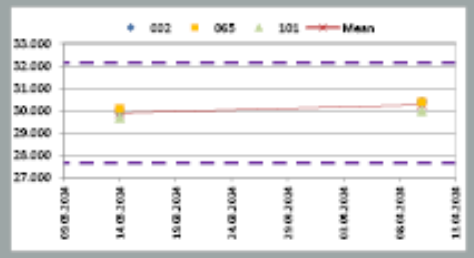
Material collapsed and hardened during shipment with dry ice

(Note: Temp. at sample receipt often <-40°C due to dry ice)

Fortunately: When material was left to warm up a bit it became easy to handle again

Homogeneity TEST/ Stability TEST

Homogeneity and Stability Test Results – COMPULSORY COMPOUNDS

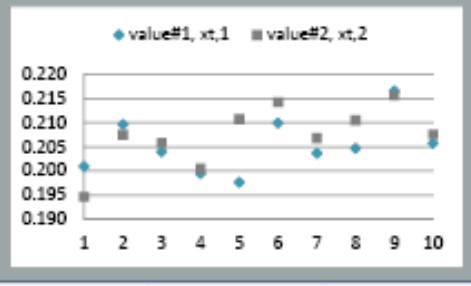
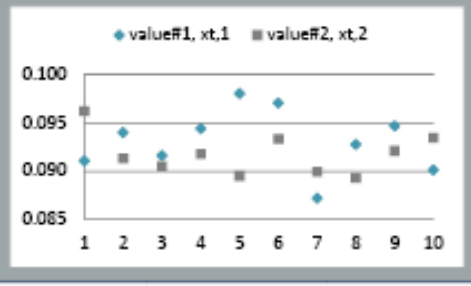
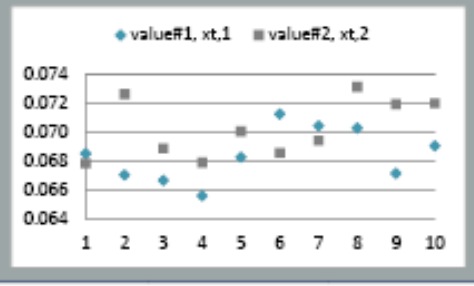
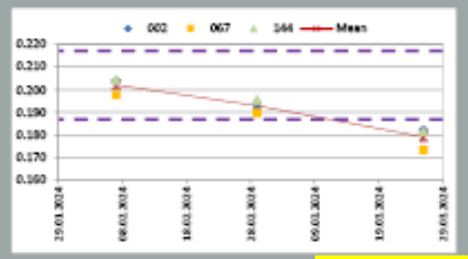
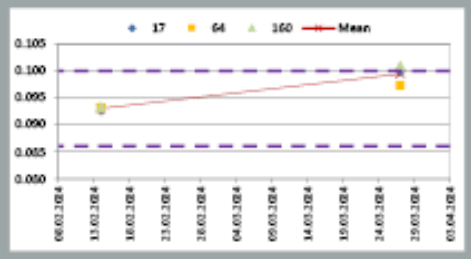
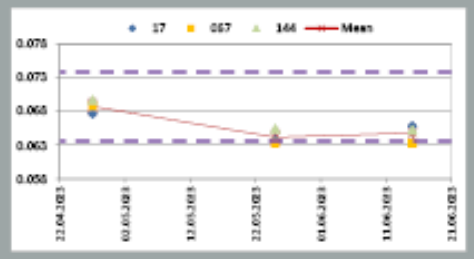
Analyte	Avermectin B1a	Clopyralid	Copper
Homogeneity Distribution n=10 duplicates			
Mean Homogeneity [mg/kg]	0.0703	0.1883	30.1445
AV	0.0711	0.192	29.9
RSD%	3.4%	8.1%	1.3%
S_{sam}^2< (c) ?	0.00116<0.00527	0.01212<0.01412	0.22865<2.26084
Homogeneity Test	passed	passed	passed
Stability Test n=3 duplicates			

	Homogeneity d=0	Stability 2 d=22	Stability3 d=48	Homogeneity d=0	Stability 2 d=22	Stability3 d=48	Homogeneity d=0	Stability 2 d=	Stability3 d=27
StDev based on 5 Inj.		6.8%			1.1%			-	
Deviation to 1. Analysis	-	1.0%	6.9%	-	-6.2%	-6.4%	-	-	1.2%
Stability Test	-	passed	passed	-	passed	passed	-	-	passed

S_{sam}^2: between-samples STD
(c): Check Value (0.3* σ PT):

Homogeneity TEST/ Stability TEST

Homogeneity and Stability Test Results – COMPULSORY COMPOUNDS

Analyte	Dithianon	DTCs (expr. as CS_2)	Ethephon
Homogeneity Distribution n=10 duplicates			
Mean Homogeneity [mg/kg]	0.2063	0.0924	0.0694
AV	0.236	0.1	0.0582
RSD%	2.6%	2.0%	2.1%
S_{sam}^2< (c) ?	0.00461<0.01547	0<0.00693	0<0.0052
Homogeneity Test	passed	passed	passed
Stability Test n=3 duplicates			

	Homogeneity d=0	Stability 2 d=22	Stability3 d=48	Homogeneity d=0	Stability 2 d=	Stability3 d=42	Homogeneity d=0	Stability 2 d=25	Stability3 d=42
StDev based on 5 Inj.		1.0%			-			1.6%	
Deviation to 1. Analysis	-	-4.5%	-11.4%	-	-	6.9%	-	-6.7%	-5.7%
Stability Test	-		failed	-	-	passed	-	passed	passed

S_{sam}^2: between-samples STD
(c): Check Value (0.3* σ PT):

Homogeneity TEST/ Stability TEST

Stability of DITHIANON

NOTES:
PT-Period: 38 d (shipping day not counted)!
Max. allowed deviation: +/- 7.5%
(=30% of target SD of 25%)

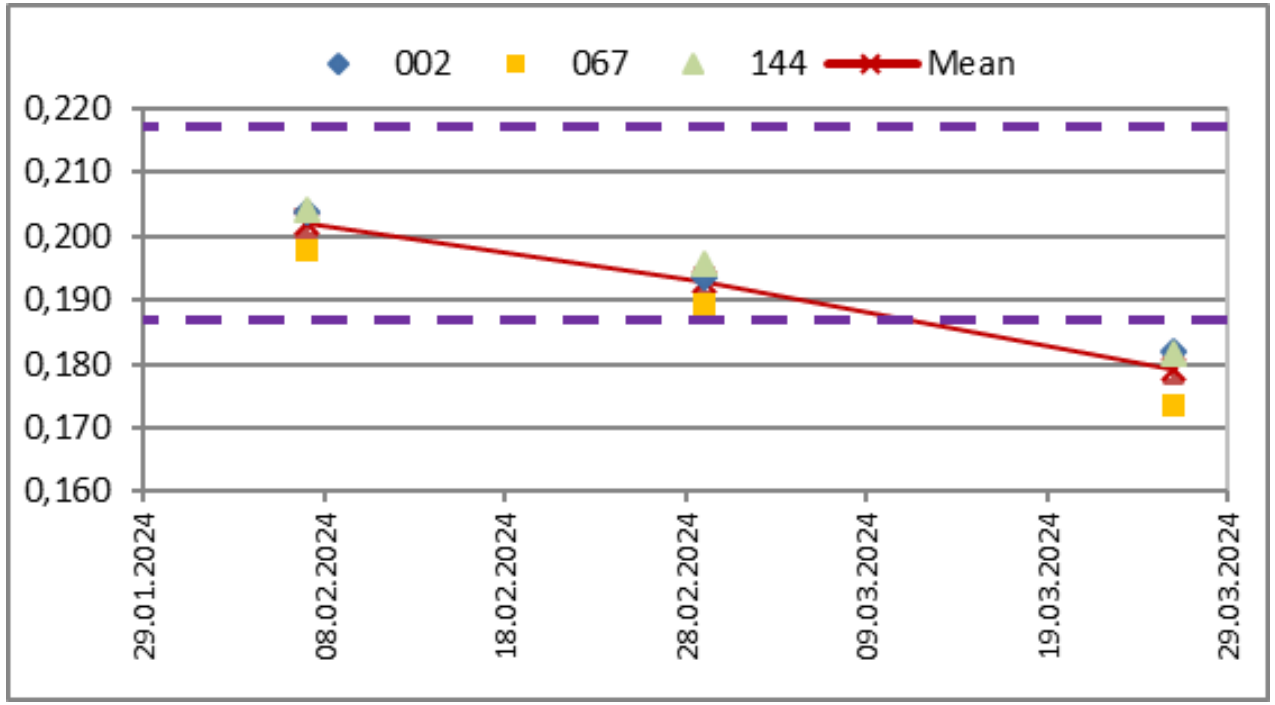
Extrapolation of stability based on slope

a) Slope of entire curve (D1-D3):
Deviation Limit of -7.5% reached after ~**31 d.**

b) Slope of (D1,D2):
Deviation Limit of -7.5% reached after ~**37 d.**

Conclusion:
Stability of Dithianon was not sufficient !

S_{sam}^2: between-samples STD
(c): Check Value (0.3* σ PT):

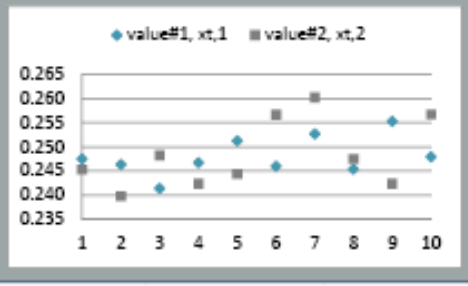
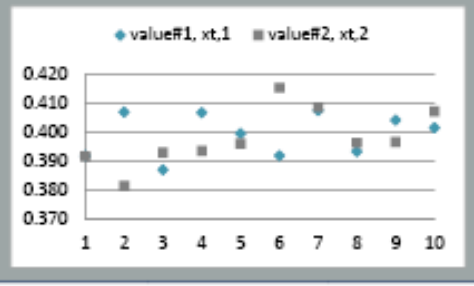
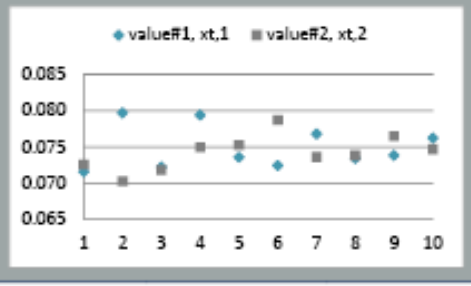
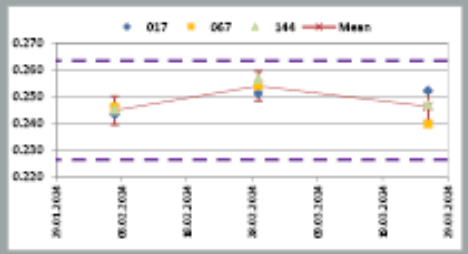
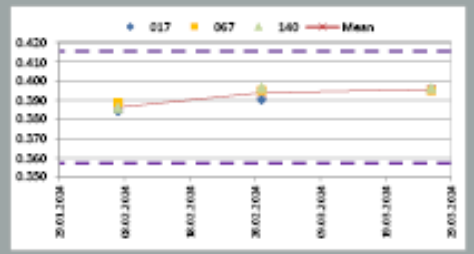
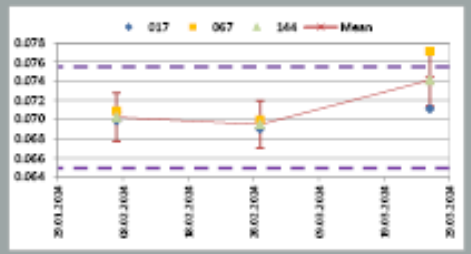


	Homogeneity d=0	Stability 2 d=22	Stability3 d=48
StDev based on 5 Inj.	1.0%		
Deviation to 1. Analysis	-	-4.5%	-11.4%
Stability Test	-		failed

Homogeneity TEST/ Stability TEST

Homogeneity and Stability Test Results – COMPULSORY COMPOUNDS

S_{sam}^2: between-samples STD
(c): Check Value (0.3* σ PT):

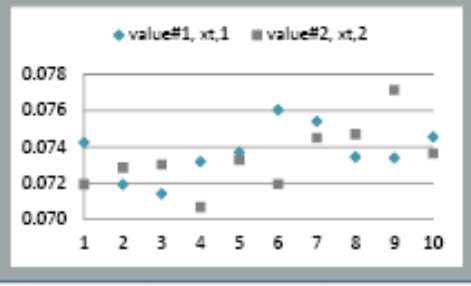
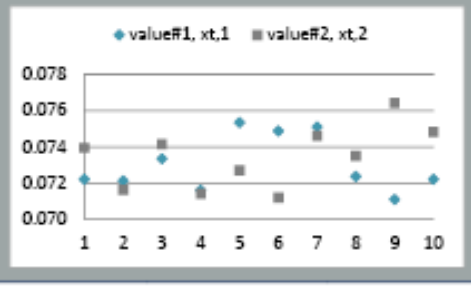
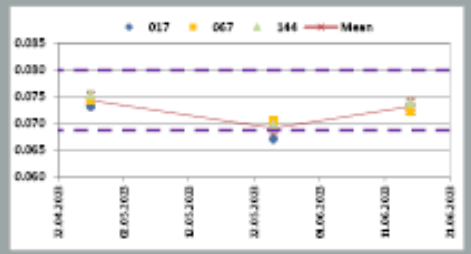
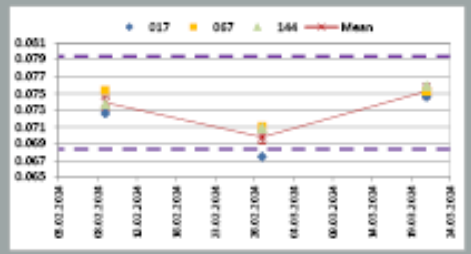
Analyte	Folpet	Folpet (sum calc.)	Phthalimide
Homogeneity Distribution n=10			
Mean Homogeneity [mg/kg]	0.248	0.3990	0.0746
AV	0.225	0.421	0.082
RSD%	1.7%	1.5%	2.1%
S_{sam}^2< (c) ?	0.00158<0.01862	0<0.02989	0<0.00559
Homogeneity Test	passed	passed	passed
Stability Test n=3			

	Homogeneity d=0	Stability 2 d=22	Stability3 d=48	Homogeneity d=	Stability 2 d=	Stability3 d=	Homogeneity d=0	Stability 2 d=28	Stability3 d=49
StDev based on 5 Inj.		2.2%			-			3.6%	
Deviation to 1. Analysis	-	3.7%	0.6%	-	2.0%	2.4%	-	-1.1%	5.5%
Stability Test	-	passed	passed	-	passed	passed	-	passed	passed

Homogeneity TEST/ Stability TEST

Homogeneity and Stability Test Results – COMPULSORY COMPOUNDS

S_{sam}^2: between-samples STD
(c): Check Value (0.3* σ PT):

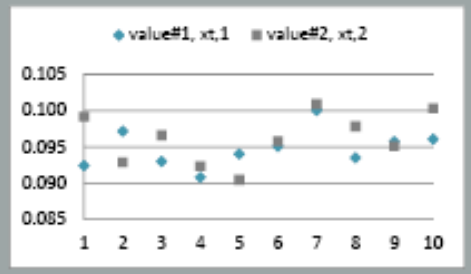
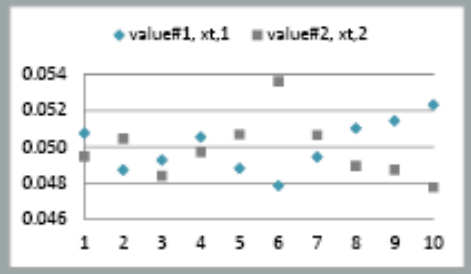
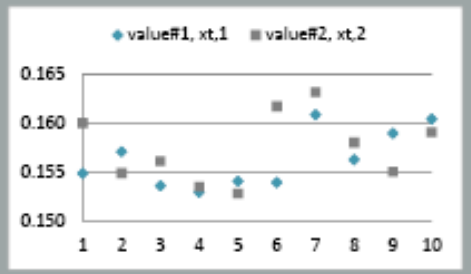
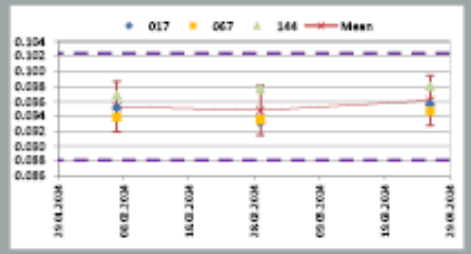
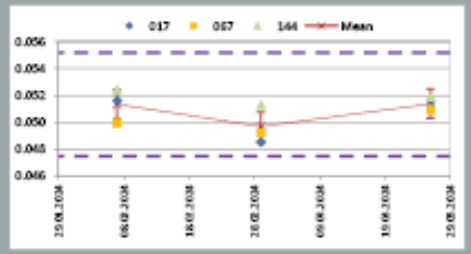
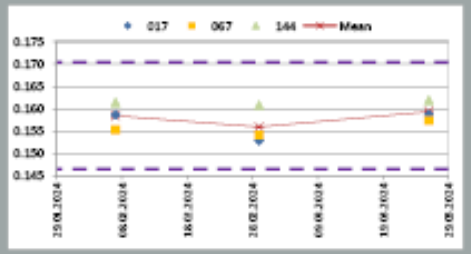
Analyte	MPP	N-Actelyl glufosinate
Homogeneity Distribution n=10		
Mean Homogeneity [mg/kg]	0.0735	0.3990
AV	0.0819	0.421
RSD%	1.5%	1.5%
S_{sam}^2< (c) ?	0.00024<0.00552	0<0.02989
Homogeneity Test	passed	passed
Stability Test n=3		

	Homogeneity d=0	Stability 2 d=25	Stability3 d=42	Homogeneity d=0	Stability 2 d=25	Stability3 d=42	Homogeneity d=0	Stability 2 d=	Stability3 d=
StDev based on 5 Inj.		2.0%			1.1%				
Deviation to 1. Analysis	-	-7.0%	-1.5%	-	-5.5%	1.8%			
Stability Test	-	passed	passed	-	passed	passed			

Homogeneity TEST/ Stability TEST

Homogeneity and Stability Test Results – OPTIONAL COMPOUNDS

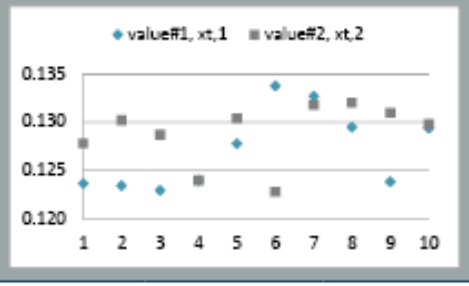
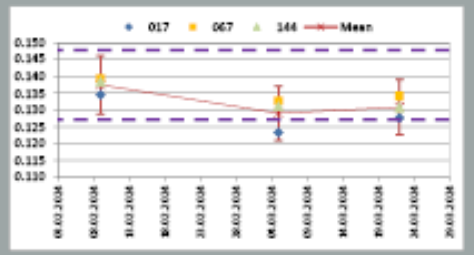
S_{sam}^2: between-samples STD
(c): Check Value (0.3* σ PT):

Analyte	Meptyldinocap	Meptyldinocap m. 2,4-DNOP	Meptyldinocap (sum calc.)
Homogeneity Distribution n=10			
Mean Homogeneity [mg/kg]	0.0955	0.0499	0.1569
AV	0.086	0.0647	0.15
RSD%	2.7%	1.0%	1.7%
S_{sam}^2< (c) ?	0.00181<0.00716	0<0.00375	0.00204<0.01177
Homogeneity Test	passed	passed	passed
Stability Test n=3			

	Homogeneity d=0	Stability 2 d=22	Stability3 d=48	Homogeneity d=0	Stability 2 d=22	Stability3 d=48	Homogeneity d=0	Stability 2 d=22	Stability3 d=48
StDev based on 5 Inj.		3.5%			2.1%			-	
Deviation to 1. Analysis	-	-0.5%	0.9%	-	-3.2%	0.1%	-	-1.6%	0.5%
Stability Test	-	passed	passed	-	passed	passed	-	passed	passed

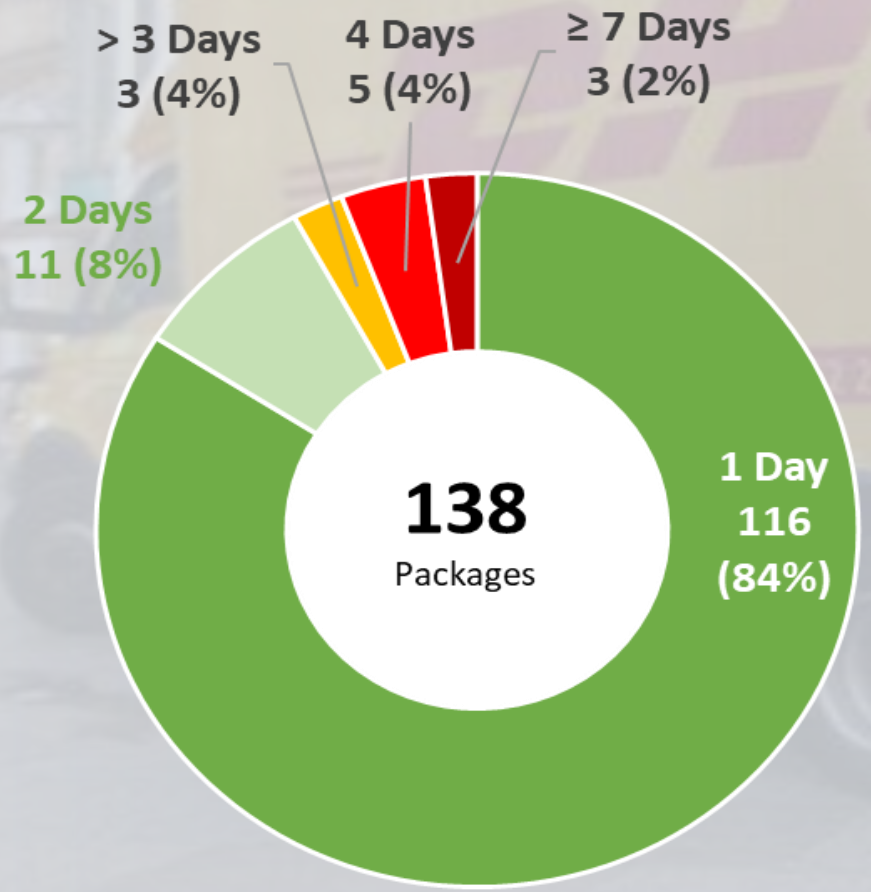
Homogeneity and Stability Test Results – EXTRA ANALYTE

S_{sam}^2: between-samples STD
(c): Check Value (0.3* σ PT):

Analyte	Difluoroacetic acid (DFA)								
Homogeneity Distribution n=10									
Mean Homogeneity [mg/kg]	0.1280								
AV	0.146								
RSD%	2.0%								
S_{sam}^2< (c) ?	0<0.0096								
Homogeneity Test	passed								
Stability Test n=3									
	Homogeneity d=0	Stability 2 d=22	Stability3 d=48	Homogeneity d=0	Stability 2 d=22	Stability3 d=48	Homogeneity d=0	Stability 2 d=22	Stability3 d=48
StDev based on 5 Inj.		6.3%							
Deviation to 1. Analysis	-	-6.1%	-4.8%						
Stability Test	-	passed	passed						

Stability during shipping

Shipment Duration



Sample Dispatch: Mo. 5 Feb. 2024 (with dry ice in all cases)

EU and EFTA-labs:

Arrival within …

1 day (Tuesday): 84 %

2 days (Wednesday): 8 %

4 days (Friday): 1 lab from PL (IT problems in DHL-System)

☛ **All but one package arrived within 2 days (sample frozen)**

Labs in Other Countries:

Arrival within …

3 days (Thursday): 3 labs (CR, PE, RS) **2 %**

4 days (Friday): 4 labs (AU, IN and 2x RS) **4 %**

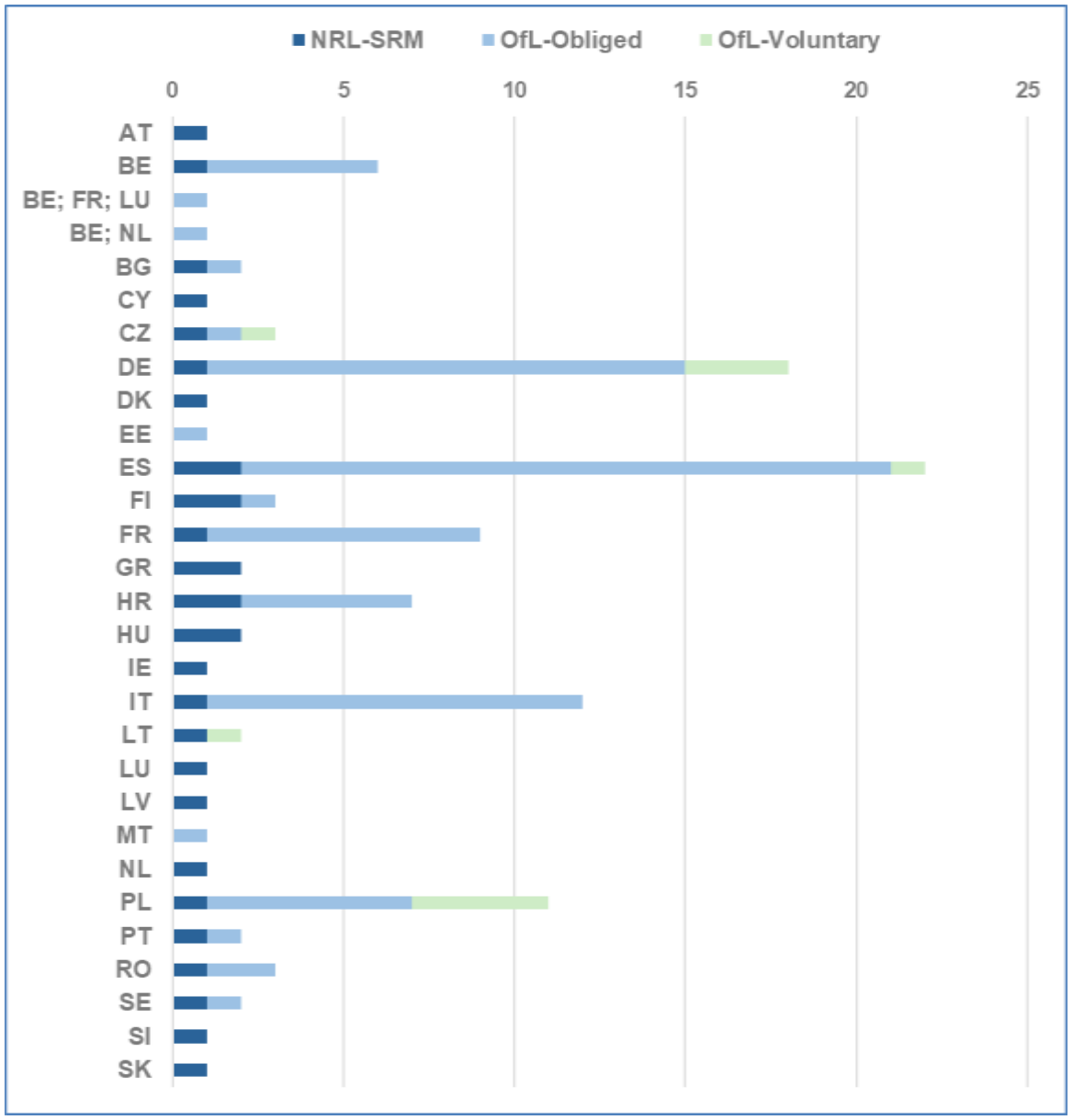
≥ 7 days: (7 d: PE, VN; 9 d RS)

Participating labs / countries

		Labs submitting results	Registered WITHOUT submitting results
EU OfLs		119	1* + 1
EFTA OfLs		4	0
3rd Countries + EU Candidates		12	0
	SUM	76	2

* EU-OfLs stated in Webtool, that all ***analytes were out of lab's scope***, therefore it didn't analyze any of the compounds

Participating labs / countries



EFTA-Countries	Participated in EUPT-SRM19
CH	2
NO	1
IS	1
EFTA-Total	4

EU Candidate & 3rd countries	Participated in EUPT-SRM19
AU	1
CR	1
IN	1
PE	2
RS	4
VN	1
UK	2
EU Cand. & 3rd C. Total	4

- EE: Re-organisation **(to be NRL-SRM took part)**
- MT (designation of new proxy NRL-SRM is pending)

Frequency of analysis

COMPULSORY, OPTIONAL and EXTRA Compounds

EU+EFTA

Percentage based on 123 (119 EU + 4 EFTA) labs registered and submitting results

Present in Test Material	No. of Labs Analysed
Abamectin B1a	99
Ethephon	96
DTC (expr. as CS2)	92
Folpet	88
Phthalimide	87
Folpet (sum)	83
Dithianon	81
N-Acetyl glufosinate	79
Clopyralid	77
Copper	75
MPP (=aka MPPA)	75
Meptyldinocap	19
Meptyldinocap (sum, follo	19
Gamma Cyhalothrin	16
2,4-DNOP (free phenol)	14
Meptyldinocap (sum, calcu	14
Difluoroacetic acid (DFA)	10

≥ 80 %

50 – 79 %

25 – 49 %

< 25 %

Only one of these labs analyzed Gamma Cyh. (via Chiral Chr/phy)

NOT Present in Test Material	No. of Labs Analysed
2,4-D (free acid)	100
Emamectin B1a	100
Chlormequat-Cl	99
Mepiquat-Cl	99
Glufosinate	91
MCPA (free acid)	90
Captan	88
THPI	87
Captan (sum)	84
Triclopyr (free acid)	63
Trimethylsulfonium cation	33
Amitrole	16

False negatives

34x Compulsory, 5x Optional and 2x Extra analytes

EU+EFTA

Compulsory Analytes	AV [mg(kg]	No. of FNs/FN*	Lab-Code	RL [mg(kg]	Judgement
Abamectin B1a	0.0711	2	75	0.01	FN
			94	0.001	FN
Clopyralid	0.192	2	71	0.01	FN
			134	0.5	FN* (AV < RL)
Dithianon	0.236	4	46	0.01	FN
			54	0.01	FN
			87	0.01	FN
			125	0.01	FN
DTC (expr. as CS2)	0.1	5	2	0.2	FN* (AV < RL)
			27	0.1	FN* (AV < RL)
			53	0.01	FN
			104	0.3	FN* (AV < RL)
			108	0.05	FN
Ethephon	0.0582	3	67	0.05	FN
			84	0.05	FN
			114	0.01	FN
Folpet	0.225	8	13	0.01	FN
			58	0.01	FN
			72	0.01	FN
			80	0.01	FN
			111	0.05	FN
			114	0.01	FN
			125	0.005	FN
			137	0.01	FN
Folpet (sum)	0.421	2	15	0.03	FN
			58	0.03	FN

Compulsory Analytes	AV [mg(kg]	No. of FNs/FN*	Lab-Code	RL [mg(kg]	Judgement
MPP (=aka MPPA)	0.0819	2	60	0.01	FN
			127	0.01	FN
N-Acetyl glufosinate	0.0773	4	52	0.01	FN
			78	0.01	FN
			124	0.01	FN
			132	0.10	FN* (AV < RL)
Phthalimide	0.082	2	15	0.01	FN
			72	0.01	FN

Optional Analytes	AV [mg(kg]	No. of FNs/FN*	Lab-Code	RL [mg(kg]	Judgement
2,4-DNOP (free phenol)	0.0647	2	59	0.01	FN
			96	0.01	FN
Meptyldinocap	0.086	1	125	0.005	FN
Meptyldinocap (sum, calculated)	0.15	1	59	0.02	FN
Meptyldinocap (sum, follow. hydr.)	0.188	1	59	0.01	FN

Extra Analytes	AV [mg(kg]	No. of FNs/FN*	Lab-Code	RL [mg(kg]	Judgement
Difluoroacetic acid (DFA)	0.146	1	137	0.01	FN
Cyhalothrin (sum)	0.0754	1	89	0.01	FN

False negatives

EU+EFTA

32 labs reported 41 FN results

Therein …

5 FNs due to RLs > AVs

marked with asterisk

3x DTCs,

1x Clopyralid

1x N-Acetyl-Glufosinate

Lab-Code	Abamectin B1a	Clopyralid	Dithianon	DTC (expr. as CS2)	Ethephon	Folpet	Folpet (sum)	MPP (=aka MPPA)	N-Acetyl glufosinate	Phthalimide	2,4-DNOP (free phenol)	Meptyldinocap	Meptyldinocap (sum, calculated)	Meptyldinocap (sum, follow. hydr.)	Difluoroacetic acid (DFA)	Cyhalothrin (sum)	Sum
2				1*													1
13						1											1
15							1			1							2
27				1*													1
46			1														1
52									1								1
53				1													1
54			1														1
58						1	1										2
59											1		1	1			3
60								1									1
67					1												1
71		1															1
72						1				1							2
75	1																1
78									1								1
80						1											1
84					1												1
87			1														1
89																1	1
94	1																1
96											1						1
104				1*													1
108				1													1
111						1											1
114					1	1											2
124									1								1
125			1			1						1					3
127								1									1
132									1*								1
134		1*															1
137						1									1		2

False positives / False reporting Details

FALSE POSITIVES

EU+EFTA

8 x FP for 6 Compulsory Analytes (thereof 2x FR)

Compulsory Analytes	No. of FPs/FRs	Lab-Code	Conc. [mg(kg]	MRRL [mg(kg]	RL [mg(kg]	Judgement
2,4-D (free acid)	1	76	0.007	0.01	0.025	FR (result < RL)
Captan	2	39	0.0276	0.01	0.01	FP
		89	0.033	0.01	0.01	FP
Captan (sum)	2	39	0.0276	0.03	0.03	FR (result < RL)
		89	0.033	0.03	0.03	FP
Chlormequat-Cl	1	114	0.054	0.01	0.01	FP
Glufosinate	1	72	0.014	0.01	0.01	FP
Mepiquat-Cl	1	114	0.119	0.01	0.01	FP

1x FP for one Optional Analyte

Compulsory Analytes	No. of FPs/FRs	Lab-Code	Conc. [mg(kg]	MRRL [mg(kg]	RL [mg(kg]	Judgement
Amitrole	1	125	0.10	0.01	0.005	FP

False positives / False reporting

EU+EFTA

6 labs reported 9 numerical results for analytes not present in test material.

Therein …2 “false reporting” (result < RL) marked with ‡

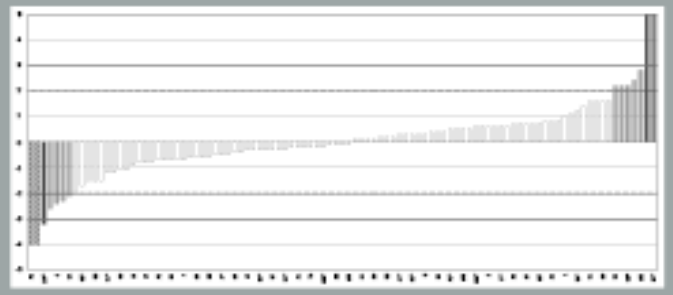
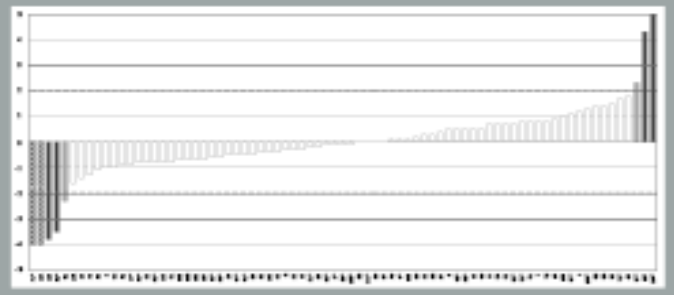
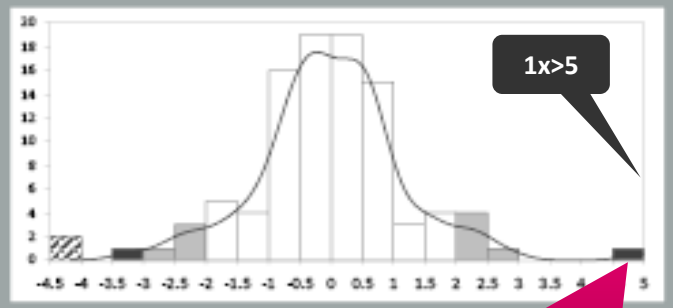
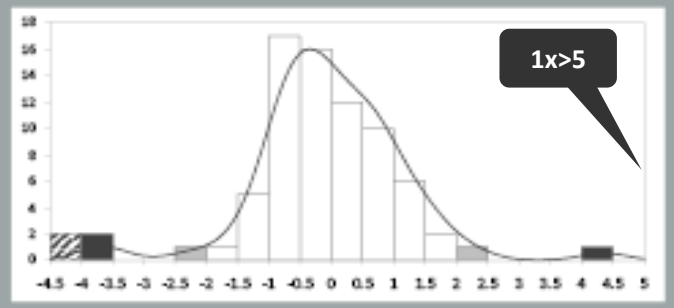
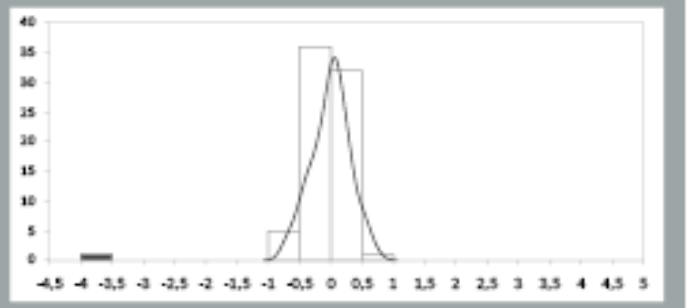
1x captan (sum)
1x 2,4-D (free acid)

Lab-Code	2,4-D (free acid)	Captan	Captan (sum)	Chlormequat-Cl	Glufosinate	Mepiquat-Cl	Amitrole	Sum
39		1	1‡					1
72					1			1
76	1‡							0
89		1	1					2
114				1		1		2
125							1	1

Consequential FPs

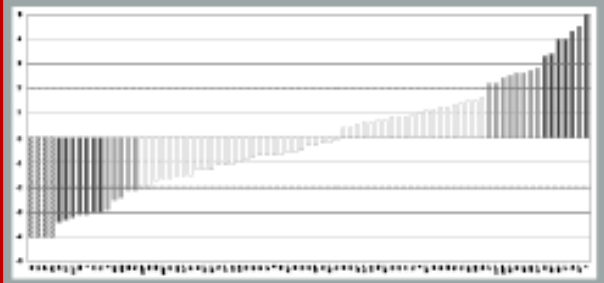
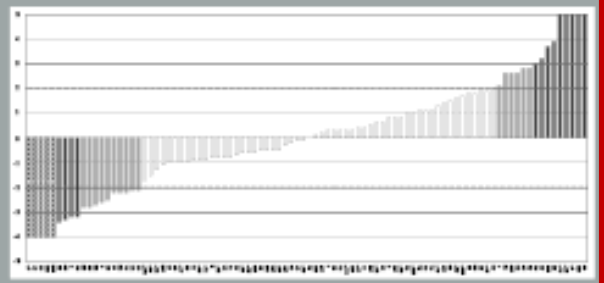
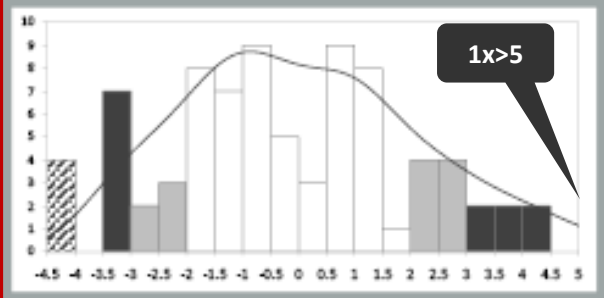
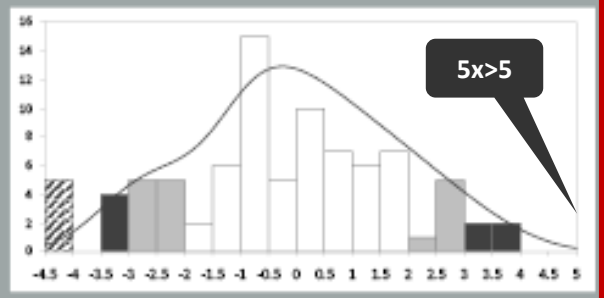
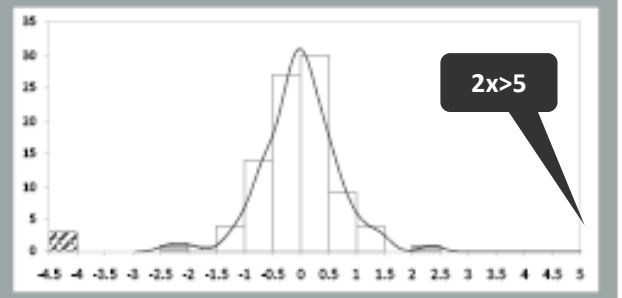
RESULTS OVERVIEW

Results Overview

Analyte	Avermectin B1a	Clopyralid	Copper
Histogram of z scores			
Kernel Density of z-scores			
No. of numerical results	97	75	75
Outlier(s)	1	1	1
False negatives	2	2	0
AV based on	Whole population excl. outliers	Whole population excl. outliers	Whole population excl. outliers
AV [mg/kg]	0.071	0.192	29.9
CV*	24.6%	23.4%	7.7%
MRRL [mg/kg]	0.01	0.01	0.20
UAV Test	passed	passed	passed

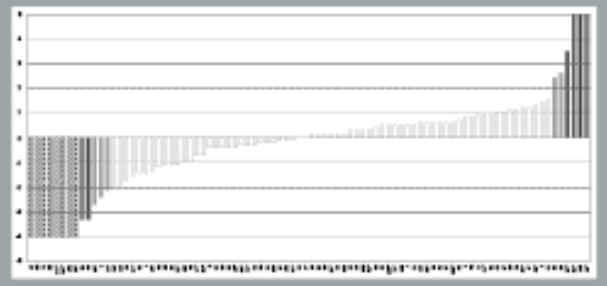
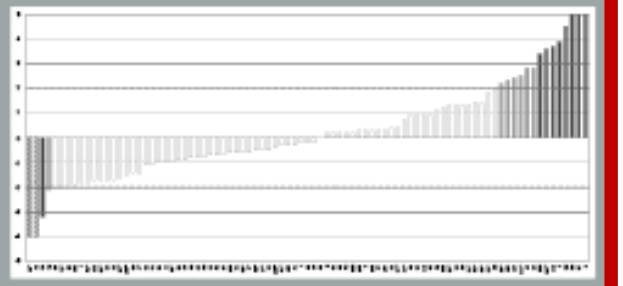
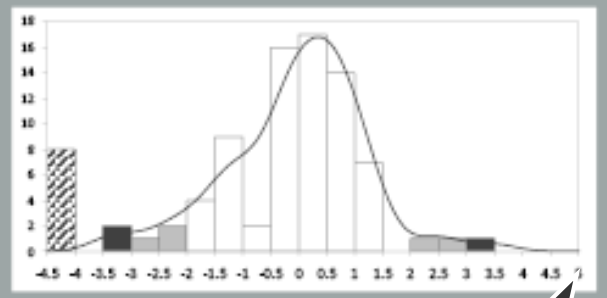
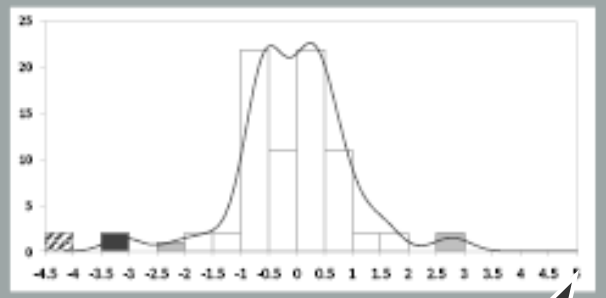
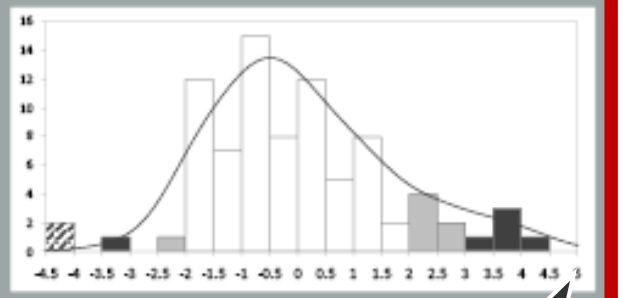
This Lab reported issues w. Standard purity (confirmed by EURL-SRM)

Results Overview

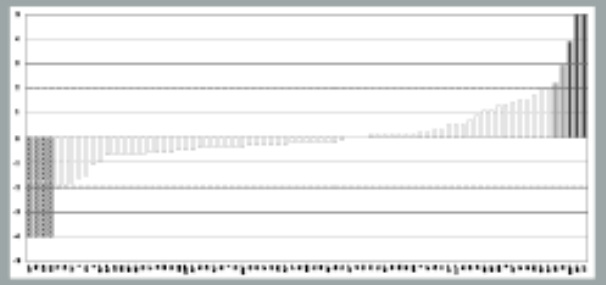
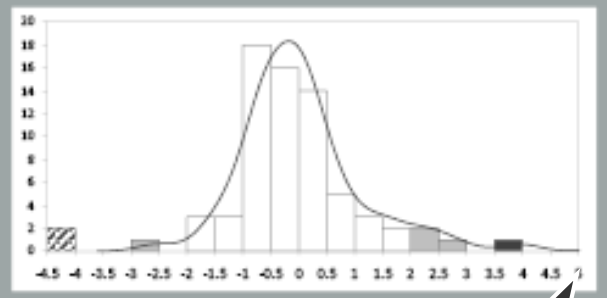
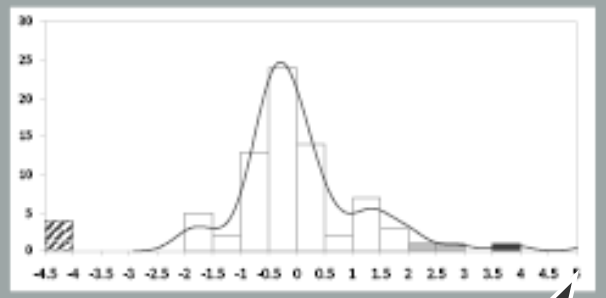
Analyte	Dithianon	DTCs (expr. as CS_2)	Ethephon
Histogram of z scores			
Kernel Density of z-scores			
No. of numerical results	77	87	93
Outlier(s)	0	5	2
False negatives	4	5	3
AV based on	Whole population excl. outliers	Whole population excl. outliers	Whole population excl. outliers
AV [mg/kg]	0.181	0.068	0.058
CV*	54.6%	46.7%	14.7%
MRRL [mg/kg]	0.01	0.01	0.01
UAV Test	failed	passed	passed

EURL-SRM

Results Overview

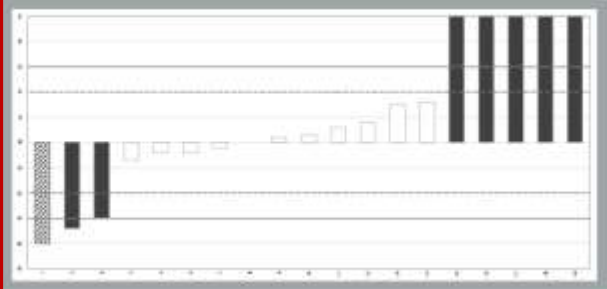
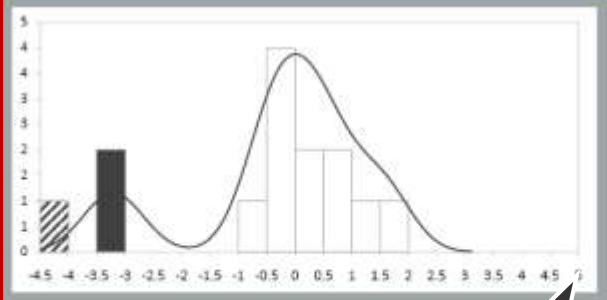
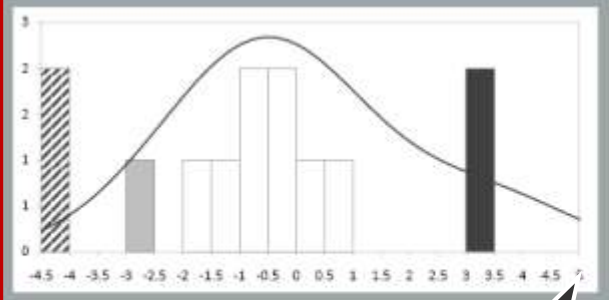
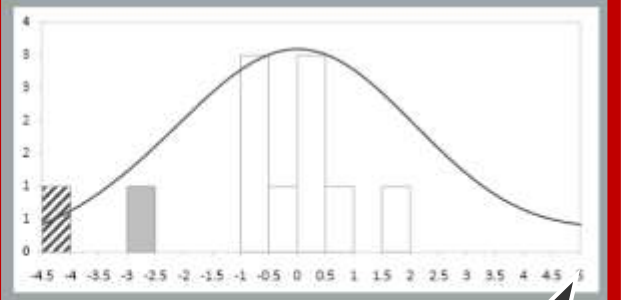
Analyte	Folpet	Folpet (sum calc.)	Phthalimide
Histogram of z scores			
Kernel Density of z-scores	 3x>5	 2x>5	 3x>5
No. of numerical results	80	81	85
Outlier(s)	3	3	3
False negatives	8	2	2
AV based on	Whole population excl. outliers	Whole population excl. outliers	Whole population excl. outliers
AV [mg/kg]	0.225	0.421	0.106
CV*	26.8%	18.4%	38.3%
MRRL [mg/kg]	0.01	0.03	0.01
UAV Test	passed	passed	passed

Results Overview

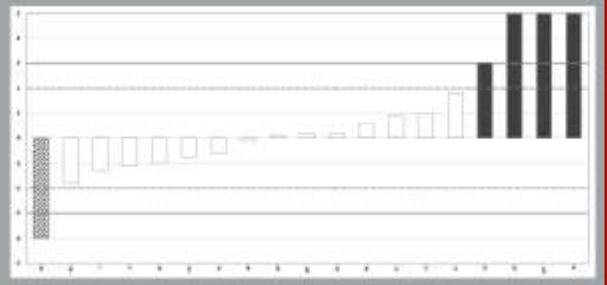
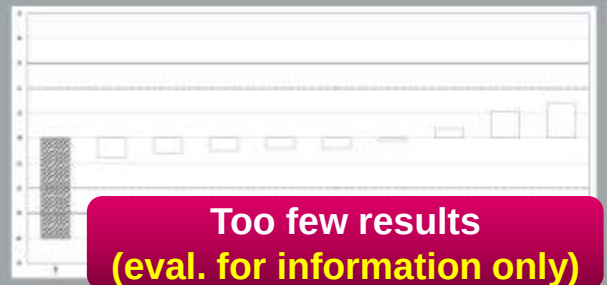
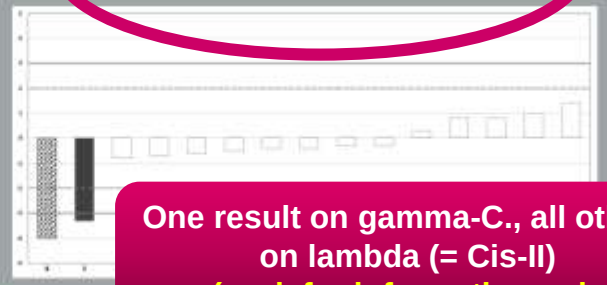
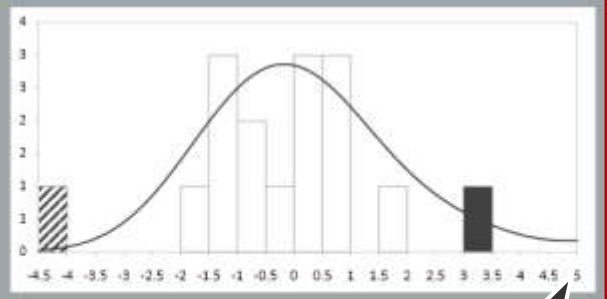
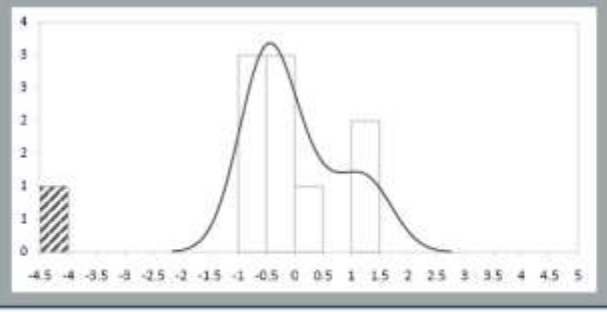
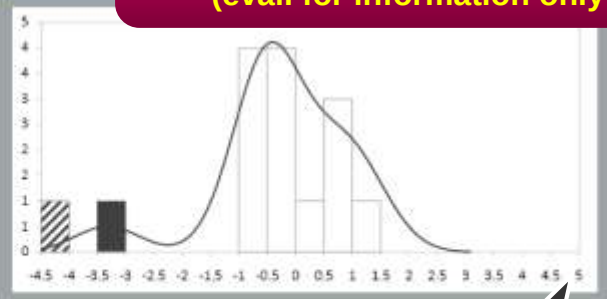
Analyte	MPP	N-Acetyl glufosinate
Histogram of z scores		
Kernel Density of z-scores	 4x>5	 2x>5
No. of numerical results	73	75
Outlier(s)	2	1
False negatives	2	4
AV based on	Whole population excl. outliers	Whole population excl. outliers
AV [mg/kg]	0.082	0.077
CV*	22.8%	21.9%
MRRL [mg/kg]	0.01	0.01
UAV Test	passed	passed

EURL-SRM

Results Overview

Analyte	Meptyldinocap	Meptyldinocap m. 2,4-DNOP	Meptyldinocap (sum calc.)
Histogram of z scores			
Kernel Density of z-scores			
No. of numerical results	18 (5x>5)	12 (1x>5)	13 (3x>5)
Outlier(s)	5	1	3
False negatives	1	2	1
AV based on	Whole population excl. outliers	Whole population excl. outliers	Whole population excl. outliers
AV [mg/kg]	0.086	0.065	0.150
CV*	29.6%	46.9%	23.4%
MRRL [mg/kg]	0.01	0.01	0.02
UAV Test	failed	failed	failed

Results Overview

Analyte	Mep. (sum fol. hydrolysis)	Difluoroacetic acid (DFA)	Lambda Cyhalothrin
Histogram of z scores			
Kernel Density of z-scores			
No. of numerical results	18	9	14
Outlier(s)	3	0	1
False negatives	1	1	1
AV based on	Whole population excl. outliers	Whole population excl. outliers	Whole population excl. outliers
AV [mg/kg]	0.188	0.146	0.0773
CV*	30.9%	21.7%	20.5%
MRRL [mg/kg]	0.01	0.02	0.01
UAV Test	failed	failed	passed

3x>5

3x>5

Too few results
(eval. for information only)

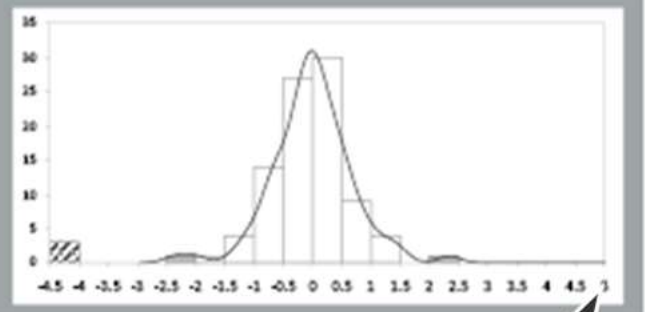
One result on gamma-C., all others on lambda (= Cis-II)
(eval. for information only

Actual Spiking
Gamma: 0.061
isomer: 0.026
SUM: 0.087

Closer LOOK on individual Analytes

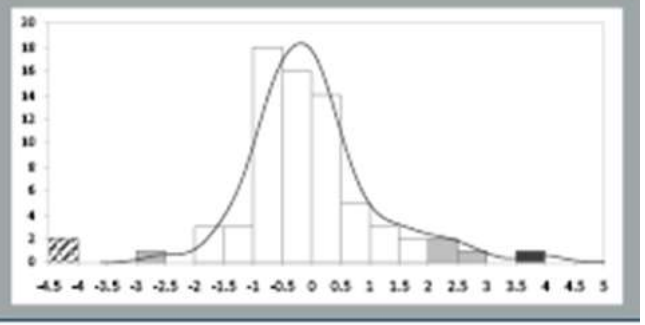
QuPPe - Compounds

Impact of using ILIS on Accuracy

Analyte	Ethephon
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	93
Outlier(s)	2
False negatives	3
AV based on	Whole population excl. outliers
AV [mg/kg]	0.058
CV*	14.7%
MRRL [mg/kg]	0.01
UAV Test	passed

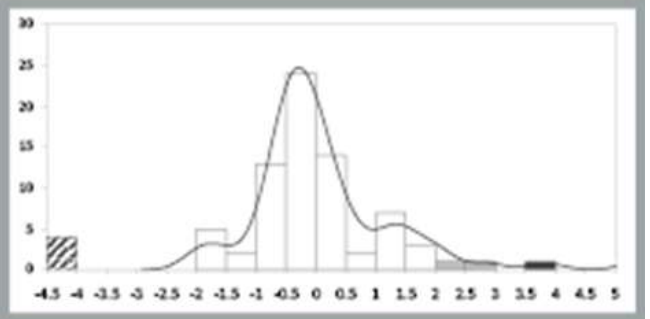
Ethephon	ILIS-Yes	ILIS-No
Results (n=)	55	38
Median	0.0590	0.0565
Robust Mean	0.0589	0.0578
CV*	**9.4%**	**24.9%**

Impact of using ILIS on Accuracy

Analyte	MPP
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	73
Outlier(s)	2
False negatives	2
AV based on	Whole population excl. outliers
AV [mg/kg]	0.082
CV*	22.8%
MRRL [mg/kg]	0.01
UAV Test	passed

MPP (=aka MPPA)	ILIS-Yes	ILIS-No
Results (n=)	28	45
Median	0.0807	0.0826
Robust Mean	0.0105	0.0117
CV*	**17.8%**	**32.3%**

Impact of using ILIS on Accuracy

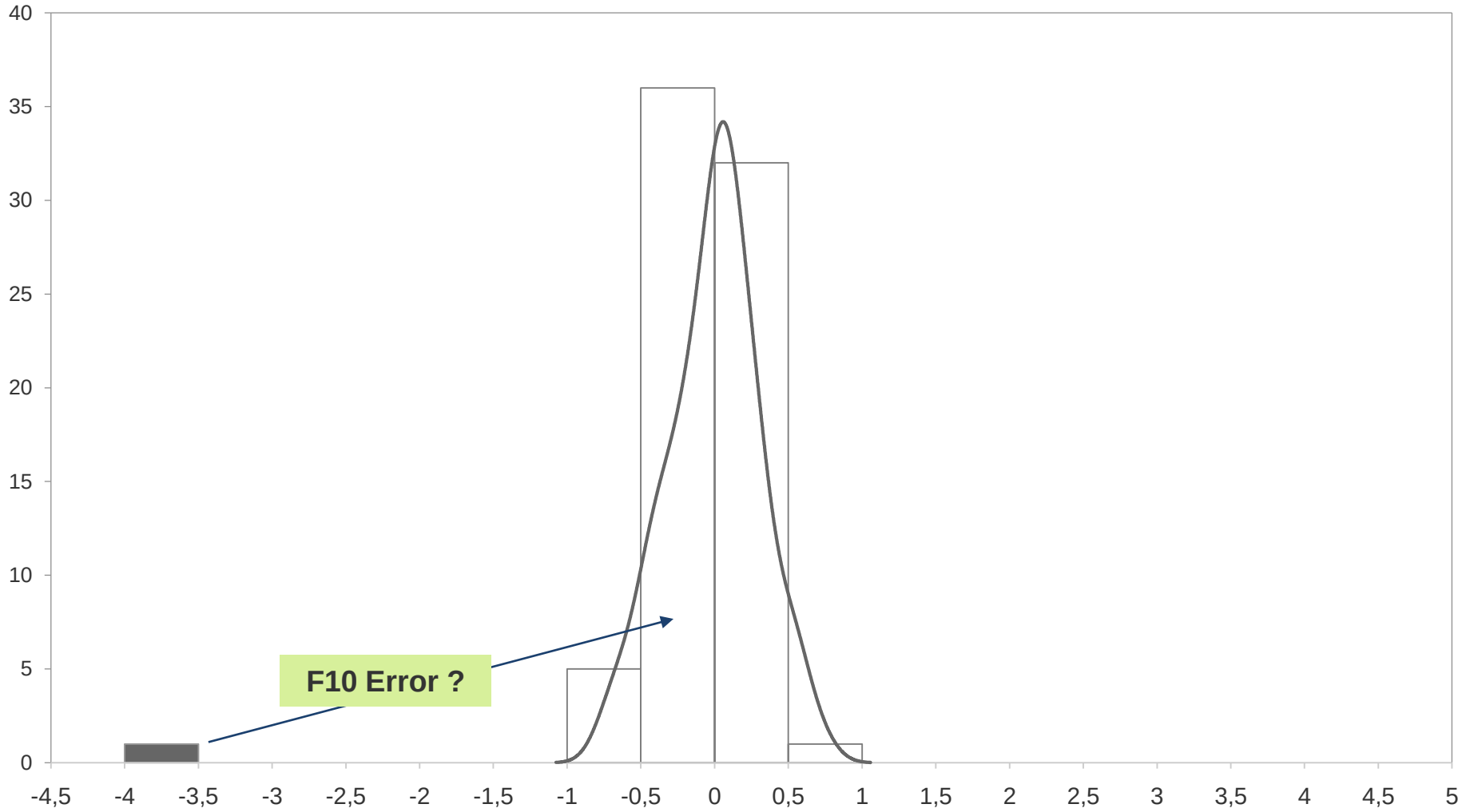
Analyte	N-Acetyl glufosinate
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	75
Outlier(s)	1
False negatives	4
AV based on	Whole population excl. outliers
AV [mg/kg]	0.077
CV*	21.9%
MRRL [mg/kg]	0.01
UAV Test	passed

N-Acetyl glufosinate	ILIS-Yes	ILIS-No
Results (n=)	32	43
Median	0.0775	0.0721
Robust Mean	0.0771	0.0785
CV*	**13.5%**	**30.8%**

COPPER

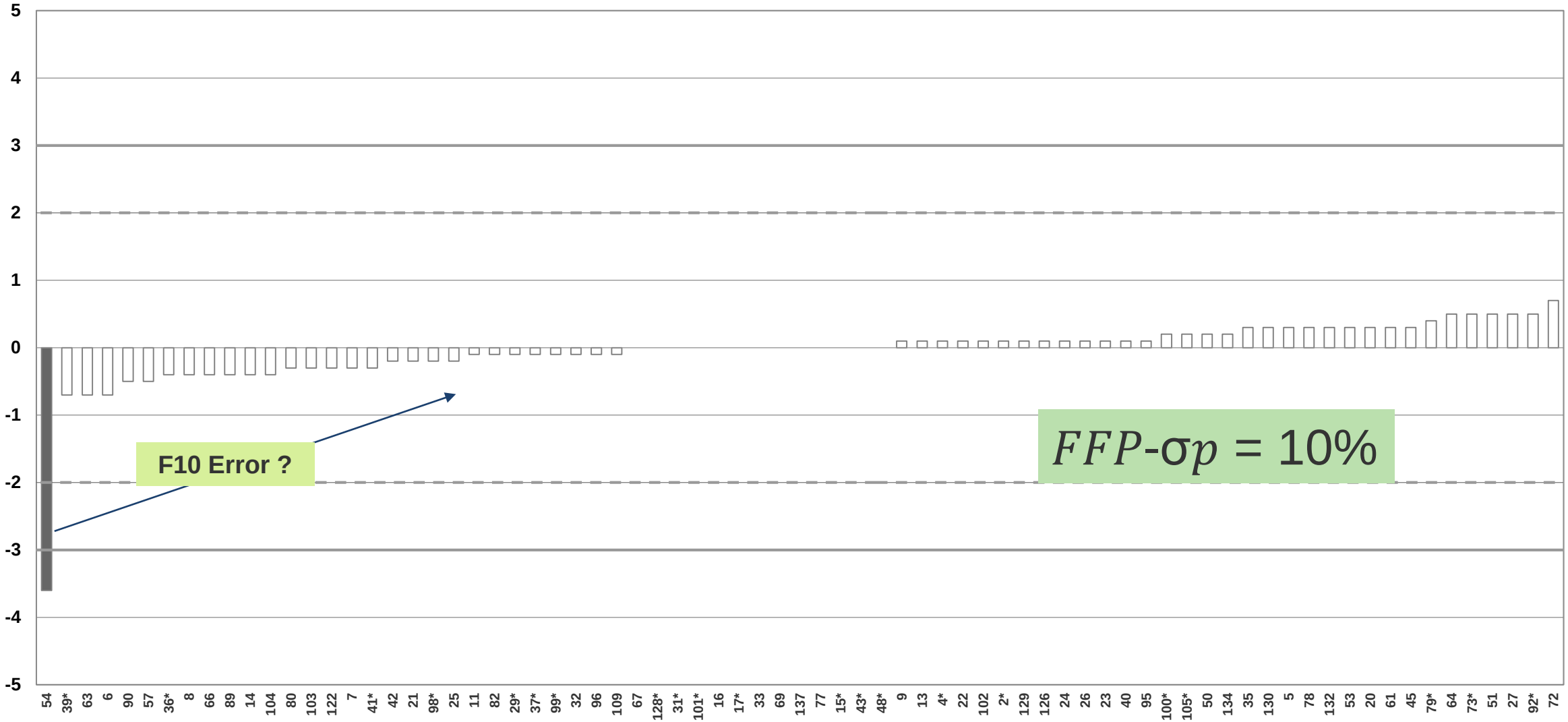
Results Overview

Copper



Results Overview

Copper



Expanded MU Reported by Labs

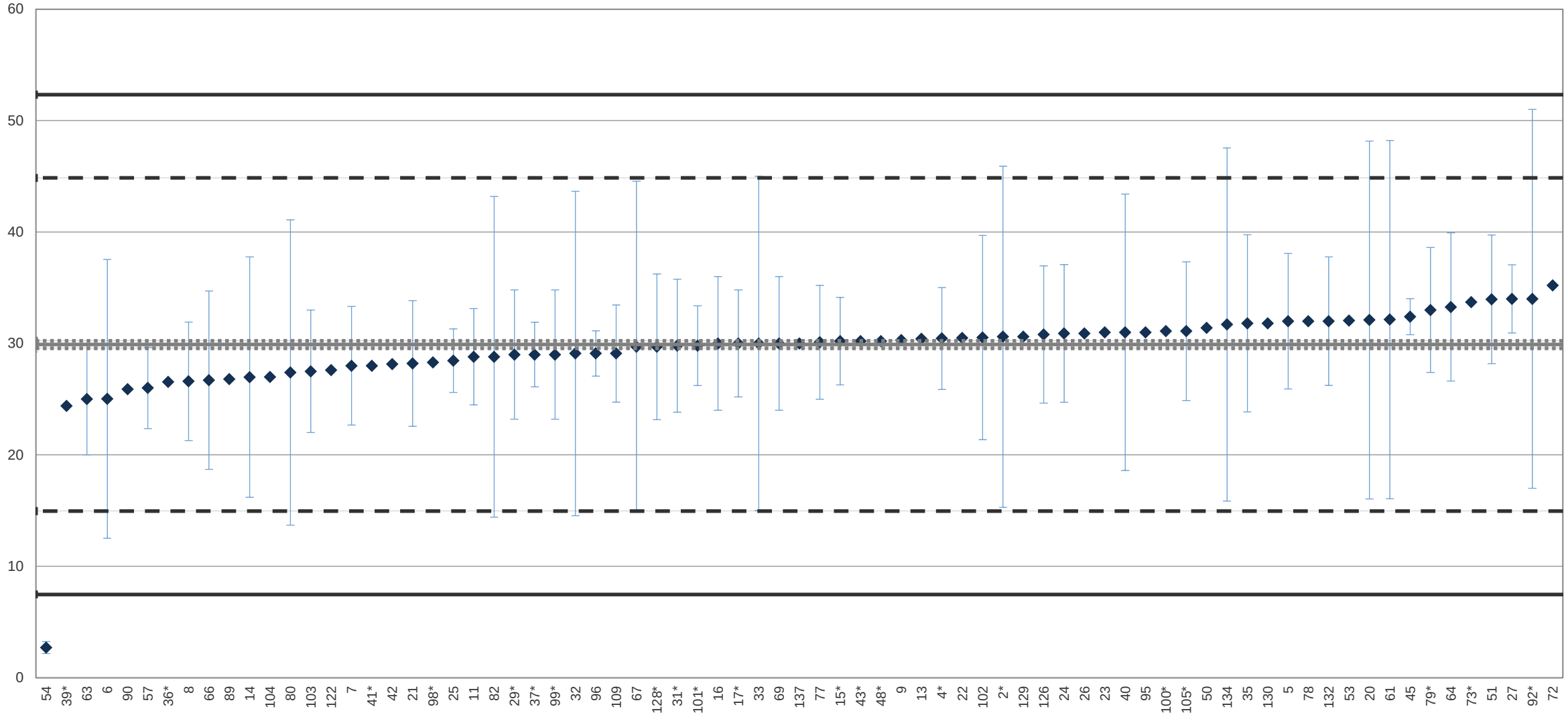
MU %	2,4-DNOP (phenol)	Abamectin B1a	Clopyralid	Cu	DFA	Dithianon	DTC (as CS2)	Ethephon	Folpet	Folpet (sum)	Gamma Cyhalothrin	Meptyl-dinocap	Meptyl-dinocap (sum, calc.)	Meptyl-dinocap (sum hydr.)	MPP (=aka MPPA)	N-Acetyl glufosinate	Phthalimide	Gesamtergebnis
2		1																1
3				1		1	1											3
4								1										1
5				1														1
7				1												1		2
9				2													1	3
10		1		2		1									1			5
12		1		1											1			3
13				1														1
14				1			1									1		3
15				3								1						4
16				1														1
17				3														3
18	1	1	1	2				1	1	1	1			1		1	1	12
19				2														2
20		**1**	**1**	**14**		**1**	**2**	**1**	**1**	**1**				**1**	**2**	**2**	**1**	**28**
21				2														2
22				1														1
25		2	2	3		1	1	1	1		1							12
26							1											1
27																	1	1
28			1															1
29						1												1
30		1	1	2		1	3	2	1	1					2	2	1	17
35							2	1							1	2		6
40				2		1	1											4
42							1											1
45							1											1
47															1			1
48								1										1
50	**8**	**62**	**44**	**11**	**3**	**45**	**50**	**57**	**49**	**49**	**10**	**10**	**9**	**10**	**44**	**45**	**49**	**555**
Gesamtergeb	9	70	50	56	3	52	64	65	53	52	12	11	9	12	52	54	54	678
20% MU	0%	1%	2%	**25%**	0%	2%	3%	2%	2%	2%	0%	0%	0%	8%	4%	4%	2%	
50% MU	89%	89%	88%	**20%**	100%	87%	78%	88%	92%	94%	83%	91%	100%	83%	85%	83%	91%	

Questionably low expanded MUs

Median MU

Results Overview

Copper



Copper

Could be errorneous, due to „Copy Method“ function in Webtool

MU %	All Data		Excluding 50% MU	
	N	calc. basis N=56	N	calc. basis N=45
≤ 20%	35	63%	35	78%
≤ 25%	41	73%	41	91%
>20%	21	38%	10	22%
>25%	15	27%	4	9%
SUM	56		45	

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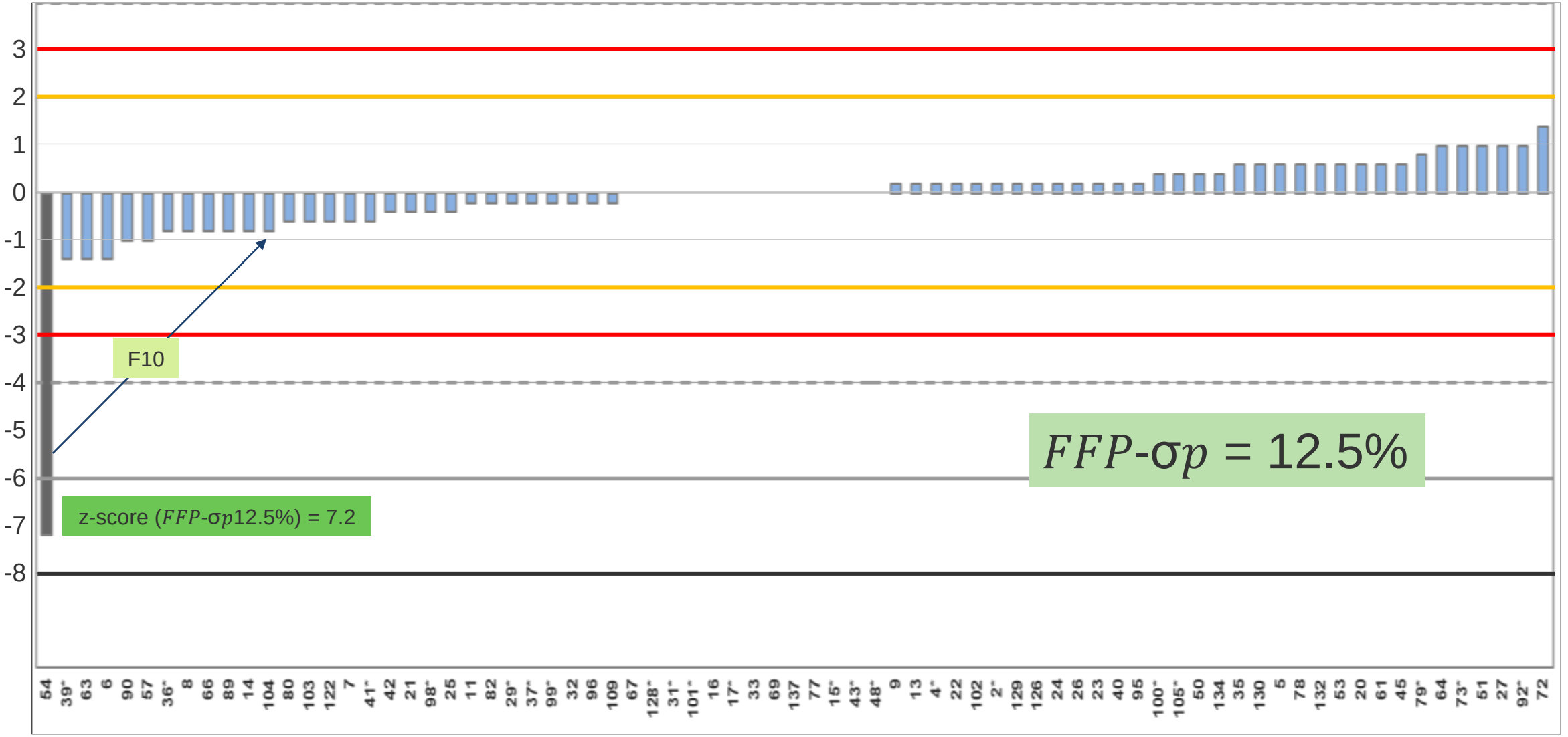
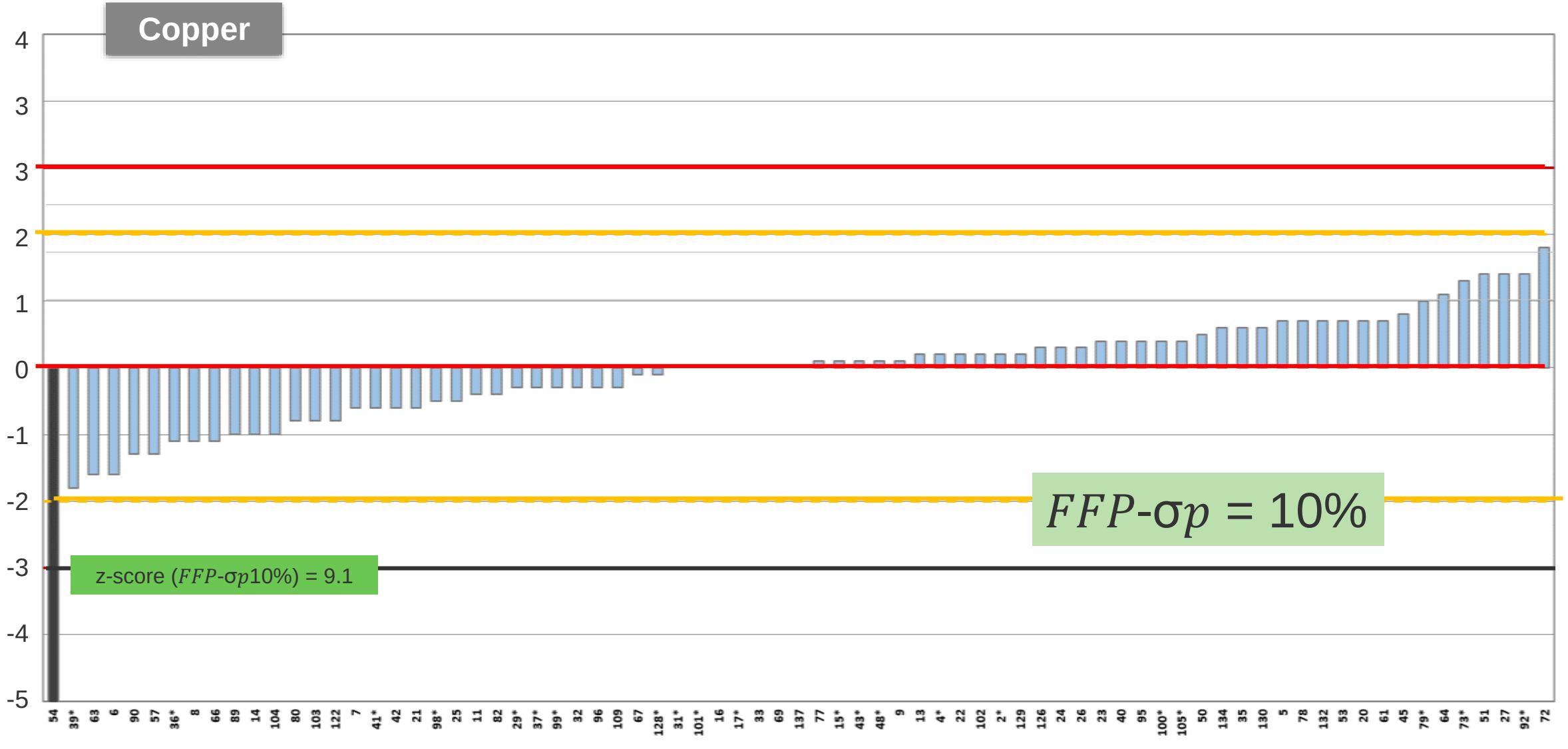
Results Overview using FFP-σp of 12.5%

Copper



Results Overview using FFP-σp of 10%



Overview of EUPT-Results from the Contaminants Sector

PT	Matrix	Assigned value (mg/kg)	Robust PT RSD %	Target RSD % (Horwitz)
2019-02	Liver	392	5,7	6,6
2020-02	Cocoa	31,1	5,4	9,6
2021-03	Feed pellets	4,72	16,3	12,6

The AdvG agreed to **introduce a FFP-Expanded MU for Copper** in the next revision of the **AQC-Document**. This FFP-MU is to be **derived from multiple PT data** (from various PT providers) according to the **top-down approach**.

Based on a preliminary evaluation, a **FFP-Target Std Dev. of 10%** along with a **20% FFP-MU** seem to be adequate figures for Copper in Food and Feed.

DITHIANON

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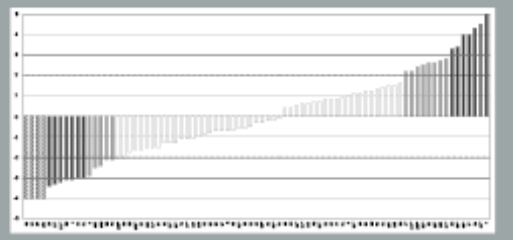
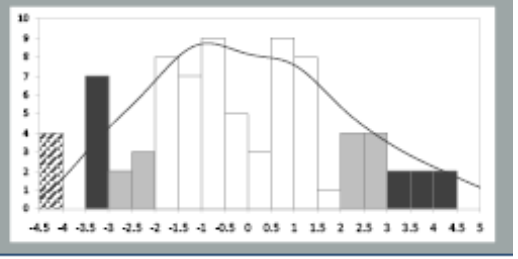
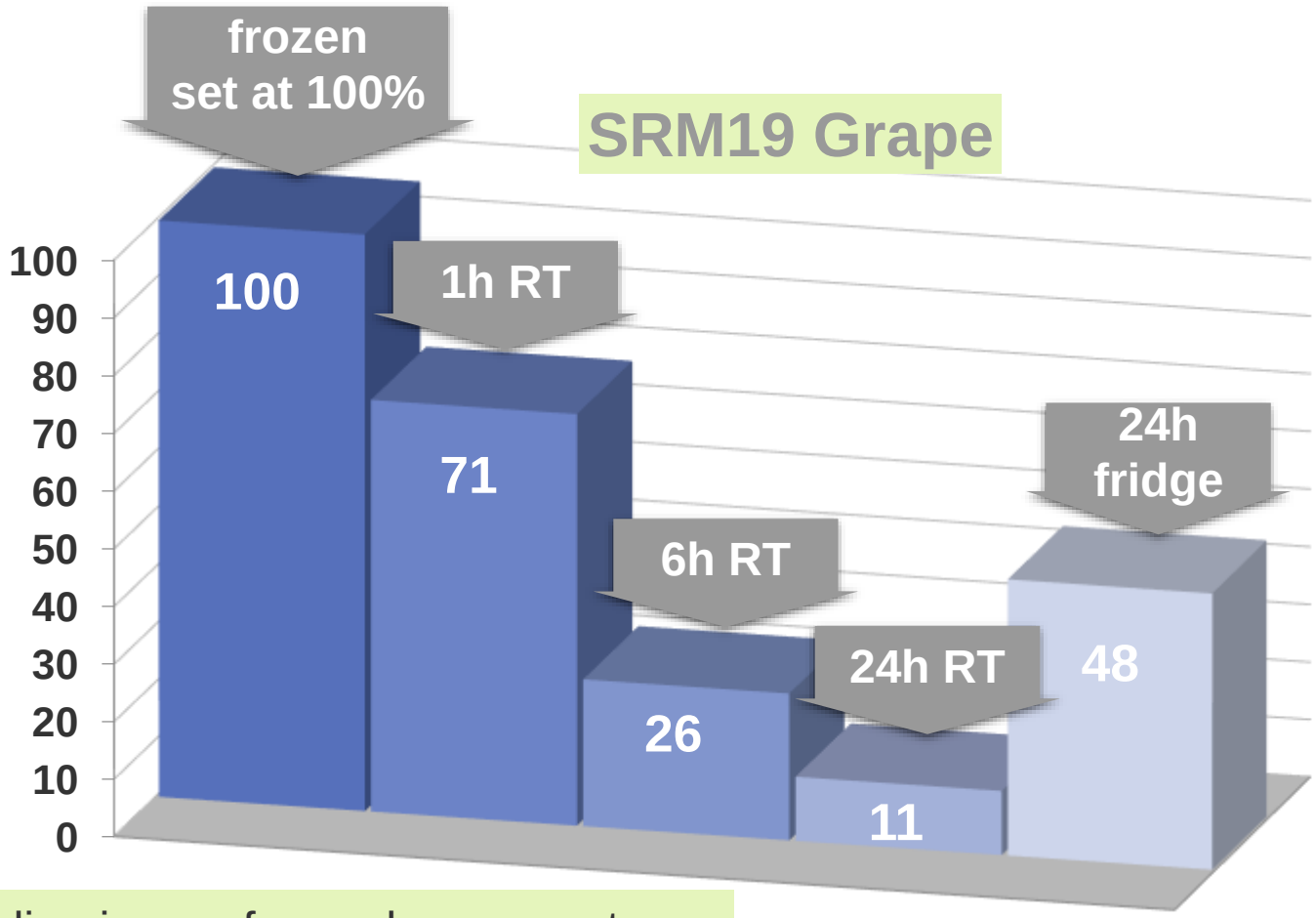
Dithianon

Analyte	Dithianon
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	77
Outlier(s)	0
False negatives	4
AV based on	Whole population excl. outliers
AV [mg/kg]	0.181
CV*	54.6%
MRRL [mg/kg]	0.01
UAV Test	failed

Impact of Sample Treatment on Dithianon Stability



Message: Dithianon degrades when left standing in non-frozen homogenates.
Great care needed to minimize degradation ► Keep Sample Frozen !!

European Commission
EURL-SRM
EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

SRM-13

EURL-SRM - Analytical Observations Report

concerning the following…

- **Compound(s)**: Dithianon, Dithianon D4
- **Commodities**: Fruit and vegetables, cereals
- **Extraction Method(s)**: QuEChERS, QuEChERS (variations)
- **Instrumental analysis**: LC-MS/MS, ESI (neg.)

Analysis of Dithianon by the QuEChERS Method - Impact of pH on recovery rates

Version 2.1 (last update: 09.05.2016)

Background information / Initial Observations:

Using QuEChERS (EN 15662), dithianon often shows low or variable recovery rates from various commodities. Especially from commodities exhibiting high natural pH, recoveries are often very low. In acidic commodities recoveries are typically acceptable (see examples in Table 1). However, cleanup with PSA also leads to low recoveries.

Dithianon Losses in non-frozen Homogenates

Extraction Method	IS	Delay between spiking native dithianon and spiking of ILIS	Delay between spiking native dithianon and extraction	Recovery rates [%]						RSD (%)
				1	2	3	4	5	Avg	
QuEChERS + 1 % FA	ILIS	No delay	No delay	118	109	103			110	6,7
	BNPU			67	70	60			66	7,4
QuEChERS + 1 % SA	ILIS	No delay	No delay	114	97	108	98	97	103	7,4
	BNPU			93	79	85	83	79	84	6,9
	ILIS	No delay	ca. 10 min	115	100	94	-	-	103	10,4
	BNPU			73	67	62	-	-	68	8,1
	ILIS	ca. 10 min	ca. 10 min (shortly after ILIS-addition)	57	57	54	-	-	56	3,5
	BNPU			51	49	50	-	-	50	2,3

Already a **10 min delay in extraction leads to considerable losses**
The ILIS will not correct for these losses if added afterwards

delayed ILIS addition leads to losses !

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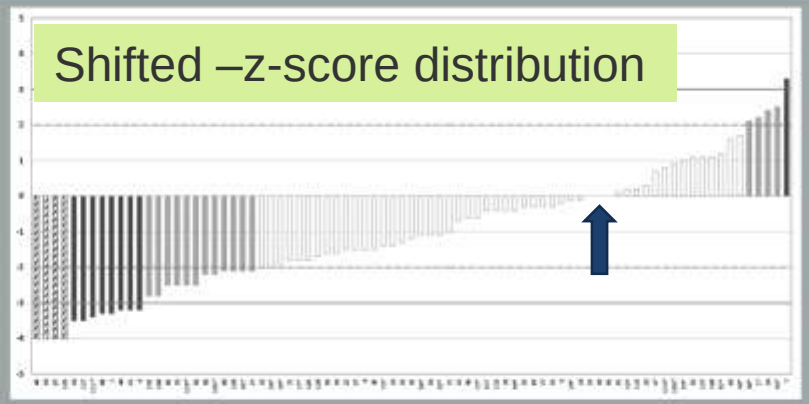
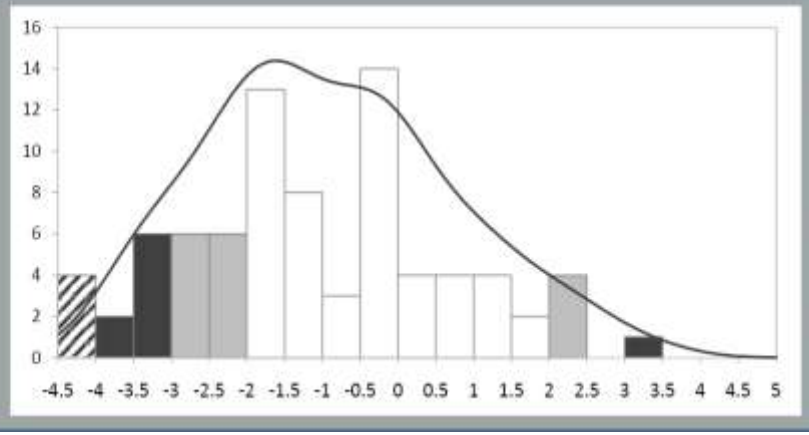
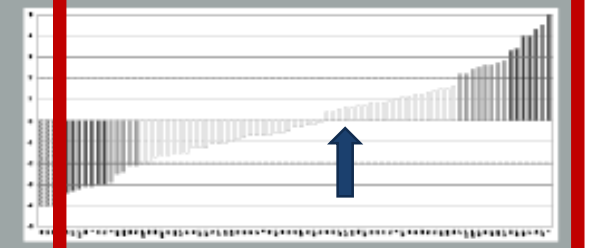
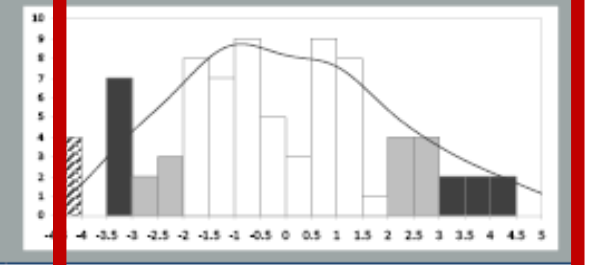
Dithianon

Alternative AV for Dithianon based on Subpopulation employing Protective Conditions (keeping sample frozen prior to extraction)

Analyte	Dithianon
Histogram of z-scores	
Kernel Density of z-scores	
No. of numerical results	40
Outlier(s)	0
False negatives	2
AV based on	40 labs results generated under strong protection
AV [mg/kg]	+30% 0.236
CV*	more narrow 38.1%
MRRL [mg/kg]	0.01
UAV Test	failed

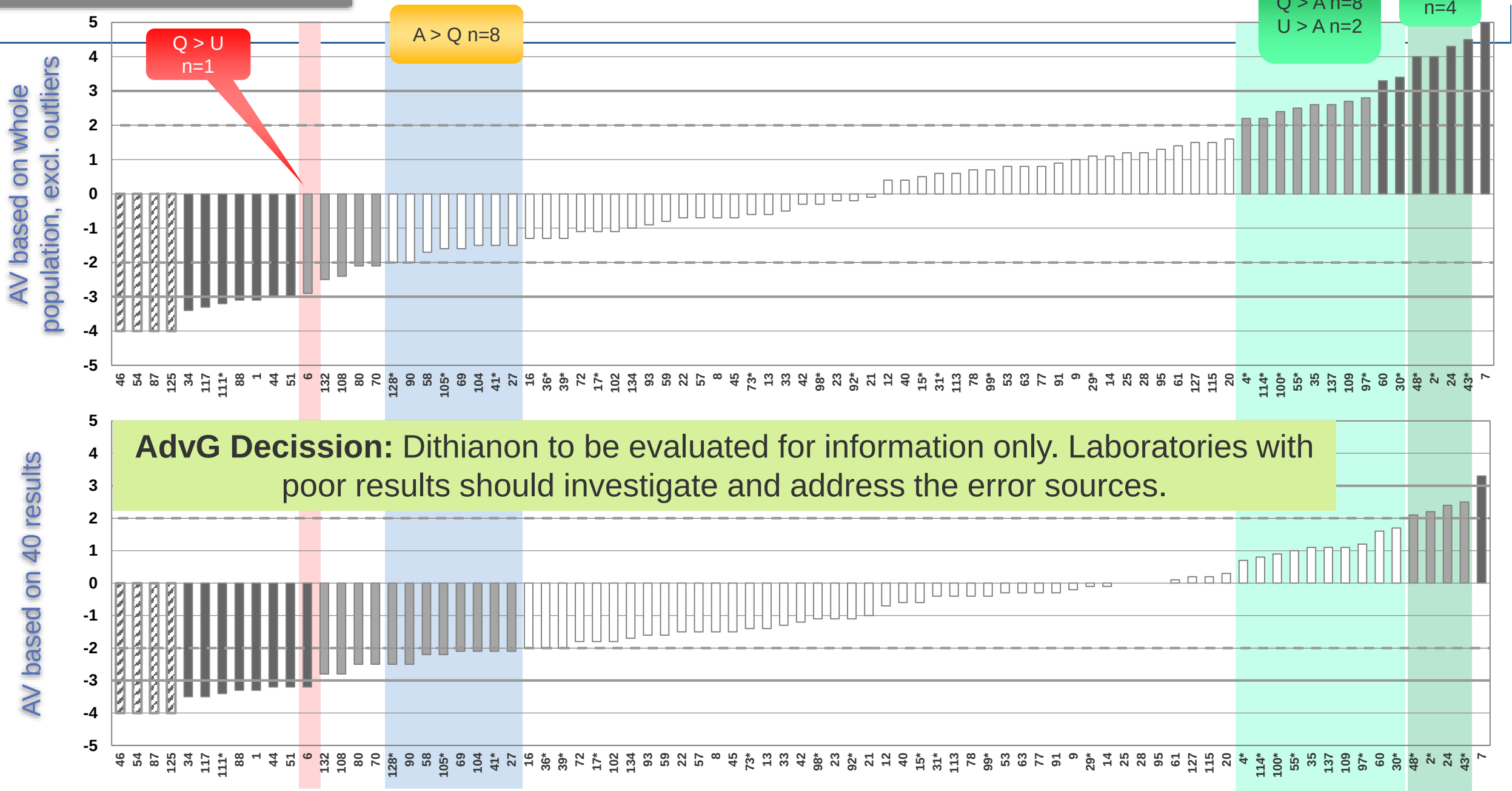
Still failed

Preliminary Evaluation based of whole population of results

Analyte	Dithianon
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	77
Outlier(s)	0
False negatives	4
AV based on	Whole population excl. outliers
AV [mg/kg]	0.181
CV*	54.6%
MRRL [mg/kg]	0.01
UAV Test	failed

Dithianon

Shift of Result Jusgement



AdvG Decission: Dithianon to be evaluated for information only. Laboratories with poor results should investigate and address the error sources.

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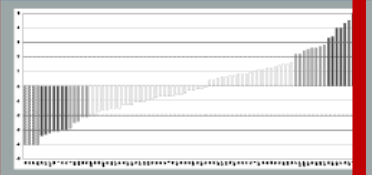
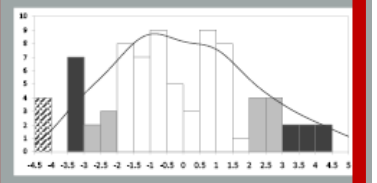
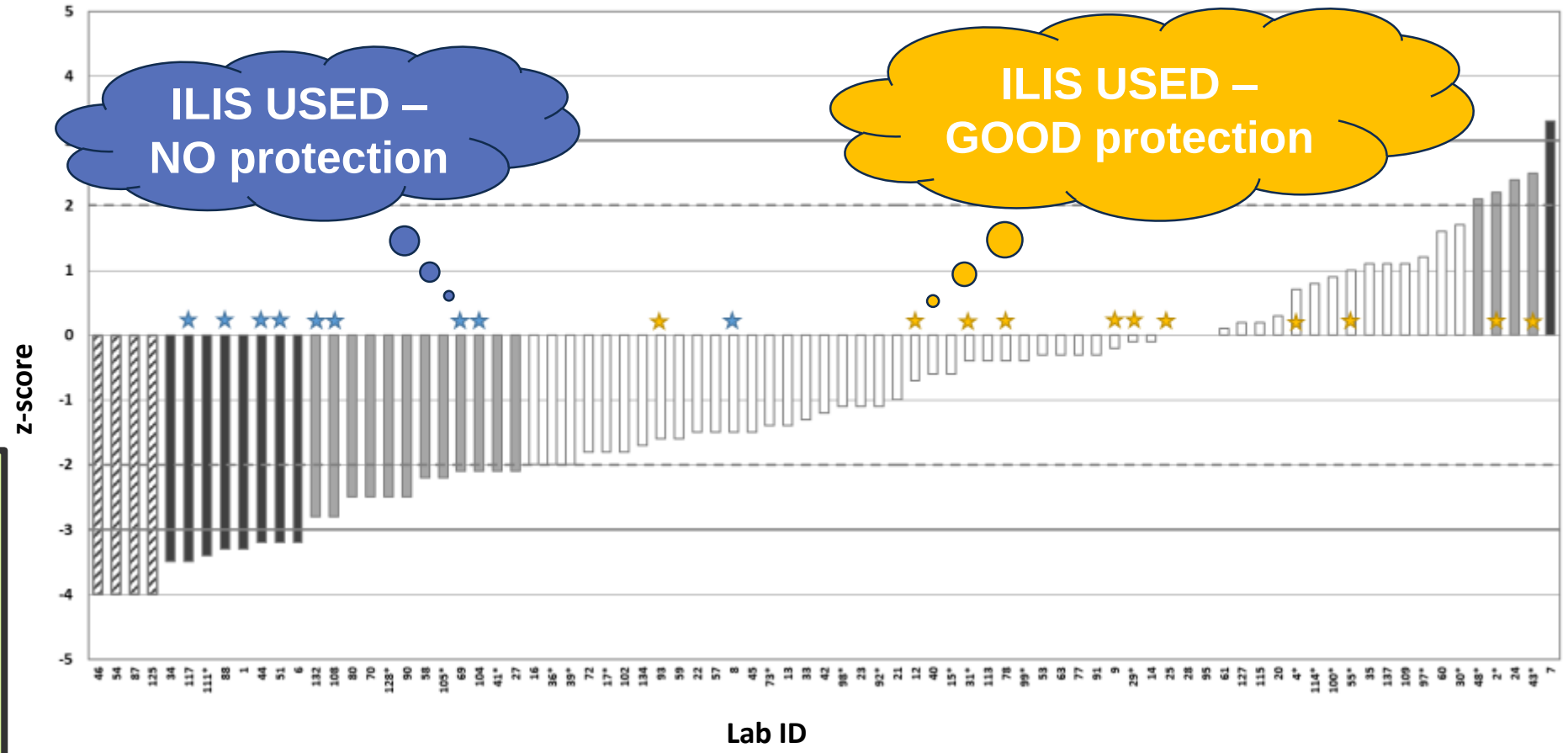
Dithianon

Analyte	Dithianon
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	77
Outlier(s)	0
False negatives	4
AV based on	Whole population excl. outliers
AV [mg/kg]	0.181
CV*	54.6%
MRRL [mg/kg]	0.01
UAV Test	failed

TAKE HOME MESSAGE: ILIS will only correct for losses in steps following its addition.
Any looses priot to its addition are not addressed.

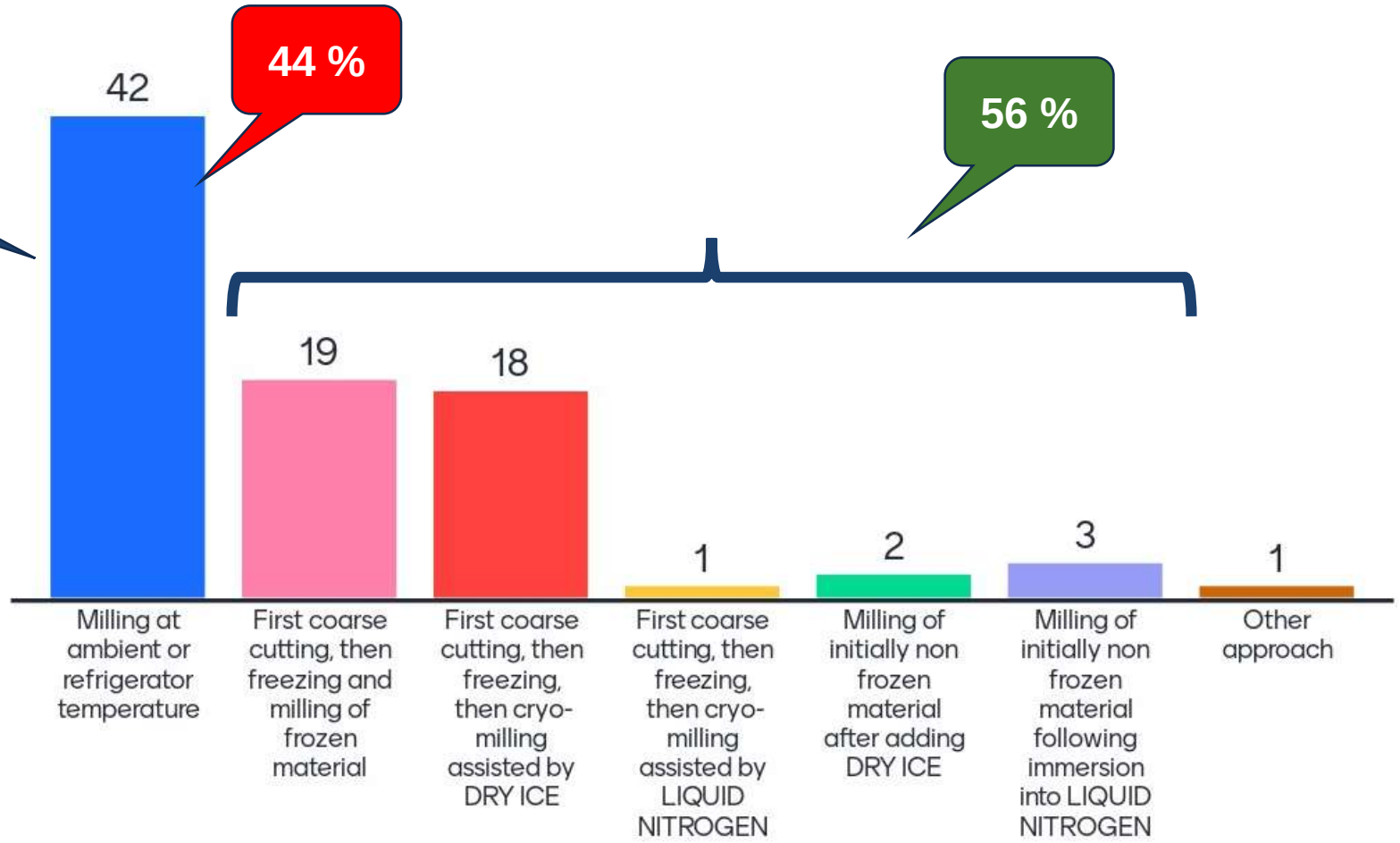
Limitations of ILIS



Joint Workshop-Survey 2023

Which is the MAIN approach your lab follows to HOMOGENIZE FRESH PRODUCE ?

Critical in the case of Dithianon



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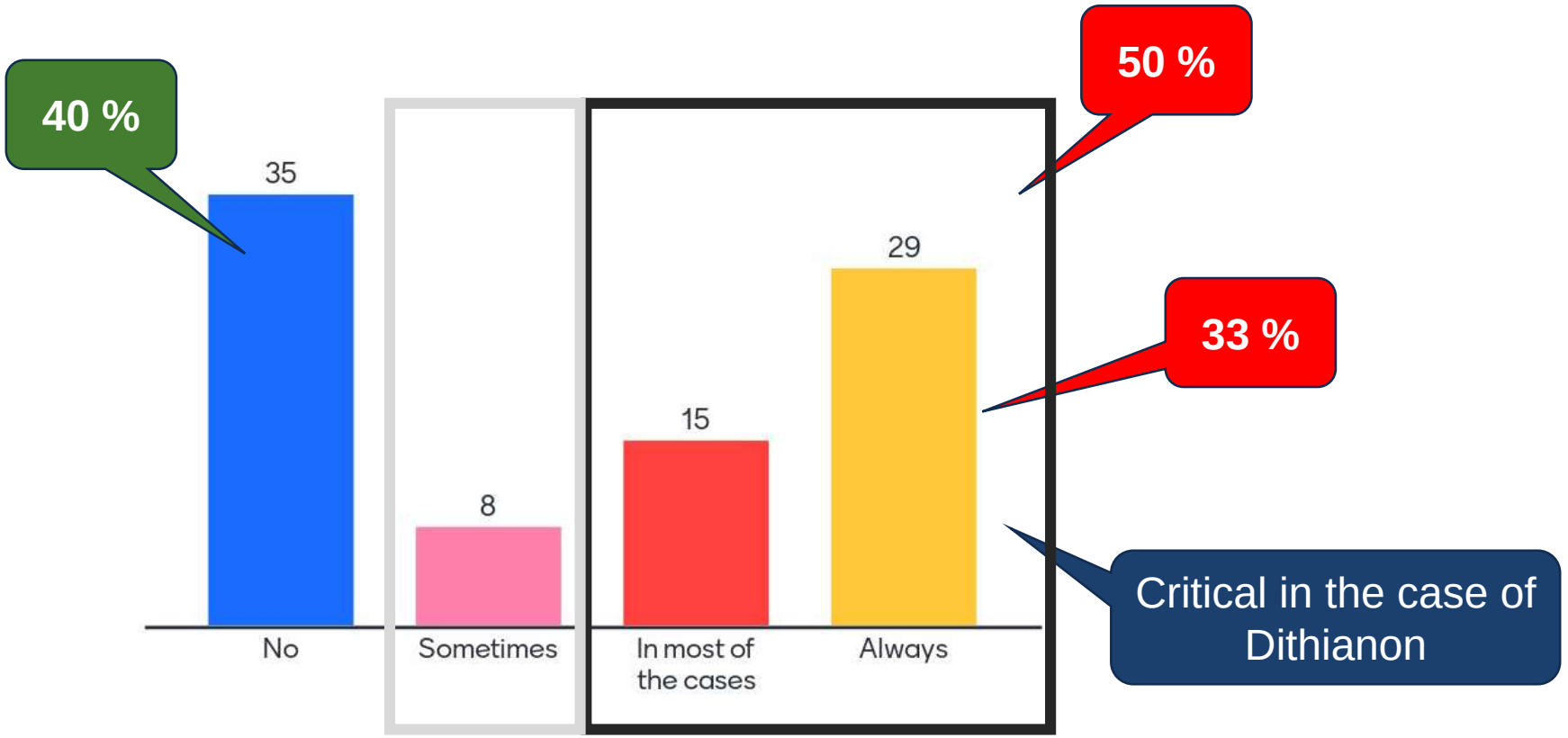
Joint Workshop-Survey 2023

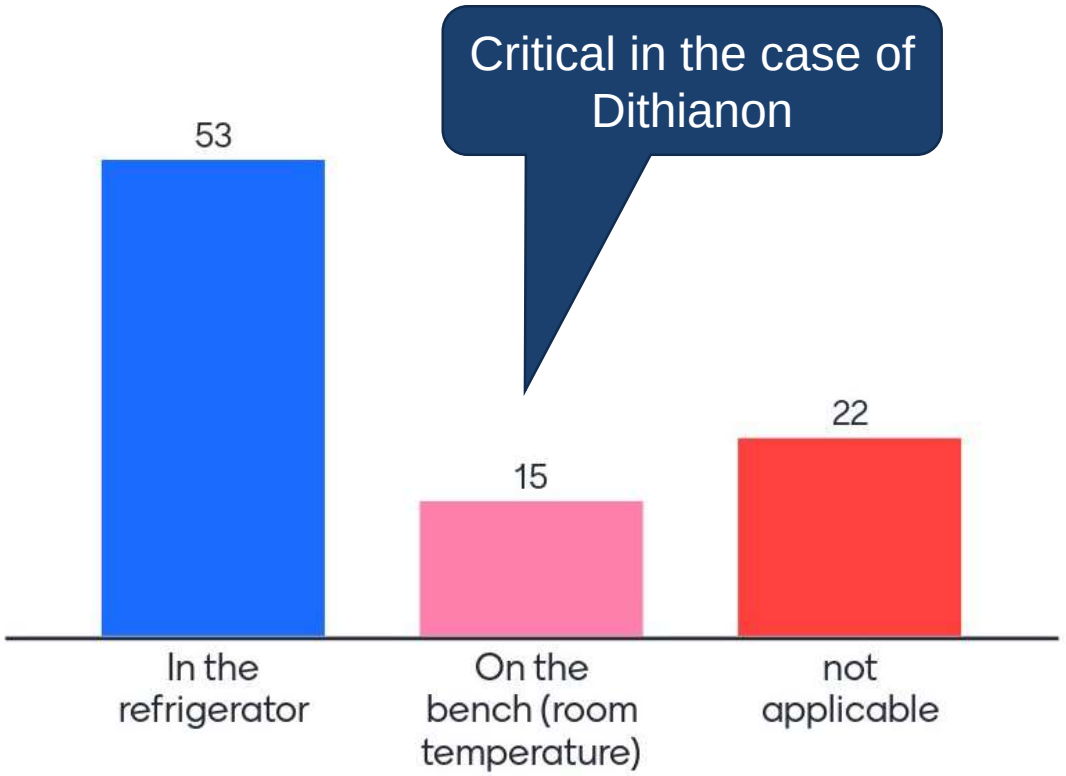
Do you let previously frozen homogenates OF FRESH PRODUCE to DEFROST prior to extraction?



EURL-SRM

Joint Workshop-Survey 2023

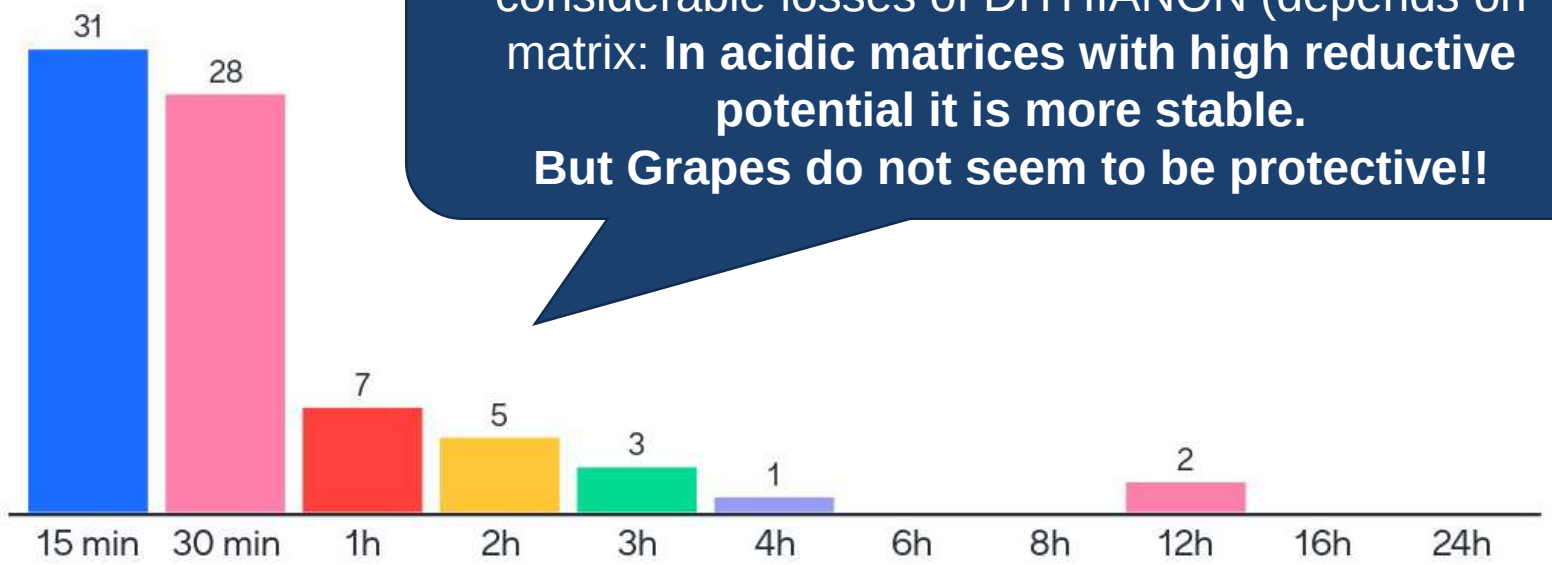
If you leave non-frozen homogenates standing before starting analysis, where do you typically leave them?



Abandoned

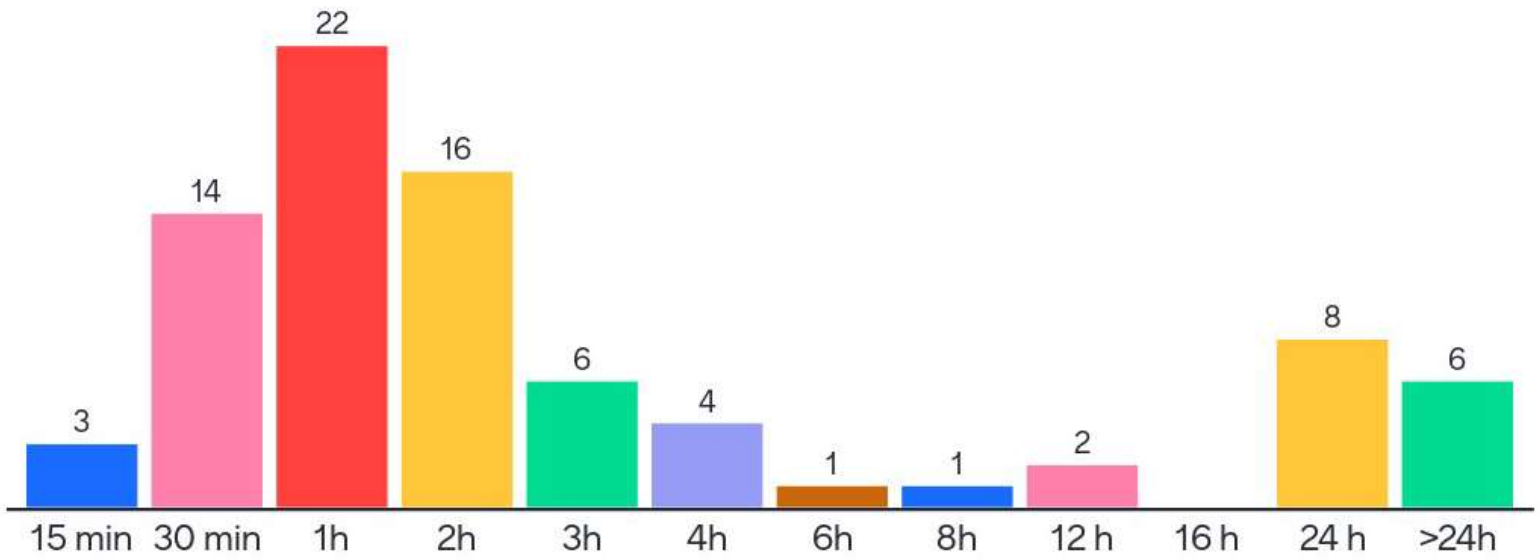
Joint Workshop-Survey 2023

In a TYPICAL CASE, how long do you leave NON-FROZEN HOMOGENATES of fresh produce standing before starting analysis, (chose closest value)



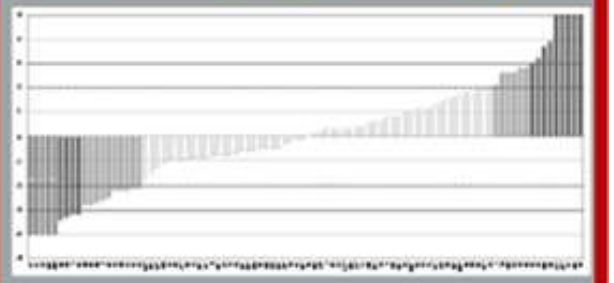
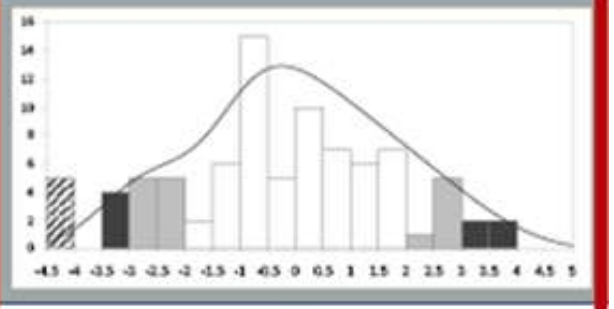
Note: Even a few minutes can make cause considerable losses of DITHIANON (depends on matrix: **In acidic matrices with high reductive potential it is more stable.**
But Grapes do not seem to be protective!!

In a RATHER BAD CASE, how long do you leave NON-FROZEN HOMOGENATES standing before starting analysis, (chose closest value)



DTC

EURL-SRM

Analyte	DTCs (expr. as CS_2)
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	87
Outlier(s)	5
False negatives	5
AV based on	Whole population excl. outliers
AV [mg/kg]	0.068
CV*	46.7%
MRRL [mg/kg]	0.01
UAV Test	passed

Analytical Approaches used by SRM19 Participants

Appoach	No. Labs	% of Labs
LLP (isooctane)	48	47%
Headspace	26	25%
Headspace-SPME	10	10%
Spectroph. (Xanthogenate)	11	11%
Spectroph. (Cu-Acetate)	5	5%
Derivatization + QuEChERS	2	2%
ALL	102	100%

AdvG considers that the **Overall Robust Mean** cannot be used for evaluation as it most propably underestimates the real level of DTC as CS_2

DTCs – Modified Procedure of Reductive Cleavage

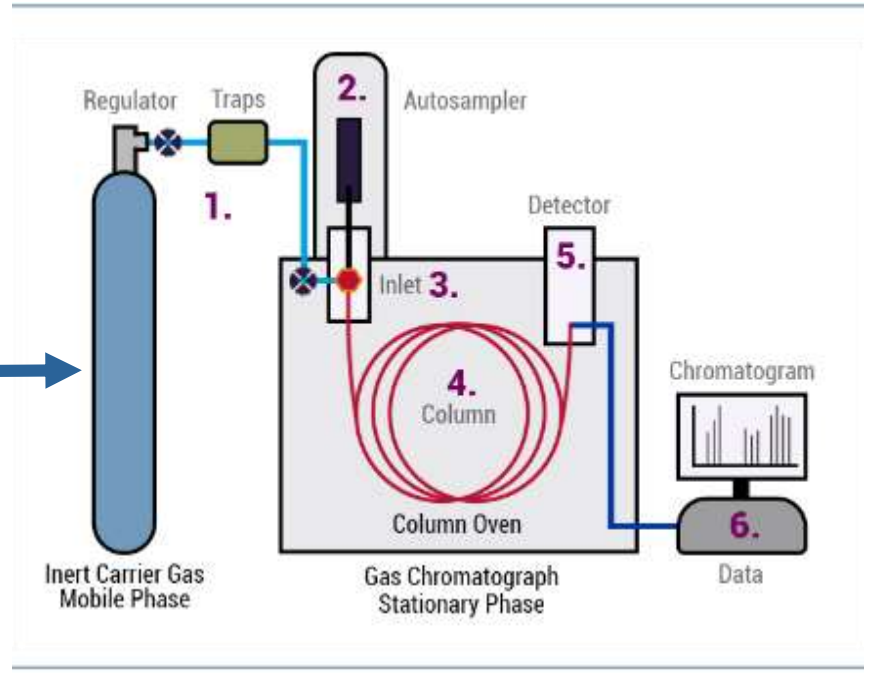
Reductive cleavage with $SnCl_2$/HCl

Former conditions:

50 g of sample homogenate
+**150 mL** hydrolysis agent
(Agent:Sample-Ratio: 3:1)
+ **25 mL** isooctane (2g sample/mL)
→**2 h @ 80 °C** in a water bath

New conditions:

10 g of sample homogenate
+**75 mL** hydrolysis agent
(Agent:Sample-Ratio: 7.5:1)
+ **10 mL** isooctane (1g sample/mL)
→**3 h @ 80-90 °C** in a **water bath or heated shaker**



Hydrolysis agent (0.66 M $SnCl_2$ /4 M HCl)

Preliminary Report Note on DTC (Metiram to CS_2)

Overall, **the experiments have shown that the robust mean value of the entire population of results** (0.0677 mg/kg) **is considerably lower than the actual concentration of DTCs in the EUPT-SRM19 test item.**

Based on a large number of experiments conducted by the EURL-SRM, and taking into account results submitted by participants employing strong reaction conditions, **the EURL-SRM estimates that the actual concentration of DTCs in the test item (expressed as CS_2) is around 0.10 mg/kg.** This value was therefore taken as the **preliminary reference value** and the **preliminary z-scores** in this report were calculated based on this value.

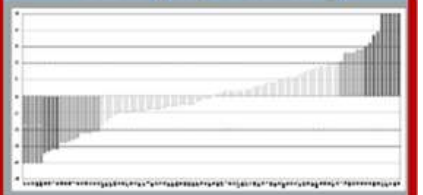
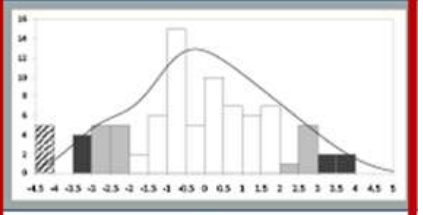
Laboratories having been allocated abs. z scores > 2 for this analyte within this report are requested to seek for the sources of errors and to undertake corrective actions. This information is to be reported in the Poor Performance Surve of the organizer (see page 6).

The decision about the final assigned value, and on whether an official scoring will be allocated to the labs, will be taken following consultations with the EUPT advisory group.

EURL-SRM

DITHIOCARBAMATES

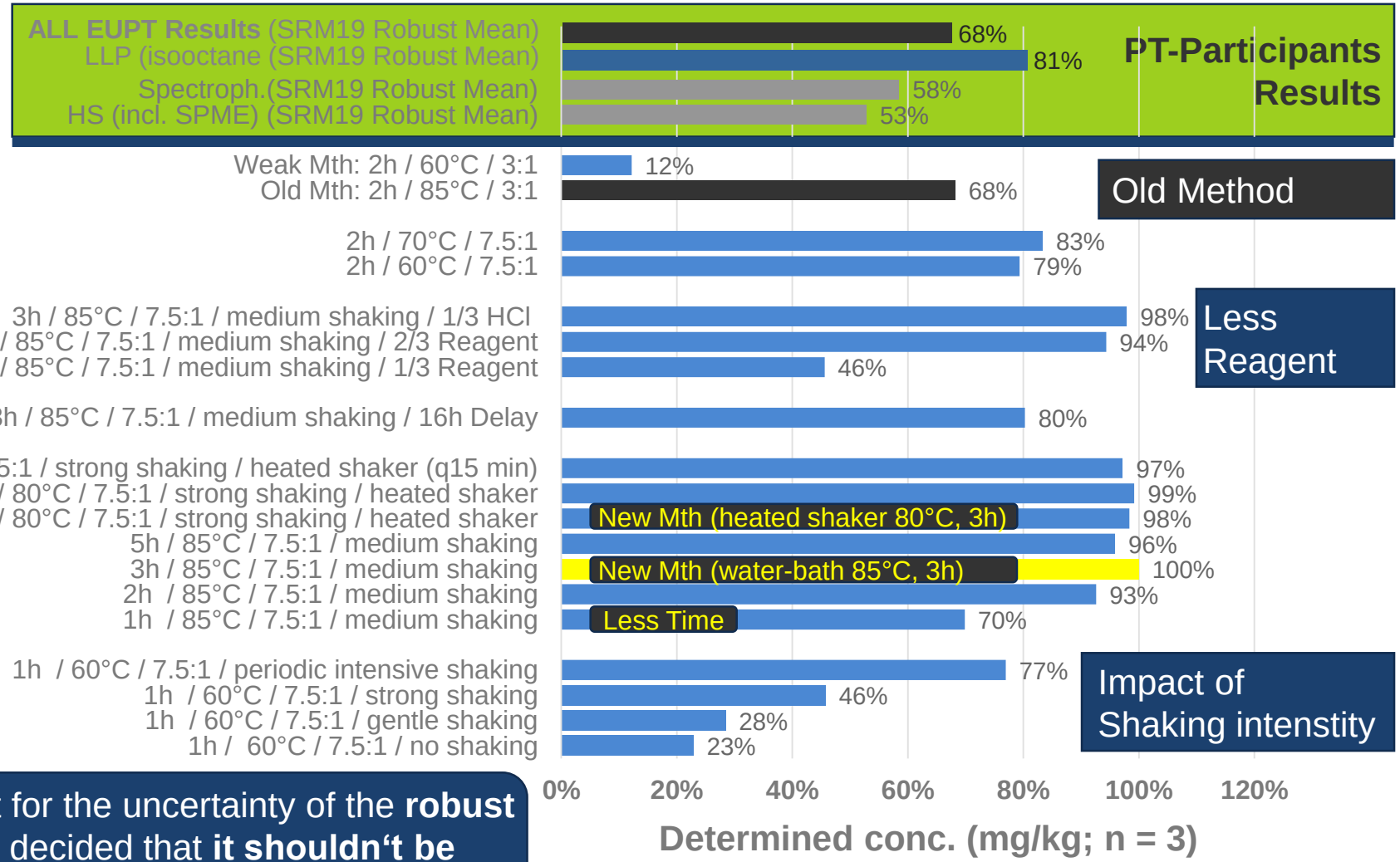
Original Evaluation with biased Robust Mean (underestimated)

Analyte	DTCs (expr. as CS_2)
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	87
Outlier(s)	5
False negatives	5
AV based on	Whole population excl. outliers
AV [mg/kg]	0.068
CV*	46.7%
MRRL [mg/kg]	0.01
UAV Test	passed

Despite the large variation, the statistical test for the uncertainty of the **robust mean passed the threshold**. Still, the AdvG decided that **it shouldn't be used as the AV** for the official EUPT-evaluation of this parameter

EURL-SRM Experiments using SRM19 Material

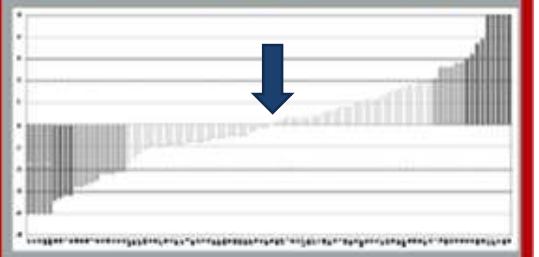
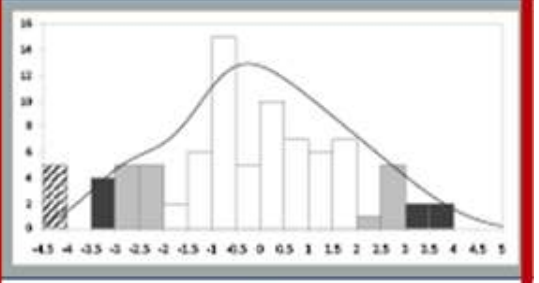
Impact of Sample Treatment on Conversion yields of Metiram to CS_2



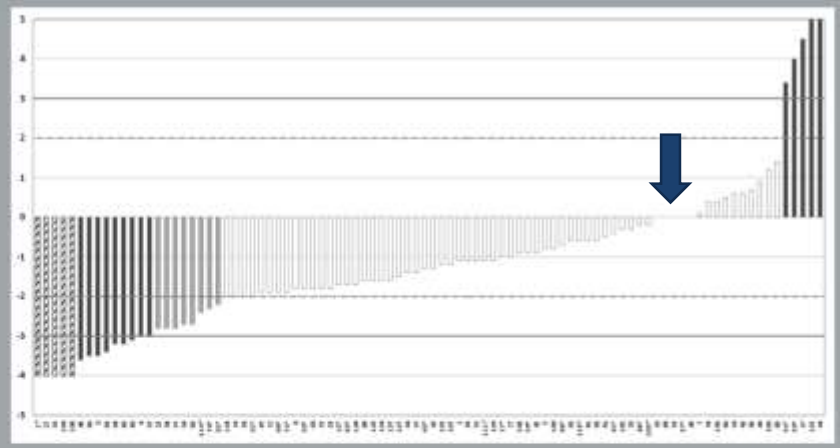
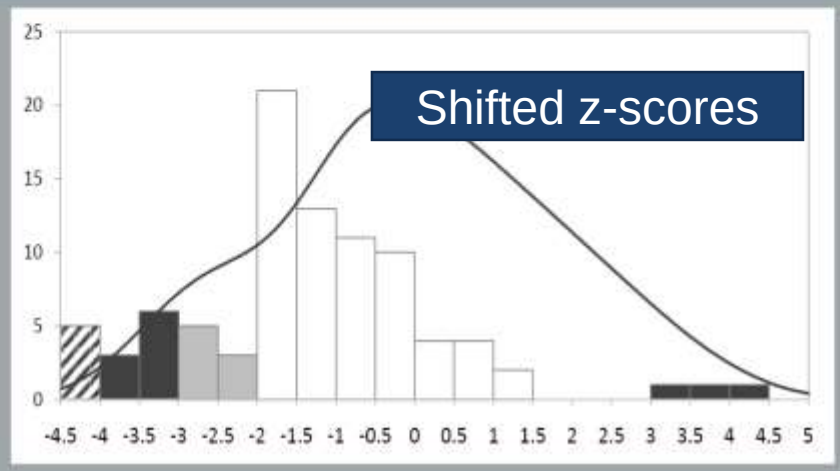
EURL-SRM

Results Overview

Original Evaluation with biased Robust Mean (underestimated)

Analyte	DTCs (expr. as CS_2)
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	87
Outlier(s)	5
False negatives	5
AV based on	Whole population excl. outliers
AV [mg/kg]	0.068
CV*	46.7%
MRRL [mg/kg]	0.01
UAV Test	passed

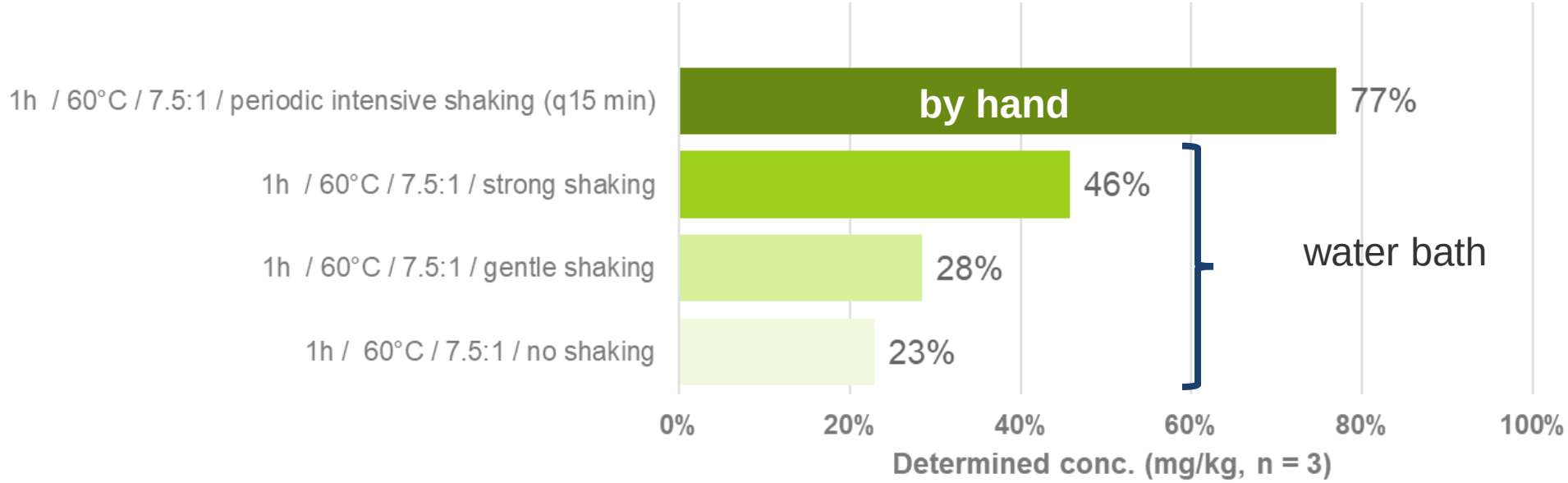
Alternative Reference Value for DTCs Set at 0.1 mg/kg considering all available Info

Analyte	DTCs (expr. as CS2)
Histogram of z-scores	
Kernel Density of z-scores	
No. of numerical results	87
Outlier(s)	-
False negatives	5
AV based on	preliminary reference value
AV [mg/kg]	0.1
CV*	-
MRRL [mg/kg]	0.01
UAV Test	-

Results Overview

Impact of Sample Treatment on Conversion yields of Metiram to CS_2

Impact of SHAKING in Method using LLP to Isooctan

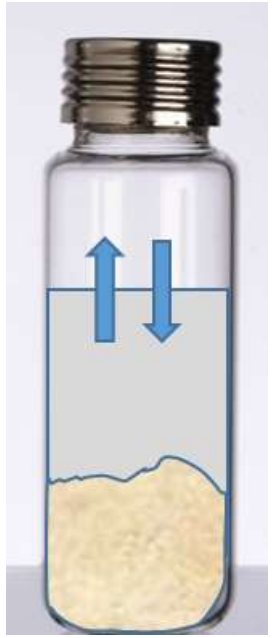


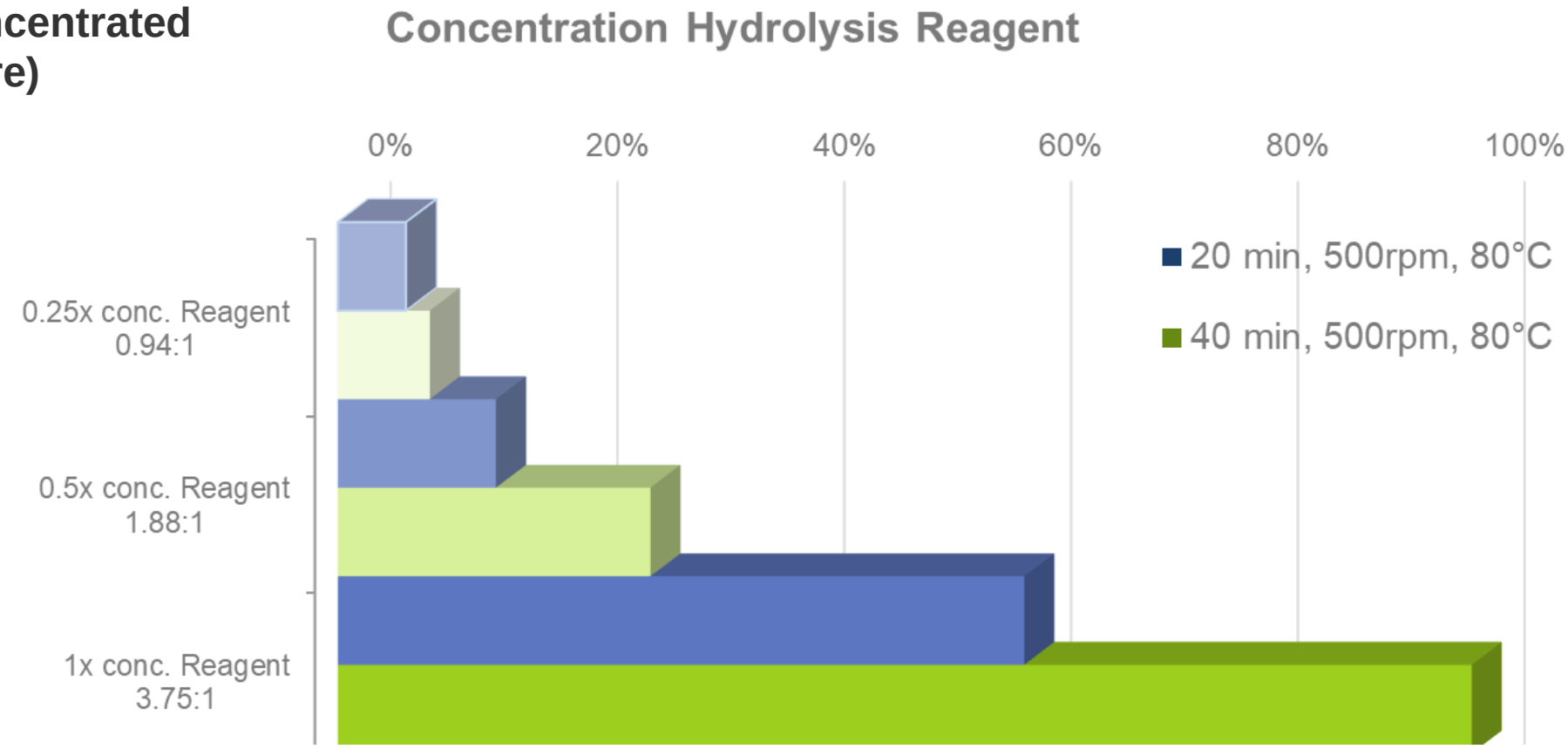
TAKE HOME MESSAGE:
The shaking Intensity plays an important role in the conversion of DTC-polymers to CS_2

Low Reaction Temperature to better highlight the impact of shaking

Headspace Analysis – Impact of Reagent Concentration

3 g Sample + 11,2 mL Reagent
(Reagent double as concentrated as in new LLP procedure)



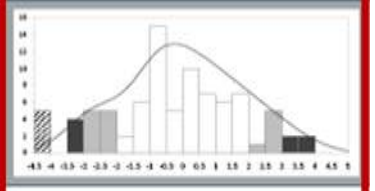


TAKE HOME MESSAGE:
Reagent conc. also plays a role in Headspace analysis

SRM19 Grape, Metiram

EURL-SRM

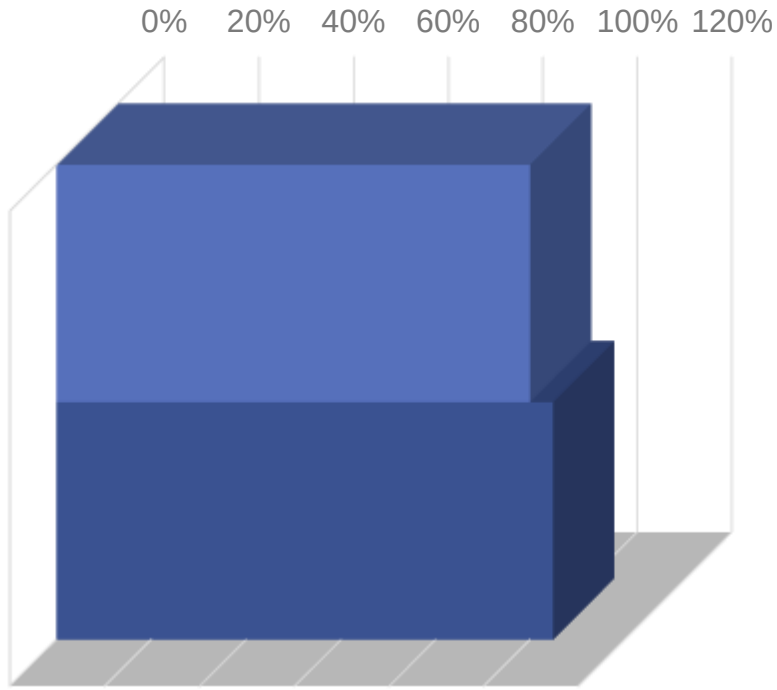
Results Overview

Analyte	DTCs (expr. as CS_2)
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	87
Outlier(s)	5
False negatives	5
AV based on	Whole population excl. outliers
AV [mg/kg]	0.068
CV*	46.7%
MRRL [mg/kg]	0.01
UAV Test	passed

Impact of Sample Treatment on Conversion yields of Metiram to CS_2

HS Sample Preparation + GC-MS/MS

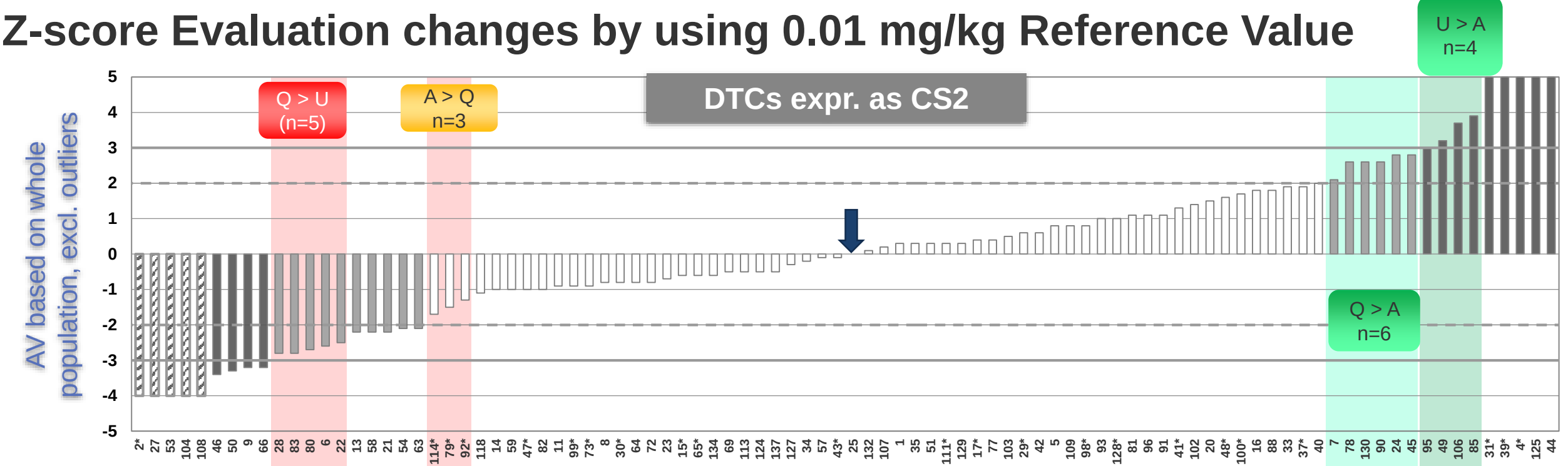
Impact of defrosting

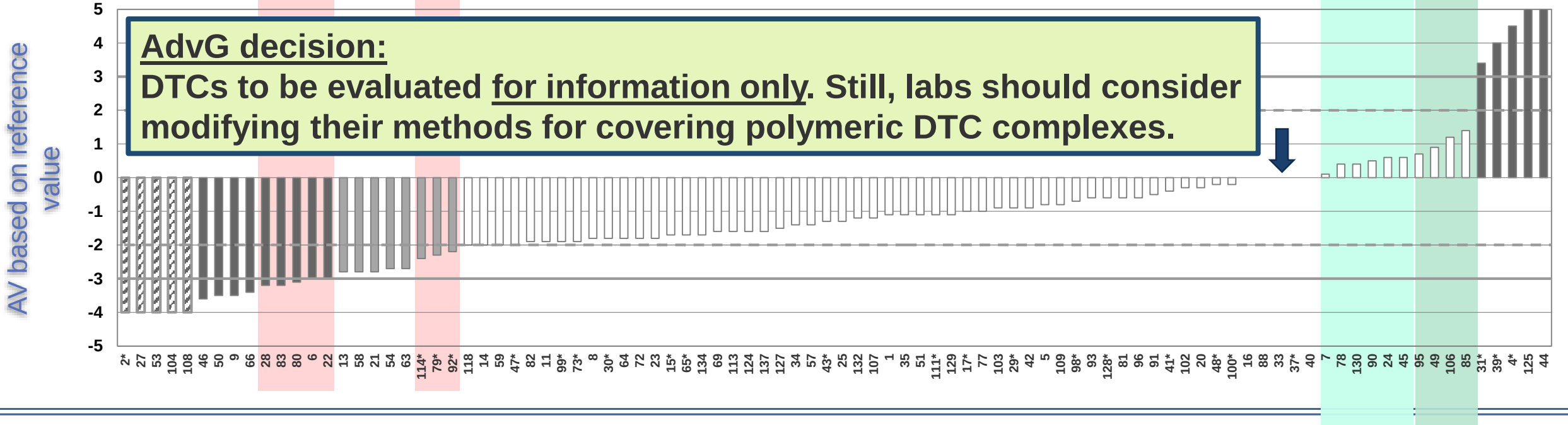


TAKE HOME MESSAGE:
In the case of polymeric DTCs (Maneb, Metiram etc.)
DEFROSTING is not as critical as with Thiram and Ziram

SRM19 Grape, Metiram

Z-score Evaluation changes by using 0.01 mg/kg Reference Value



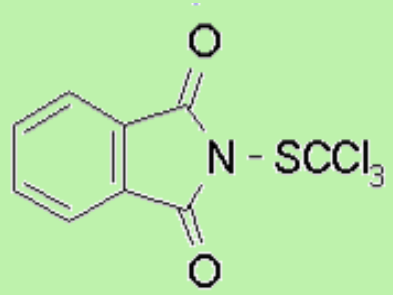


AdvG decision:

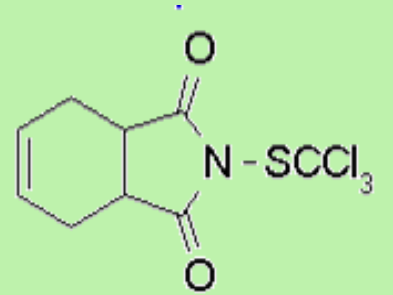
DTCs to be evaluated for information only. Still, labs should consider modifying their methods for covering polymeric DTC complexes.

Folpet / PI

DEGRADATION OF CAPTAN AND FOLPET DURING ANALYSIS



FOLPET



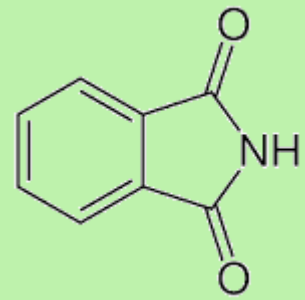
CAPTAN

Degradation especially at

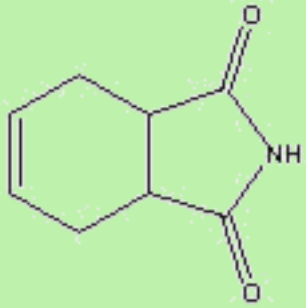
- ***High pH***
- ***High temperature***

e.g. during:

- ***Homogenization***
- ***Storage of defrosted Homogenates***
- ***Extraction/Cleanup***
- ***Storage of Extracts***
- ***GC-injectiion***



Phthalimide



Tetrahydrophthalimide

Analysis of Captan (sum) and Folpet (sum)

EU Residue Definitions since 2016:

Captan including tetrahydrophthalimid (THPI), calculated as captan

Folpet including phthalimid (PI), calculated as folpet

ERROR SOURCES IN THE ANALYSIS OF FOLPET AND PI

PT-Matrix was acidic (grapes) thus decomposition of Folpet to PI was moderate

Comparison of PT-Data: Labs protecting vs. labs defrosting >1h
→ Folpet Losses: ~5% ; PI increase: ~15% **WHY ?**

Reason:
Folpet present at a higher molarity than PI (F=2.6)

Decrease of Folpet and corresp. increase of PI, exemplarily visualized for 2.6:1 mol-ratio (as in PT),

Folpet AV (mg/kg) 0,421		Folpet vs. PI	PI AV (mg/kg) 0,082	
		Conc. Factor 5,13		
Loss	Folpet Losses	Mol Factor 2,6	Generated PI	Increase PI
0,021	-5%		0,0105	13%
0,042	-10%		0,0211	26%
0,063	-15%		0,0316	39%
0,084	-20%		0,0421	51%
0,126	-30%		0,0632	77%
0,168	-40%		0,0842	103%
0,211	-50%		0,1053	128%
0,337	-80%		0,1684	205%

Assuming quantitative conversion

GC-ANALYSIS: OVERESTIMATION OF PI AND THPI IN PRESENCE OF PARENTS

FOLPET	PI	PI measured (calibrated w. PI)	overestimation of PI
spiked in one vial [ppm]		[ppm]	error [%]
0,1	0,1	0,11	27%
0,2	0,1	0,11	22%
0,3	0,1	0,14	53%
0,6	0,1	0,19	116%
1	0,1	0,24	178%

CAPTAN	THPI	THPI measured (calibrated w. THPI)	overestimation of THPI
spiked in one vial [ppm]		[ppm]	error [%]
0,1	0,1	0,13	31%
0,2	0,1	0,12	20%
0,3	0,1	0,15	50%
0,6	0,1	0,19	102%
1	0,1	0,25	159%

Tomato blank extract (QuEChERS, d-SPE, AP)
Spiked w. Folpet/ Captan and PI/THPI at different levels
Simultaneous measurement by GC-MS/MS

Situation in PT-material

		Captan/ THPI	Folpet/ PI
Parent (mg/kg)		0,172	0,249
Degradant (mg/kg)		0,59	0,10
Ratio Parent/ Degradant	Conc.	1 : 3.5	2.5 : 1
	Mols	1 : 7	1.3 : 1

Proportionally More parent

PROBLEM IN GC-ANALYSIS

THE HIGHER THE PARENT: DEGRADANT RATIO
THE MORE PRONOUNCED THE OVERESTIMATION
OF THE RESPECTIVE DEGRADANT !!!

Bias between robust mean values for Phthalimid depending on Analysis Approach

Analyte	Folpet			Phthalimid		
Population for Robust Mean (RM)	entire population	GC based	LC based	entire population	GC based	LC based
No. of numerical results	80	66	14	85	69	16
therein Outliers	3	3	0	3	1	2
No. results for RM	77	63	14	82	68	14
No. of FNs	8	8	0	2	1	1
Prelim. Assigned Value [mg/kg]	0.225	0.218	0.247	0.106	0.112	0.082
CV*	26.8%	30.6%	14.5%	38.3%	38.1%	32.4%
AV Uncertainty	0.0086	0.01050	0.012	0.0056	0.00649	0.0089
AV Tolerance	0.0169	0.0164	0.0185	0.008	0.0084	0.0062
	passed	passed	passed	passed	passed	failed

-27%

+36%

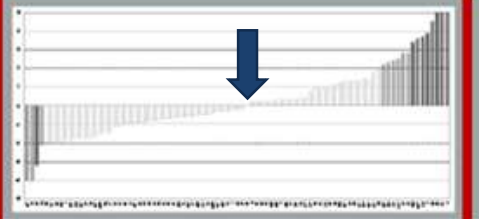
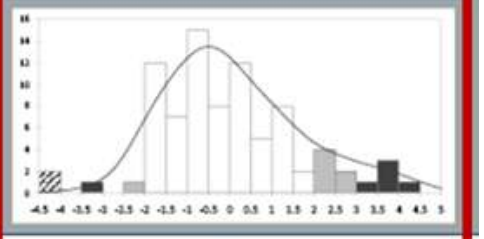
Preliminary Report Note Phthalimide

In the case of **phthalimide**, despite the numerous appeals by the EURL-SRM to consider the risk of overestimating the levels when using GC-based methods, 69 of the 85 numerical results (81%) were generated by laboratories employing GC-based methods. In fact, only 16 numerical results were generated by LC-based methods. The overall distribution of the 85 numerical results was quite broad (CV* 38.3 %) and again a certain bimodality was noticed, due to the LC-results forming a slightly shifted population with a robust mean value of 0.082 mg/kg (N=14 after elimination of two outliers). This value is roughly 23% lower than the robust mean of the total population at 0.106 mg/kg (N=82 after elimination of 3 outliers) and roughly 27% lower than the robust mean of the GC-based results of 0.112 mg/kh (N=69). This trend was expected for the reasons explained above. Unexpectedly, the LC population was rather broadly distributed (CV* 32.4 %), which increases the uncertainty of the robust mean. Still, considering that one of the main purposes of this preliminary report is to give labs the opportunity to timely localize and eliminate sources of errors, and taking into account the spiking levels, but also considering the results of numerous EURL-SRM experiments, **the robust mean of the LC-results at 0.082 mg/kg was used as a the preliminary assigned value for calculating the preliminary z scores in this report**. This value is close to mean value of the EURL-SRM homogeneity test (0.0785 mg/kg), which was also derived using LC-MS/MS measurement. Evaluating the results based on the robust mean of the entire population would be unfair towards laboratories having avoided practices leading to overestimated results for phthalimide.

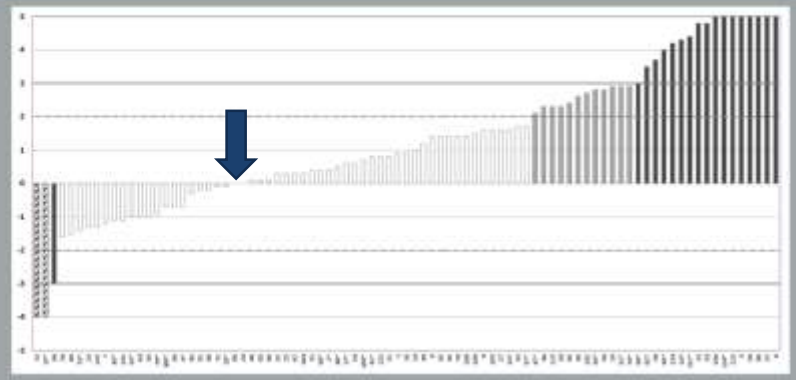
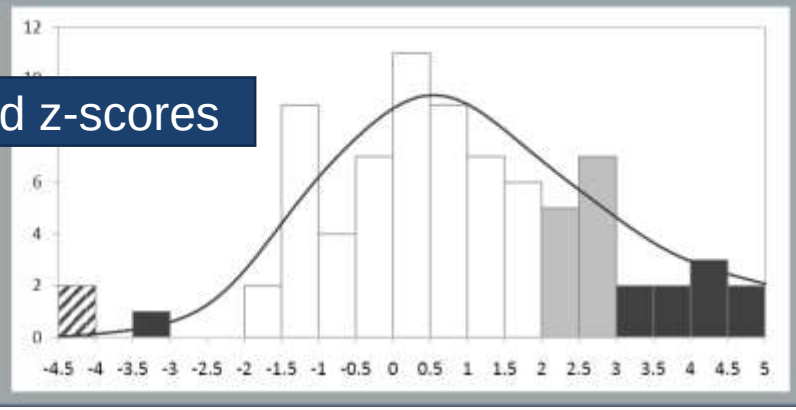
EURL-SRM

Phthalimide

Original Evaluation with biased Robust Mean (overestimated)

Analyte	Phthalimide
Histogram of z scores	
Kernel Density of z-scores	
No. of numerical results	85
Outlier(s)	3
False negatives	2
AV based on	Whole population excl. outliers
AV [mg/kg]	0.106
CV*	38.3%
MRRL [mg/kg]	0.01
UAV Test	passed

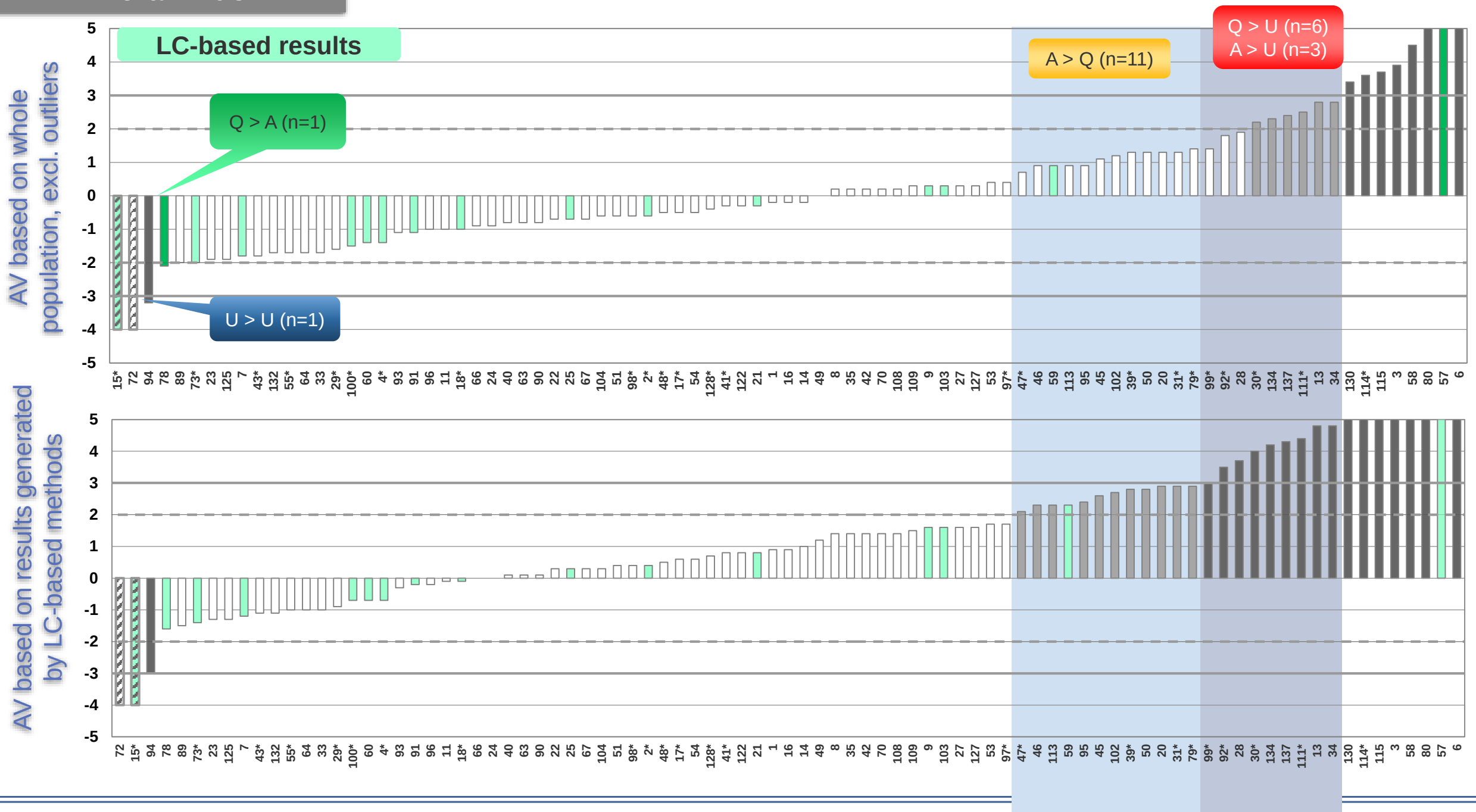
Alternative Reference Value for Phthalimide (0.082 mg/kg) considering all available information

Analyte	Phthalimide
Histogram of z-scores	
Kernel Density of z-scores	
No. of numerical results	16
Outlier(s)	2
False negatives	1
PrelimAV based on	14 results generated by LC-based methods
AV [mg/kg]	0.082
CV*	32.4%
MRRL [mg/kg]	0.01
UAV Test	failed

Shifted z-scores

The statistical test for the uncertainty of the robust mean passed the threshold. Still, the AdvG concluded that it does not qualify as an AV for the official EUPT-evaluation of this parameter

Phthalimide



Retrospective view: Results from EUPT-SRM17

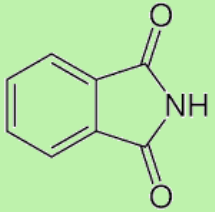
Investigation on FOLPET behavior DURING THAWING

EUPT-SRM17 (Tomato)

Rec Tomato 0.25 ppm n=2		Folpet	PI derived from Folpet NO PI Spiking calculated as Folpet
Time after Spiking	Extraction	**Rec %**	**generation rate (%)**
15h	QuEChERS	**32**	**68**
4h	QuEChERS	**92**	**19**
0h	QuEChERS	**106**	**-**
15h	QuE+1%FA	**32**	**66**
4h	QuE+1%FA	**97**	**19**
0h	QuE+1%FA	**112**	**-**

Loss of Folpet goes along with PI generation

FOLPET



Phthalimide

Thawed tomato blank was spiked with folpet and left standing at RT;
Analysis by LC-MS/MS:
Sample Preparation QuEChERS (No d-SPE) OR FA- QuEChERS (No d-SPE)

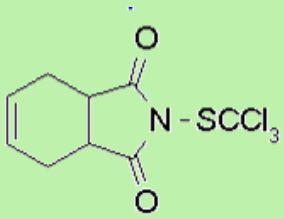
Retrospective view: Results from EUPT-SRM17

Investigation on CAPTAN behaviour DURING THAWING

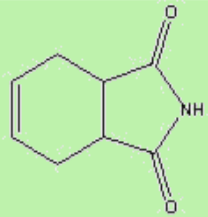
EUPT-SRM17 (Tomato)

Rec Tomato 0.25 ppm n=2		Captan	THPI derived from Captan NO THPI Spiking calculated as Captan
Time after Spiking	Extraction	**Rec %**	**generation rate (%)**
15h	QuEChERS	-	102
4h	QuEChERS	**57**	48
0h	QuEChERS	**104**	-
15h	QuE+1%FA	-	109
4h	QuE+1%FA	**59**	48
0h	QuE+1%FA	**91**	-

Loss of Captan goes along with THPI generation



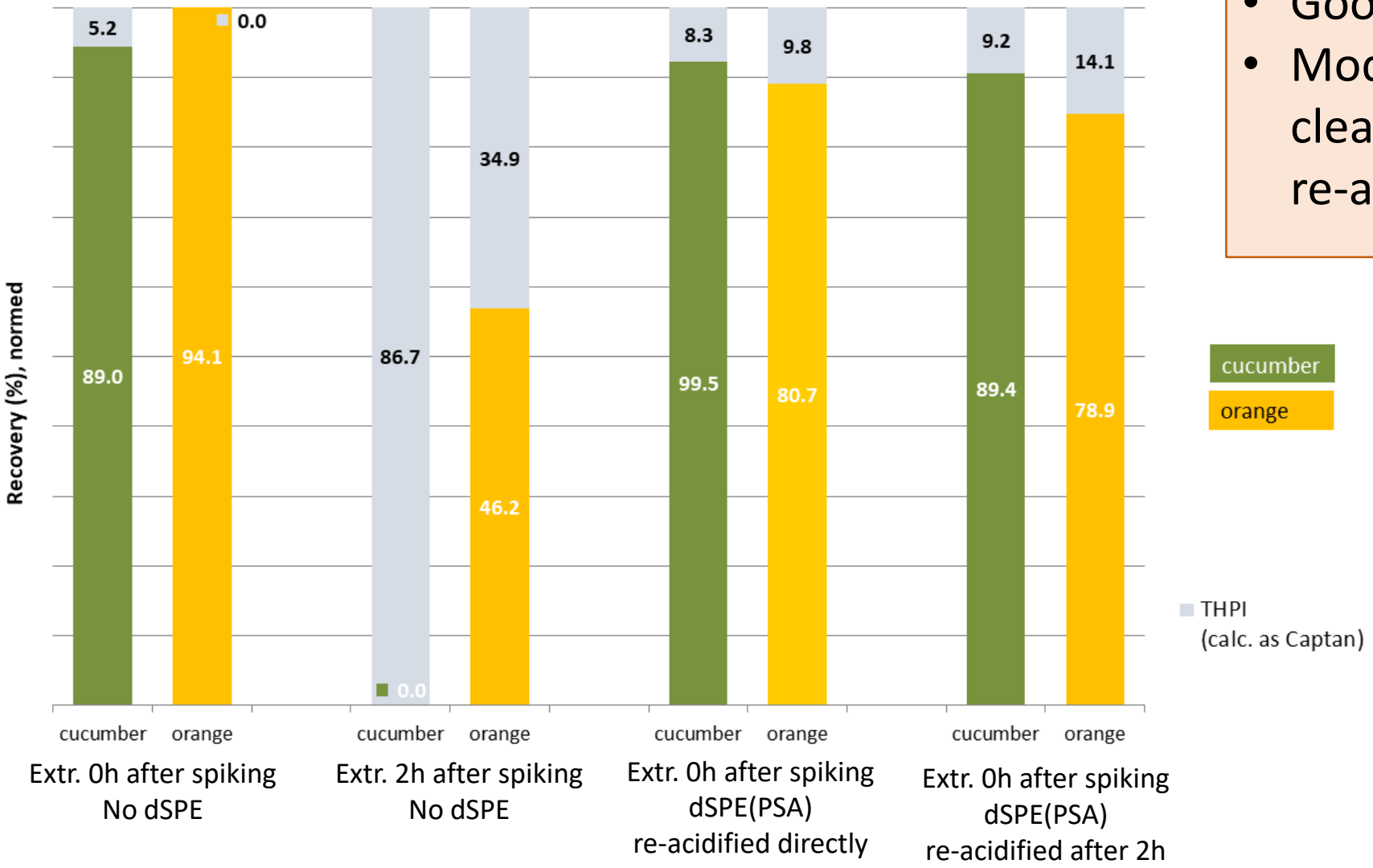
CAPTAN



Tetrahydrophthalimide

Thawed tomato blank was SPIKED WITH CAPTAN and left standing at RT;
Analysis by LC-MS/MS:
Sample Preparation QuEChERS (No d-SPE) OR FA- QuEChERS (No d-SPE)

Stability of Captan during QuEChERS-Extraction:



Avoid prolongued standing of thawed homogenates !!

- Good Rec. w. QuEChERS
- Moderate losses during PSA-cleanup and if extracts are not re-acidified

Similar results for Folpet, Captafol

Both parents and degradants determined by LC-MS/MS in this experiment

DILEMMA 3: Which Techniques to use for Measurement

Sample Contains
only THPI/PI
(absence of parents difficult to judge, if extensively degrading during procedure)

Sample Contains
Parents & THPI/PI
(often the case)

Passive or Active Transformation of parents to THPI/PI in Homogenate or Extract
(Conversion not always quantitative, No data on parent)

THPI/PI via GC-MS(/MS)

THPI/PI via LC-MS(/MS)

Approach 1:
Parents & THPI/PI via GC-MS/MS

Tricky, risk to overestimate degradants special procedure + Excel sheet (SRM-07)

Approach 2:
Parents via GC-MS/MS THPI/PI via LC-MS/MS

CURRENTLY PREFERRED but make sure to address MEs during measurement (e.g. ILIS, APs)

Approach 3:
Parents via LC-MS/MS THPI/PI via LC-MS/MS

Parent analysis via LC-MS/MS lacks sensitivity

Direct Analysis of PI/THPI using GC or LC-MS/MS - OVERVIEW

GC (see SRM-07)

Captan/Folpet (quant)

Need to Compensate MEs (e.g. using AP+ ILIS) ✓

THPI/PI (quant)

Risk of overestimation & FPs!

Formed in inlet from parents + other potential sources, e.g.

Phtalanhydride ► **PI,** ✗

Captafol ► **THPI,**

Special GC-Quantif. involving corr. of PI/THPI levels via calc. (Excel file linked in SRM-07) ✓

THPI/PI (qual)

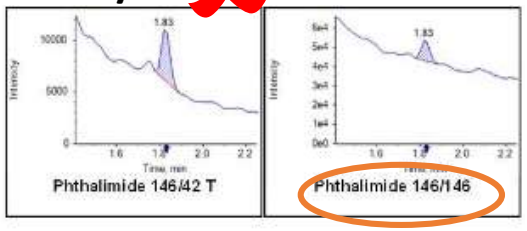
Useful for routine screening ! ✓

LC-MS/MS (see SRM-42 and SRM-49)

ESI-Mode

Neg. mode (SRM-42)

THPI/PI: ✗

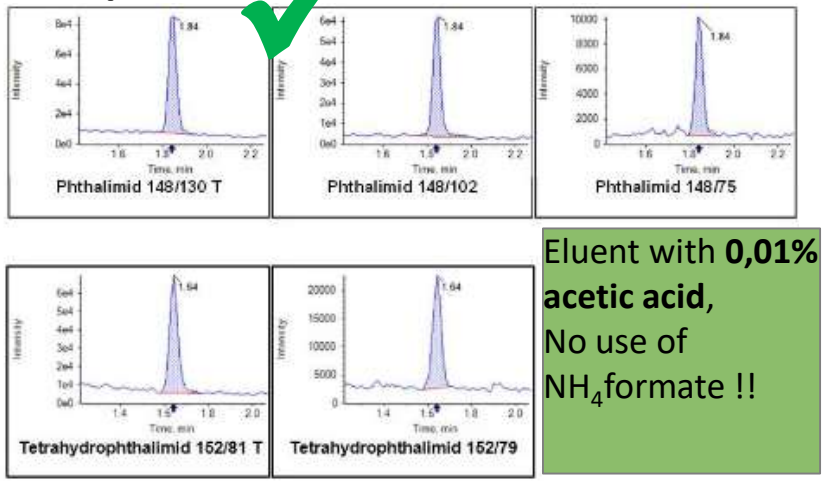


Lack of sensitivity depending on gradient and instrument, Only one useful MRM for PI

Parents: ✗

Pos. mode (SRM-49)

THPI/PI: ✓



Eluent with **0,01% acetic acid**, No use of NH_4formate !!

Parents:

$[M+H]^+$ or $[M+NH_4]$ adducts sensitivity not bad but variable ✗

APCI-Mode

Neg. mode (SRM-42)

THPI/PI and Parents

*Possible but **tricky**!! (insource effects), extra requirements, cross-interferences. e.g. Folpet D4 and PI-D4 interfere with Captan (analyzed as THPI) and THPI respectively*

✗

Topics

EURL-SRM Network
NRL-SRM Network

Proficiency Tests
EUPT-SRM Overview
EUPT-SRM18 (Honey)
EUPT-SRM17 (Tomatoes)
EUPT-SRM16 (Sesame)
EUPT-SRM15 (Rice)

Workshops
Workshop Overview
Joint Workshop 2023
Joint EURL/NRLs (SRM-FV) 2022

Services
ILISs Distribution
CheckYourScope
SRM-PinBoard
EURL-SRM Methods
Analytical Observations
Residue Observations
Downloads
Sources of Standards

Internet
EURL DataPool
QuEChERS - Website
QuPPe - Website
PestiPedia

Data Submission

Latest News

19-04-2023 | EURL-SRM
Risk of False Positives of Chloridazon-Desphenyl in Honey by LC-MS/MS
A new EURL-SRM Analytical Observations Report concerning the risk of false posit
Various chromatographic separation methods for chloridazon-desphenyl were test

17-03-2023 | EURL-SRM
QuPPe-PO-Method Version 12.1
The QuPPe-PO-Method has been updated (now includes more detailed information on Honey analysis).

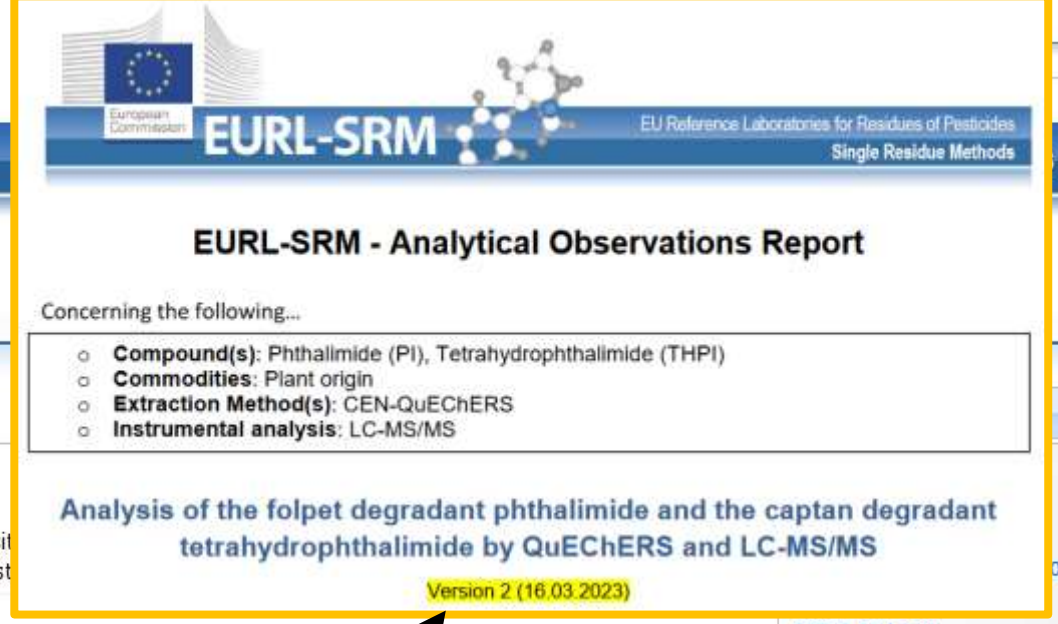
16-03-2023 | EURL-SRM
Analysis of the Folpet and Captan degradants Phthalimide (PI) and Tetrahydrophthalimide (THPI) by QuEChERS and LC-MS/MS
The Analytical Observation Report (SRM-49) on the analysis of PI and THPI via LC-MS/MS was updated by introducing additional validation data. This update also includes results of experiments concerning the transformation of Captan and Captafol to Tetrahydrophthalimide (THPI) and of Folpet to Phthalimide (PI), during various steps of the QuEChERS procedure and especially in thawed sample homogenates prior to extraction.

03-03-2023 | EURL-SRM
Determination of fluoride ion in food
Two approaches for the determination of Fluoride Ion via selective electrodes (ISE) are described: a) direct measurement in QuPPe extracts and b) measurement in diffusates derived by microdiffusion.

27-02-2023 | EURL-SRM
Compilation of Residue Observations Reports of QuPPe Compounds
A new compilation of residue findings of QuPPe compounds in food products, analysed in 2022, was uploaded. The report additionally encompasses findings of ethylene oxide / 2-chloroethanol. Aim of these annual compilations of residue findings is to help OfLs to localize analyte/matrix combinations that are worthwhile monitoring.

24-02-2023 | EURL-SRM
New Analytical Observations Report on QACs analysis
The EURL report on QACs analysis in food via QuEChERS and LC-MS/MS, was updated by introducing a simple and practical approach for separating background contaminations of QACs during LC-MS/MS analysis involving the use of a trap-column.

10-02-2023 | EURL-SRM
Joint EURLs/NRLs Workshop | 18–20 October 2023 in Stuttgart (Fellbach)
The Joint EURLs/NRLs Workshop for Pesticide Residues will be held from 18 to 20 October 2023 in Stuttgart.



CIRCA BC Login
RASFF Portal DB (COM)
How to Use CIRCA BC
InfoNote: Processed Food/Feed (COM)
EUPT Registration Website

Pinboard

Show more Pinboard Messages...

Compilation of Analytical Observations Reports

The table below compiles various observations made during the analysis of pesticide residues.

Compound(s)	No. of Method Finder List/Version/Date of Update	Link
Captan & THPI (tetrahydrophthalimide) and Folpet & PI (phthalimide)	**SRM-07/(V3)/06.07.2017** **SRM-42/(V1)/30.06.2019** **SRM-49/(V1)/16.03.2023**	SRM-07 (GC-MS/MS) **Excel files to calc. conc. of parents & degradants, based on GC-MS/MS data generated following calibration approaches described in SRM-07:** SRM-07-ExtCal (parents+degrad. by GC-MS/MS) SRM-07-StdAdd (parents+degrad. by GC-MS/MS) SRM-42 (par.+degrad.; LC-MS/MS; APCI or ESI) SRM-49 (THPI+PI by LC-MS/MS; ESI-pos)

Short Description of SRM-07 (GC-MS or GC-MS/MS): This document describes approaches for the analysis of Captan and Folpet in QuEChERS extracts via GC-MS or GC-MS/MS. Different approaches for correcting the results of the parent molecules for matrix effects during GC analysis or for losses during the entire procedure are presented and discussed. In addition two approaches for analyzing Captan and Folpet next to their legally relevant metabolites Tetrahydrophthalimide (THPI) and Phthalimide (PI) are presented and discussed.

Short Description of SRM-42 (LC-MS/MS in APCI-neg. and ESI-neg. modes): Various possibilities for the LC-MS/MS analysis of Captan/THPI and Folpet/PI were studied employing APCI and ESI interfaces. LC-MS/MS analysis circumvents problems related to GC-analysis but further efforts to improve sensitivity are required. The active hydrolysis of Captan and Folpet to their respective degradants (THPI and PI), was also studied aiming to reduce the number of analytes to be measured. Unfortunately, conversion yields were often not satisfacory and further studies are needed.

Short Description of SRM-49 (LC-MS/MS in ESI-pos. mode): A simple and sensitive method for the analysis of PI and THPI was developed based on QuEChERS extraction and LC-MS/MS determination in the ESI-pos. mode using a C18 column and a slightly acidic eluent without the addition of ammonium buffer salts for separation. Validations of THPI and PI in cucumber, grapes, wheat flour and peanut butter were successful down to 0.005 (~0.01 mg/kg expressed as corresponding parent). In wheat flour and peanut butter, THPI validation at 0.005 mg/kg and 0.010 mg/kg was only successful for one single mass-transition (m/z 152/81) as the second one (m/z 152/79) showed MS-interferences compromising identification. Further experiments are planned to increase selectivity and enable identification of THPI at low levels, both at the sample preparation (i.e. cleanup) and at the measurement stage.

Overall Conclusion: The analysis of Captan (sum) and Folpet (sum) requires special care. Homogenates of samples should not be left standing at elevated temperatures to avoid degradation. Captan and Folpet show a rather poor sensitivity in LC-MS/MS, not allowing accurate analyses at low levels, so GC-analysis needs to be endeavored. Using GC, Captan and Folpet can be sensitively analyzed but matrix effects need to be properly addressed to as these may lead to highly inaccurate results (see SRM-07). Also, care should be taken to reduce thermal decomposition in the hot injector which would lead to false negative results (see SRM-07). This thermal decompositions leads to the formation of PI and THPI, and if this aspect is not considered the GC-results of PI and THPI are overestimated. This effect is more pronounced if the parents are present at excess levels (see SRM-07). Accurate analysis of THPI and PI next to their parents is possible using a special calibration approach that deducts the share of PI and THPI formed from the decomposition of the parents within the GC-injector (see GC-Analysis of Captan-Folpet-THPI-PI via External Calibration and GC-Analysis of Captan-Folpet-THPI-PI via Standard Addition). A convenient and accurate analysis of THPI and PI, can be accomplished via LC-MS/MS in the ESI pos. mode (see SRM-49). As Captan and Folpet may degrade to THPI and PI at various stages of the procedure including the extract itself, it is important to analyse THPI/PI and Captan/Folpet

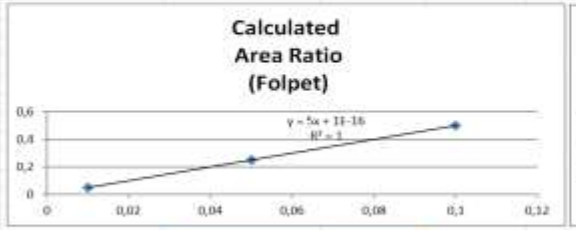
Excel Calculation Sheet

APPROACH FOR GC-ANALYSIS OF PI AND THPI IN PRESENCE OF PARENTS

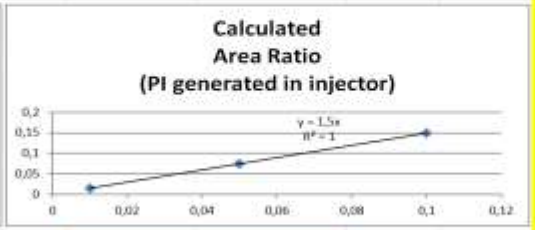
CALIBRATION DATA

Calibration Solution I: Spiked with Folpet, Folpet-D4 and Chlorpyrifos-D10 (preferably matrix-matched)

	µg/l/S	Enter Area of Folpet from Calibr. Sln I	Enter Area of ILIS (Folpet-D4) from Calibr. Sln I	Calculated Area Ratio (Folpet)	Enter Area of PI from Calibr. Sln I (generated in injector)	Enter Area of IS (e.g. Chlorpyrifos-D10) from Calibr. Sln I	Calculated Area Ratio (PI generated in injector)
Cal 1	0,01	1000	20000	0,05	1500	100000	0,015
Cal 2	0,05	5000	20000	0,25	7500	100000	0,075
Cal 3	0,1	10000	20000	0,5	15000	100000	0,15



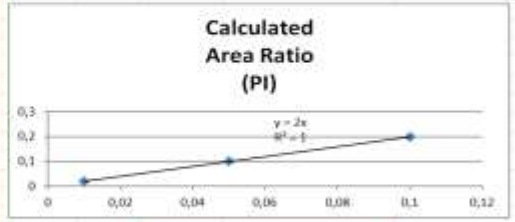
slope	5
intercept	0,0000



slope	1,5
intercept	0,0000

Calibration Solution II: Spiked with PI and Chlorpyrifos-D10 (preferably matrix-matched)

	µg/l/S	Enter Area of PI from Calibr. Sln II	Enter Area of IS (e.g. Chlorpyrifos-D10) from Calibr. Sln II	Calculated Area Ratio (PI)
Cal 1	0,01	2000	100000	0,02
Cal 2	0,05	10000	100000	0,1
Cal 3	0,1	20000	100000	0,2



slope	2
intercept	0,0000

SAMPLE DATA

Enter Sample Names / Codes here	Sample amount per IS Portion in g (typically 1 when employing 10 g for extraction)	Enter Area of Folpet from Sample Extract	Enter Area of ILIS (Folpet-D4) from Sample Extract	Calculated Area Ratio (Folpet)	Enter Area of PI (= Original + Injector-generated)	Enter Area of IS (e.g. Chlorpyrifos-D10) from Sample Extract	Calculated Area Ratio (PI)
Sample Name 1	1	2500	20000	0,125	50000	100000	0,5
Sample Name 2	1	7500	20000	0,375	75000	100000	0,75
Sample Name 3	1	5000	20000	0,25	20000	100000	0,2
Sample Name 4	1	10000	20000	0,5	30000	100000	0,3
Sample Name 5	1	30000	20000	1,5	100000	100000	1

	Folpet in Extract	Folpet in Sample
	µg/l/S	mg/kg
Sample Name 1	0,025	0,025
Sample Name 2	0,075	0,075
Sample Name 3	0,05	0,05
Sample Name 4	0,1	0,1
Sample Name 5	0,3	0,3

	PI built during injection	
	Calc. Area Ratio	µg/l/S
Sample Name 1	0,0375	0,01875
Sample Name 2	0,1125	0,05625
Sample Name 3	0,075	0,0375
Sample Name 4	0,15	0,075
Sample Name 5	0,45	0,225

	PI, total
	µg/l/S
Sample Name 1	0,25
Sample Name 2	0,375
Sample Name 3	0,1
Sample Name 4	0,15
Sample Name 5	0,5

	PI in Extract	PI in Sample	Sum of Folpet and PI, calc. as Folpet
	µg/l/S	mg/kg	mg/kg
Sample Name 1	0,23125	0,23125	0,491
Sample Name 2	0,31875	0,31875	0,718
Sample Name 3	0,0625	0,0625	0,176
Sample Name 4	0,075	0,075	0,251
Sample Name 5	0,275	0,275	0,854

SRM07-StdAdd Description in SRM-07

Excel file for the calculation Captan/THPI and Folpet/Phthalimide **using external calibration** (see Description of Procedure)

Excel file for the calculation Captan/THPI and Folpet/Phthalimide **using standard additions** (see Description of Procedure)

QUANTIFICATION OF PARENTS AND DEGRADANTS VIA GC-ANALYSIS

Principle of Approach

1) **Parent conc. in sample extr. is quantified** using external calbration and ILIS.

2) **The rate with which the degradant is formed in the injector** (through thermal decomp. of parent) is determined using standard solutions of parent (external calibration).

3) Based on the determined conc. of parent in the sample extract, the **expected signal-share of degradant formed (through parent-decomposition in the injector)** is **calculated.**

4) The **expected signal-share of degradant** is deducted from the degradant-signal measured in the sample extract.

5) Based on a separate external calibration of the degradant, the **original concentration of the degradant in the sample extract is determined**

Limitations:

Where the ratio between parent and degradant is very high, the quantification of the degradant is more prone to errors (quantification of parent and sum is less affected here)

At very low conc. of parent, the rate of decomposition may be higher than at higher conc.. And thus not accurately reflected by the rate determined at step 2)

GC-ANALYSIS OF PI AND THPI IN PRESENCE OF PARENTS

European Commission EURL-SRM EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

SRM07

EURL-SRM – Analytical Observation Report

concerning the following…

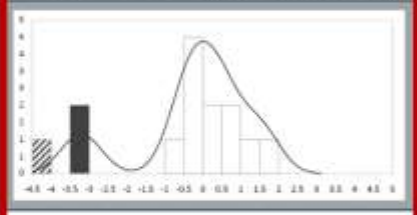
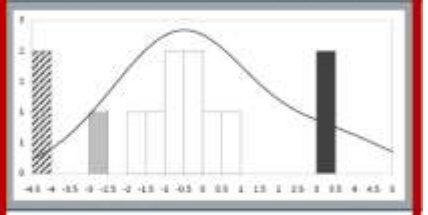
- **Compound(s)**: Captan, Folpet, Phthalimide (PI), Tetrahydrophthalimide (THPI)
- **Commodities**: Fruit and vegetables, cereals
- **Extraction Method(s)**: QuEChERS, A-QuEChERS
- **Instrumental analysis**: GC-MS, GC-MS/MS

Quantification of Residues of Folpet and Captan in QuEChERS Extracts

Version 3.1 (last update: 06.04.17)

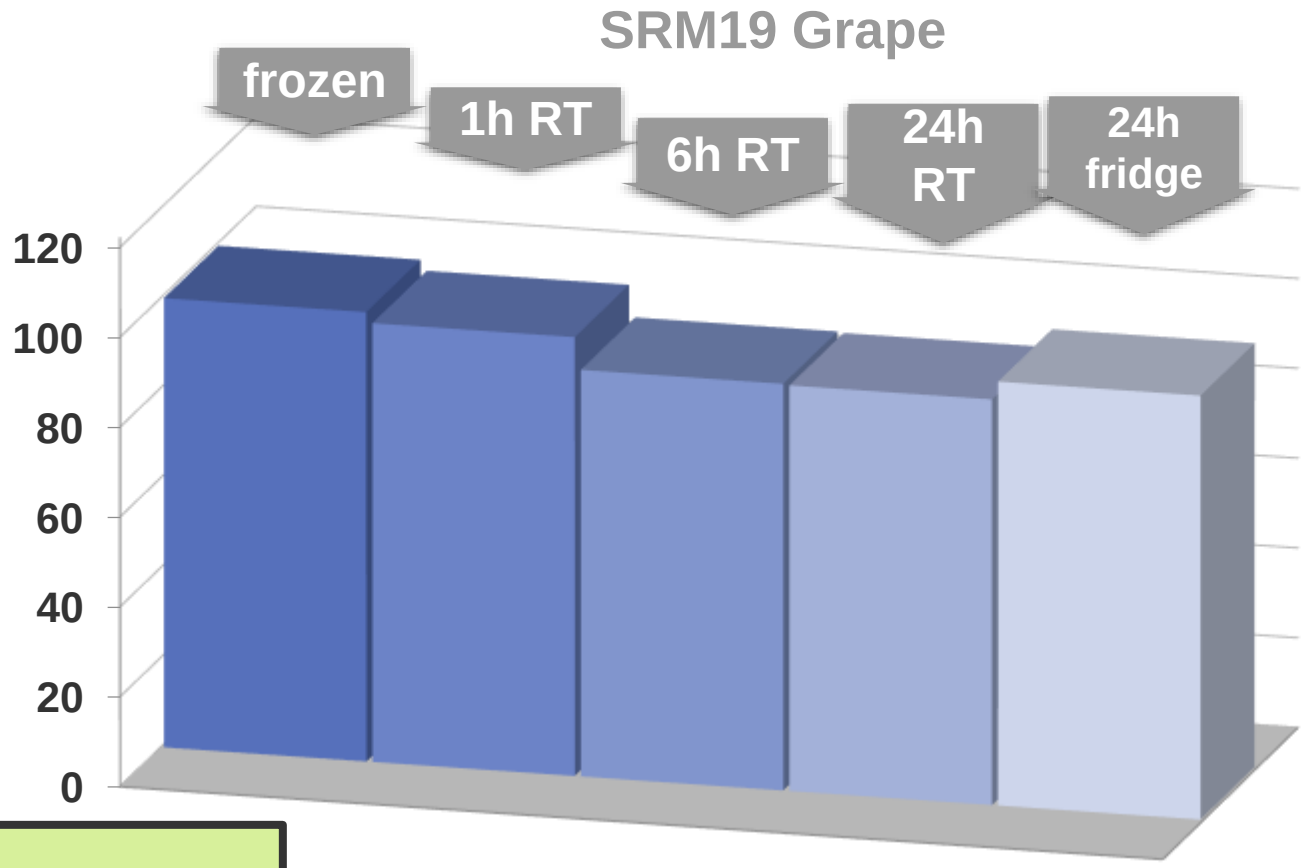
Meptyldinocap

Results Overview

Analyte	Meptyldinocap	Meptyldinocap m. 2,4-DNOP
Histogram of z scores		
Kernel Density of z-scores		
No. of numerical results	18	12
Outlier(s)	5	1
False negatives	1	2
AV based on	Whole population excl. outliers	Whole population excl. outliers
AV [mg/kg]	0.086	0.065
CV*	29.6%	46.9%
MRRL [mg/kg]	0.01	0.01
UAV Test	failed	failed

Uncertaintly of AV exceeds the limit, due to small number of results

Impact Sample Treatment on Meptyldinocap



TAKE HOME MESSAGE:
Meptyldinocap was sufficiently stable in the grape matrix
DEFROSTING not as critical as in matrices with high pH

SRM17-Report

Analytical Challenge in case of Meptyldinocap & Co.

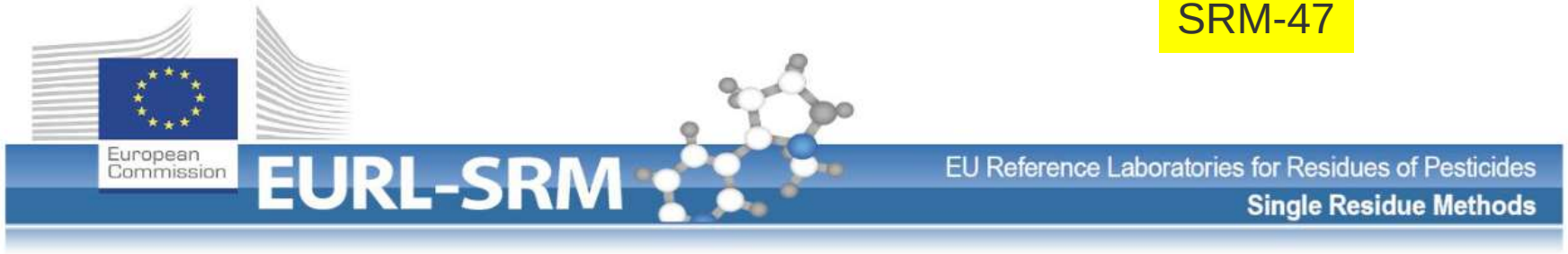
In principle, there are two approaches for the analysis: a) analysis of ***meptyldinocap*** and ***2,4-DNOP*** separately; and b) Analysis following conversion of ***meptyldinocap*** to ***2,4-DNOP***. The analysis of ***meptyldinocap*** next to its degradant ***2,4-DNOP*** is tricky as ***meptyldinocap*** is also analysed as ***2,4-DNOP*** as it readily degrades within the ESI ion source. So both compounds share the same MRM transitions and are not separated mass-spectrometrically. To avoid partial co-elution of the two compounds, it is recommended running comparably "slow" LC-gradients to ensure sufficient chromatographic separation. ***Meptyldinocap*** is sensitive to degradation and analytical standards need to be stabilized with some acid. Still, even freshly prepared ***meptyldinocap*** standards contain a small amount of ***2,4-DNOP*** (e.g. ~3 %). Despite the small share of ***2,4-DNOP*** in ***meptyldinocap*** standards, ***2,4-DNOP*** forms the largest peak upon injection. The reason for this is that ***2,4-DNOP*** when analysed as such is ca. 50 to 100-fold more sensitive than ***2,4-DNOP*** originating from ***meptyldinocap*** through in-source fragmentation which appears at a later retention time. Laboratories often get confused misallocating the retention time of ***2,4-DNOP*** to ***meptyldinocap***. This leads to wrong quantifications. Even if retention times are correctly allocated, it can happen that the peak at the retention time of ***meptyldinocap*** is overlooked as the peak for ***2,4-DNOP*** is typically much-much larger, so that the ***2,4-DNOP*** peak is taken. This scenario may happen if the two compounds elute very closely ("fast" elution gradient) so that ***2,4-DNOP*** appears close to the centre of the data review window of ***meptyldinocap***.

A method entailing conversion of ***meptyldinocap*** to ***2,4-DNOP*** was developed by the EURL-SRM (Method SRM-47).

MEPTYLDINOCAP (SUM)

Analytical Observations Report on Meptydinocap (sum)

SRM-47



EURL-SRM - Analytical Observations Report

Concerning the following…

- **Compound(s)**: Meptyldinocap
- **Commodities**: Plant origin, animal origin
- **Extraction Method(s)**: CEN-QuEChERS, QuOil
- **Instrumental analysis**: LC-MS/MS

Analysis of Meptyldinocap by QuEChERS

followed by alkaline hydrolysis and LC-MS/MS measurement

MEPTYLDINOCAP (SUM)

Weigh 10.0 g sample homogenate into 50 mL falcon tube
(5.0 g for dry commodities)

Add 100 µL internal standard solution

Adjust water content of sample to approx. 10 mL

Add 10 mL ACN

Shake thoroughly for 15 min.

Add QuEChERS salts and shake for 1 min.

QuEChERs salts:
4 g $MgSO_4$,
1 g NaCl,
1 g Na_3-Citrat-dihydrate,
0.5 g Na_2-hydrogenecitrate-sesquihydrate

Centrifuge e. g. at 4000 rpm for 5 min.

Cleanup for commodities of high lipid content:
Option 1: freeze-out and filter or decant the extract
Option 2: dSPE w. 25 mg C18-sorbent + 150 mg MgSO4 per mL extract, (shake for 1 min. and centrifuge at 4000 rpm for 5 min).
NOTE: Do not use PSA-sorbent to avod losses of phenol component!)

Transfer 1 mL of the extract into a vial

Add 25 µL (**75 µL** in case of dry commodities) **of 25% aqueous ammonia and put vial aside for 12-24 h at room temperature**

Add 25 µL (**75 µL** in case of dry commodities)
of conc. acetic acid for neutralization

In case of turbidity ► Filter or Centrifuge
In case of a well separated precipitate at vial bottom with a clear hydrolysate either proceed directly with measurement or decand into a separate vial.

LC-MS/MS

SRM-47

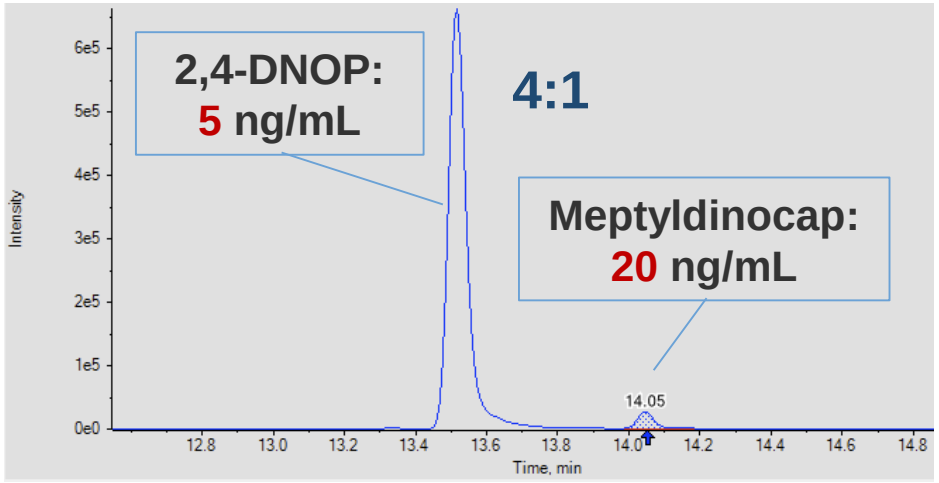
Simple alkaline hydrolysis step following Citrate buffered QuEChERS (EN 15662)

Meptyldinocap (SUM)

Meptyldinocap Analysis– ERROR SOURCES

- **Instability of Meptyldinocap in solution (standard solutions, sample extracts):**
  Degradation slows down at low pH → Acidify standards
- **Risk of Peak-Mismatch between Meptyldinocap and 2,4-DNOP:**

- **LC-MS/MS : ESI (pos.)**
  - Parent → poor sensitivity;
  - 2,4-DNOP → X
- **LC-MS/MS : ESI (neg.)**
  - Parent → moderate sensitivity (in-source fragmention to 2,4-DNOP);
  - 2,4-DNOP → **very high sensitivity (~ 80-fold more sensitive than parent !!)**



Conc. Ratio of Meptyldinocap: 2,4-DNOP

- Here 4:1
- In PT-sample: ~ 2:1

➢ **High Risk of Peak-Mismatch**
(Meptyldinocap-peak could be overlooked)

EURL-SRM

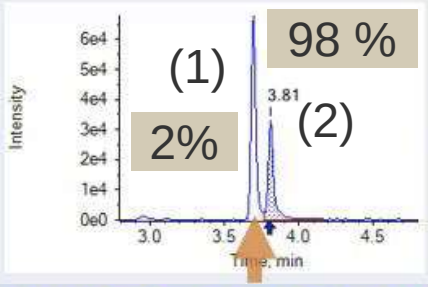
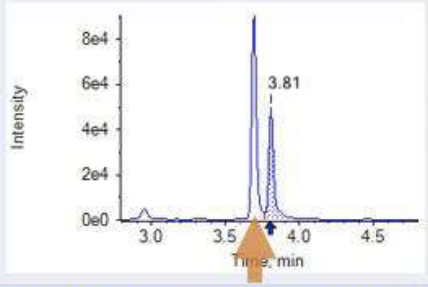
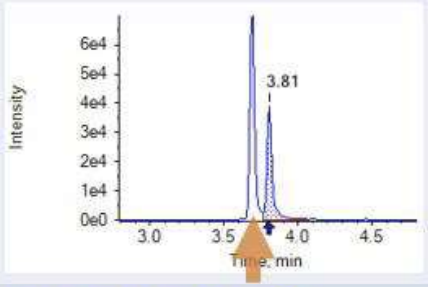
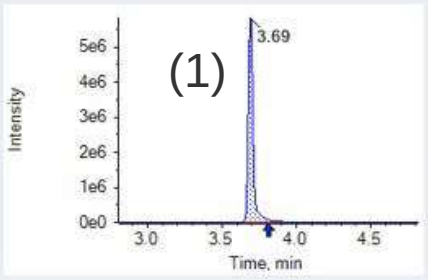
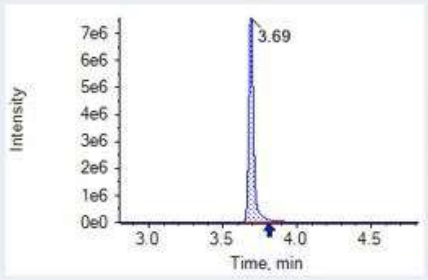
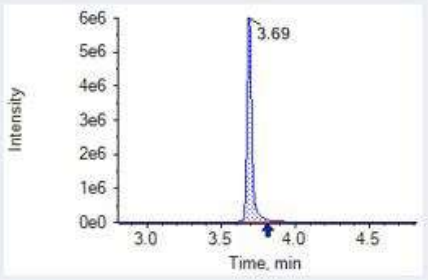
meptyldinocap (Analytical Observation)

Meptyldinocap – Error Sources

- **Meptyldinocap standards typically contain 1-2% 2,4-DNOP (as impurity):**
- **Meptyldinocap: In-source fragmentation to 2,4-DNOP in LC-MS/MS**
- **Two peaks within same mass-trace:**

  (1) 2,4-DNOP; (typically the larger peak despite being present at 1-2% !!)

  (2) In-source fragment of Meptyldinocap

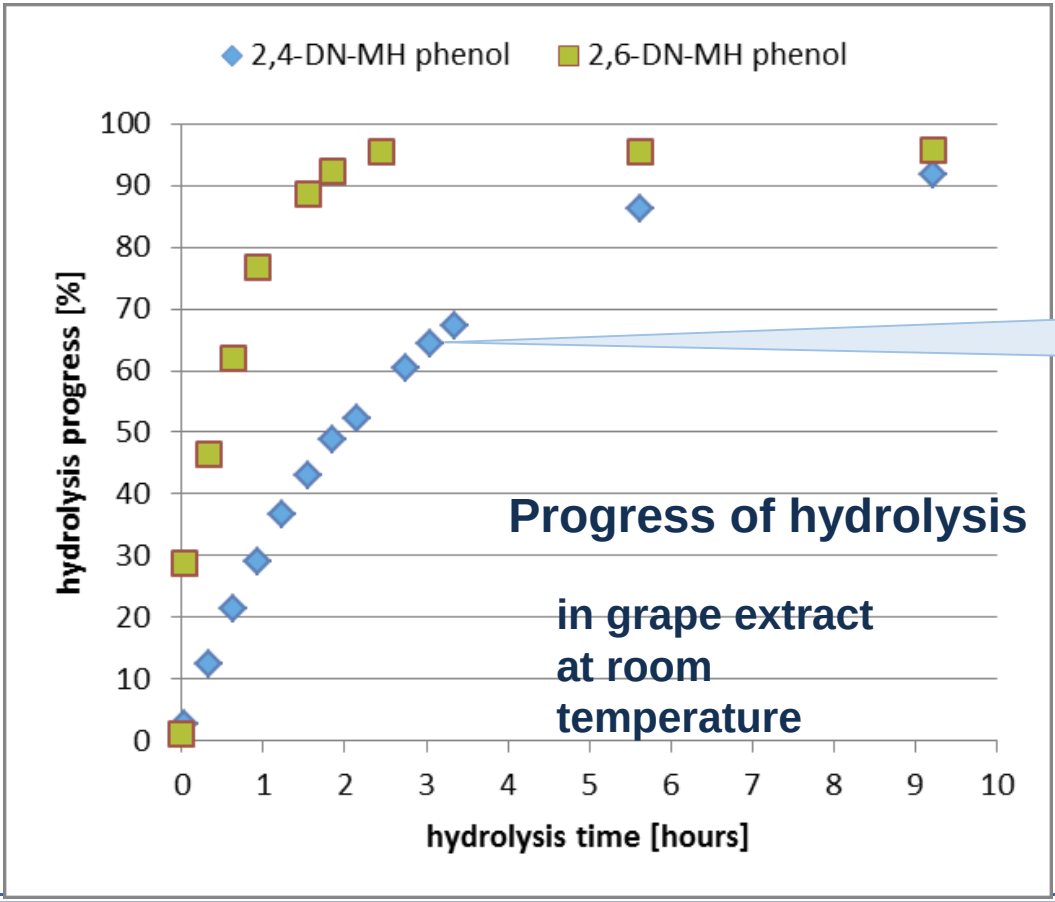
Measured solution	Detected mass traces of 2,4-DNOP		
	295/194	295/193	295/134
Meptyldinocap standard (0.06 µg/mL)			
2,4-DNOP standard (0.06 µg/mL)			

MEPTYLDINOCAP (Optimization of Hydrolysis)

Meptyldinocap (sum) – Error Sources

Incomplete Hydrolysis

+ 500µL QuEChERS extract (spiked with Meptyldinocap (and its 2,6-analogon))
+10 µl of 25% aqueous ammonia solution



2,4-DNOP more resistant to hydrolysis than its 2,6-DNOP analogon

CYHALOTHRIN

EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

EURL-SRM - Analytical Method Report

Concerning the following…

- **Compound(s)**: Lambda-Cyhalothrin (RS and SR constituent isomers)
- **Commodities**: Fruit and vegetables, cereals
- **Extraction Method(s)**: QuEChERS modified
- **Instrumental analysis**: LC-MS/MS

Analysis of Lambda- and Gamma-Cyhalothrin involving QuEChERS Extraction and Enantioselective LC-Separation of RS and SR-Isomers

Version 1 (last update: 12.04.2019)

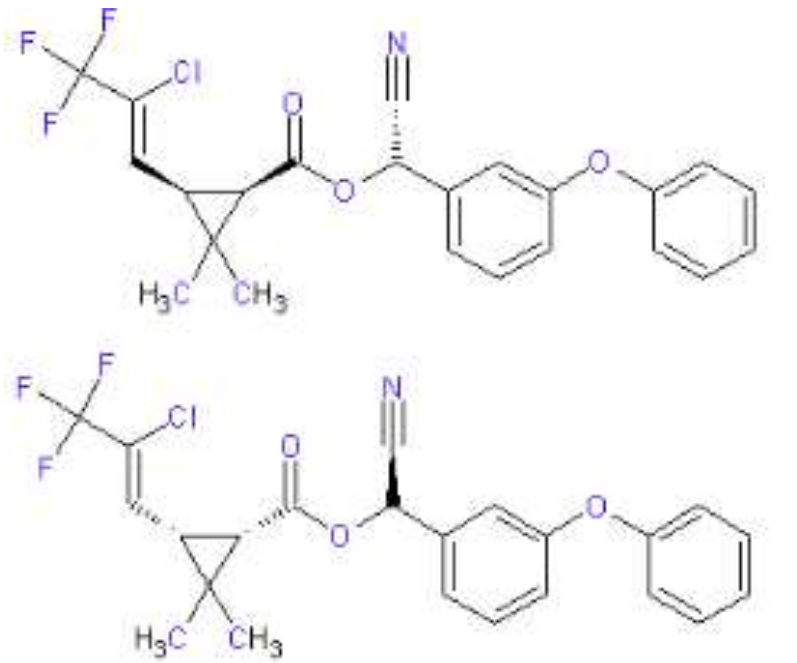
Short Description:

A QuEChERS-based procedure involving enantioselective LC-MS/MS analysis of the two isomers of lambda-cyhalothrin is presented. Separation is achieved on a cellulose-based stationary phase covered by an immobilized chiral selector.

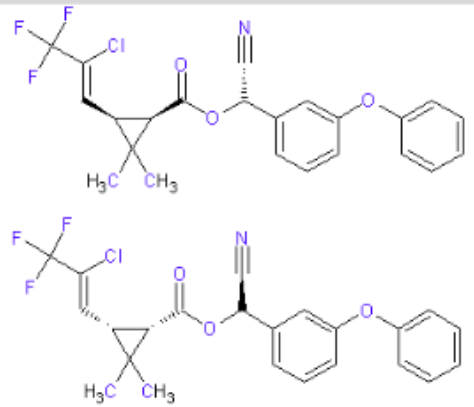
Background information:

Cyhalothrin, is an insecticide belonging to the group of synthetic pyrethroids. It is currently not approved for use in agriculture within the EU but it is still approved for veterinary purposes against ectoparasites such as ticks and mites. Cyhalothrin consists of 4 stereoisomers (RS, SR, RR, SS) in a 1:1:1:1 ratio. **Lambda-cyhalothrin** is a 1:1 mixture of 2 of the 4 cyhalothrin components (RS and SR). Its

Cyhalothrin: 4 isomers
Lambda Cyhalothrin: 2 isomers (one enantiomeric pair)
Gamma-cyhalothrin: 1 enantiomer.



Compound details:

Name: Lambda-Cyhalothrin (CAS: 91465-08-6) IUPAC: rac-(R)-cyano(3-phenoxyphenyl)methyl (1S,3S)-3-[(1Z)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl]-2,2-dimethylcyclopropane-1-carboxylate		
Parameter	**Value**	
Molecular Mass	449.9 g/mol	
Formula	$C_{23}H_{19}ClF_3NO_3$	
Exact mass	449.10055 Da	
Pka	not ionized [2]	
LogD	7 (20°C) [3]	
Residue definition EU	Lambda-cyhalothrin (includes gamma-cyhalothrin) (sum of R,S and S,R isomers) (F)	
Lambda-cyhalothrin is approved in…	AT, BE, BG, CY, CZ, DE, DK, EE, EL, ES, FI, FR, HR, HU, IE, IT, LT, LU, LV, MT, NL, PL, PT, RO, SI, SK, UK	
ADI / ARfD	0.0025 mg/kg bw per day / 0.005 mg/kg bw (Reg. (EU) 2016/146)	

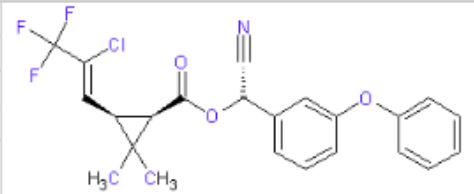
Name: Gamma-Cyhalothrin (CAS: 76703-62-3) IUPAC: (S)-α-cyano-3-phenoxybenzyl (1R)-cis-3-[(Z)-2-chloro-3,3,3-trifluoropropenyl]-2,2-dimethylcyclopropanecarboxylate		
Parameter	**Value**	
Molecular Mass	449.9 g/mol	
Formula	$C_{23}H_{19}ClF_3NO_3$	
Exact mass	449.10055 Da	
Pka	not ionized	
LogD	7 (20°C)	
Residue definition EU	Currently included in the residue definition of lambda cyhalothrin	
Gamma-cyhalothrin is approved in…	BE, BG, CZ, DE, DK, FR, HR, HU, IE, RO, SK	
ADI / ARfD	0.0012 mg/kg bw per day / 0.0025 mg/kg bw (Reg. (EU) 2016/146)	

Table 2: Instrumentation details

LC	WATERS Acquity UPLC IClass		
MS/MS	SCIEX 5500 QTrap, run in ESI positive mode		
Column	ChiralArt Cellulose-SB, 100x4.6 mm, 3 µm		
Pre-column	None		
Mobile Phase	A: 5 mmol NH_4formate in purified water + 5% methanol B: 5 mmol NH_4formate in methanol		
Gradient	**Time** (min)	**Mobile Phase A** (%)	**Mobile Phase B** (%)
	0	20	80
	15	20	80
Flow	0.6 mL/min*		
Injection volume	5 µL**		
Column temperature	35°C		

Figure 1: Sensitivity comparison of Sciex 4000 QTrap and 5500 QTrap instruments, exemplary using acetonitrile *solutions* of gamma-cyhalothrin and lambda-cyhalothrin at 0.1µg/mL each

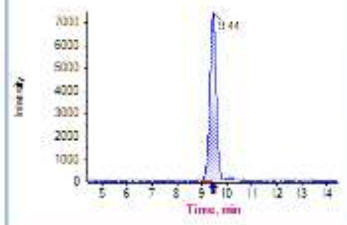
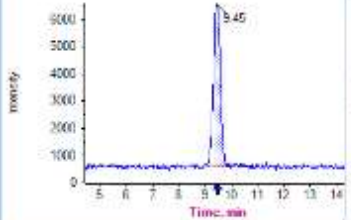
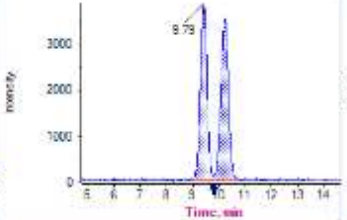
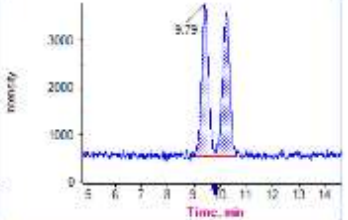
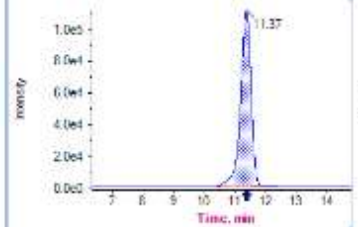
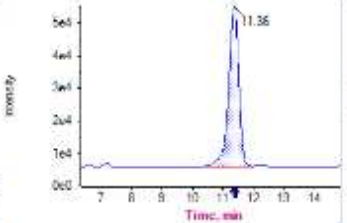
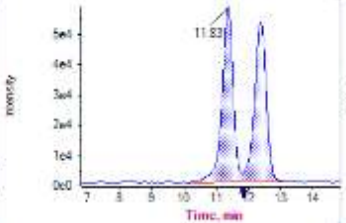
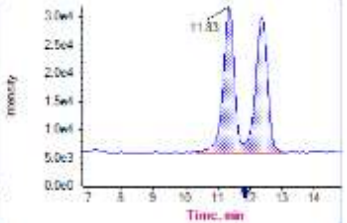
Instrument	gamma-cyhalothrin m/z 467>225 (target)	gamma-cyhalothrin m/z 467>450	lambda-cyhalothrin m/z 467>225 (target)	lambda-cyhalothrin m/z 467>450
Sciex 4000 QTrap				
Sciex 5500 QTrap				

Table 6: Validation of gamma-cyhalothrin respectively lambda-cyhalothrin on cucumber with PSA cleanup (ESI-pos. mode using Sciex API 5500 QTrap),

Compound	MRM used	Spiking Level* (mg/kg)	dSPE Cleanup (with PSA/C_{18})	Mean Recovery %
Gamma-Cyhalothrin	467>225	0.005	**Yes**	105
			No	108
Lambda-Cyhalothrin		0.010	**Yes**	103
			No	103

OVERALL PT EVALUATION

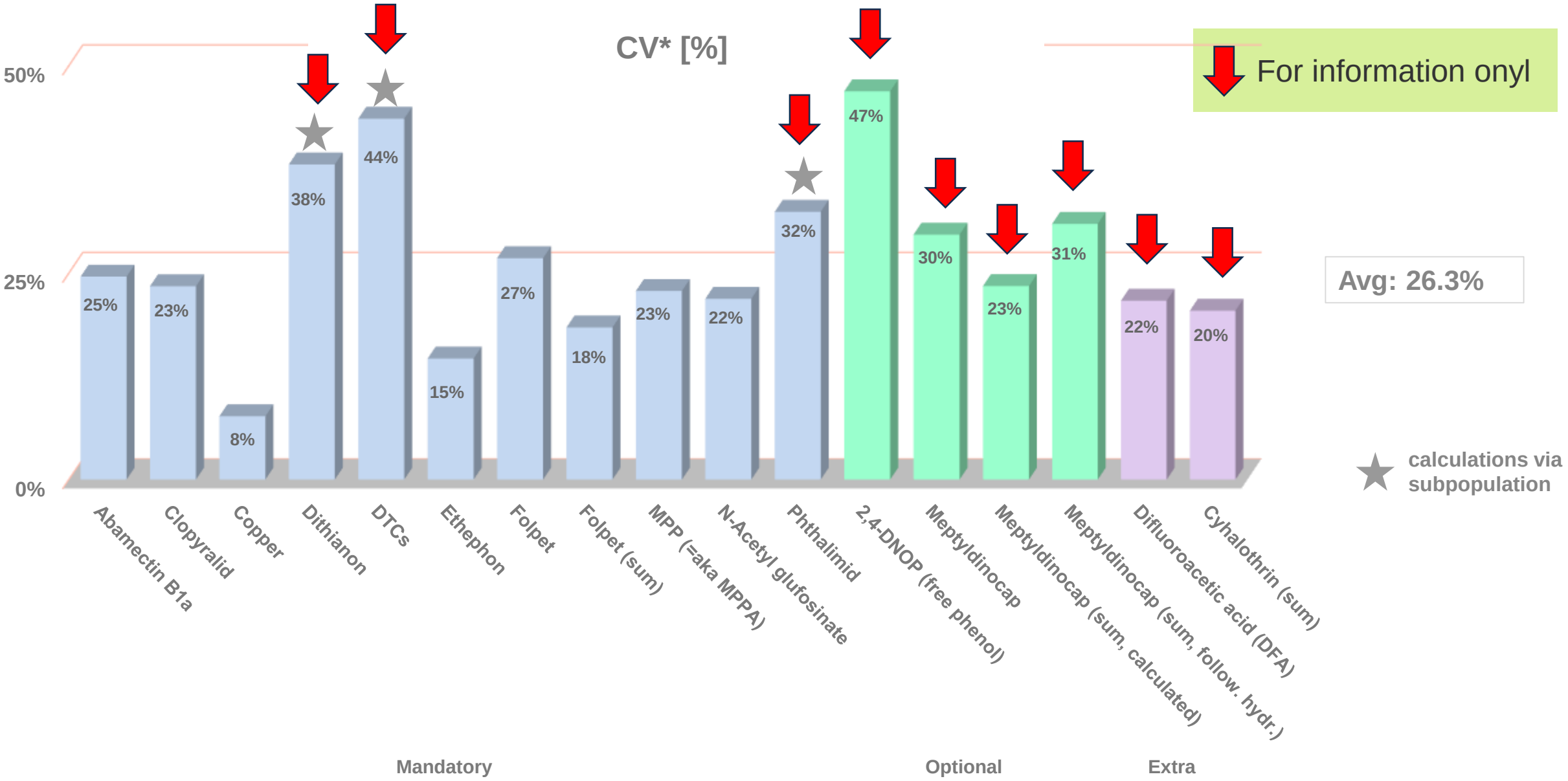
EURL-SRM

Uncertainty of assigned value

COMPULSORY / OPTIONAL / Extra Compounds

EU+EFTA

	Compound	Population for AV, if not entire population	No. of FNs | Outlier	No. of Numerical Results for AV (excl. outliers)	AV [mg/kg]	CV* [%]	Uncertainty of AV (UAV) [mg/kg]	UAV-Tolerance [mg/kg]	Judgement
Mandatory	Abamectin B1a		2 | 1	96	0.0711	24.6%	0.0022	0.0053	passed
	Clopyralid		2 | 1	74	0.192	23.4%	0.0065	0.0144	passed
	Copper		0 | 1	74	29.9	7.7%	0.3334	2.2425	passed
	Dithianon	only strong protected	2 | 0	40	0.236	38.1%	0.0178	0.0177	failed
	DTCs	entire, but AV was set at 0.1	5 | 5	82	0.1	43.6%	—	0.0075	—
	Ethephon		3 | 2	91	0.0582	14.7%	0.0011	0.0044	passed
	Folpet		8 | 3	77	0.225	26.8%	0.0086	0.0169	passed
	Folpet (sum)		2 | 3	78	0.421	18.4%	0.011	0.0316	passed
	MPP (=aka MPPA)		2 | 2	71	0.0819	22.8%	0.0028	0.0061	passed
	N-Acetyl glufosinate		4 | 1	74	0.0773	21.9%	0.0025	0.0058	passed
	Phthalimid	only LC based results	1 | 2	14	0.082	32.4%	0.0089	0.0062	failed
Optional	2,4-DNOP (free phenol)		2 | 1	11	0.0647	46.9%	0.0114	0.0049	failed
	Meptyldinocap		1 | 5	13	0.086	29.6%	0.0088	0.0065	failed
	Meptyldinocap (sum, calculated)		1 | 3	10	0.15	23.4%	0.0139	0.0113	failed
	Meptyldinocap (sum, follow. hydr.)		1 | 3	15	0.188	30.9%	0.0188	0.0141	failed
Extra	Difluoroacetic acid (DFA)		1 | 0	9	0.146	21.7%	0.0131	0.011	failed
	Cyhalothrin (sum)		1 | 1	13	0.0773	20.5%	0.0053	0.0058	passed

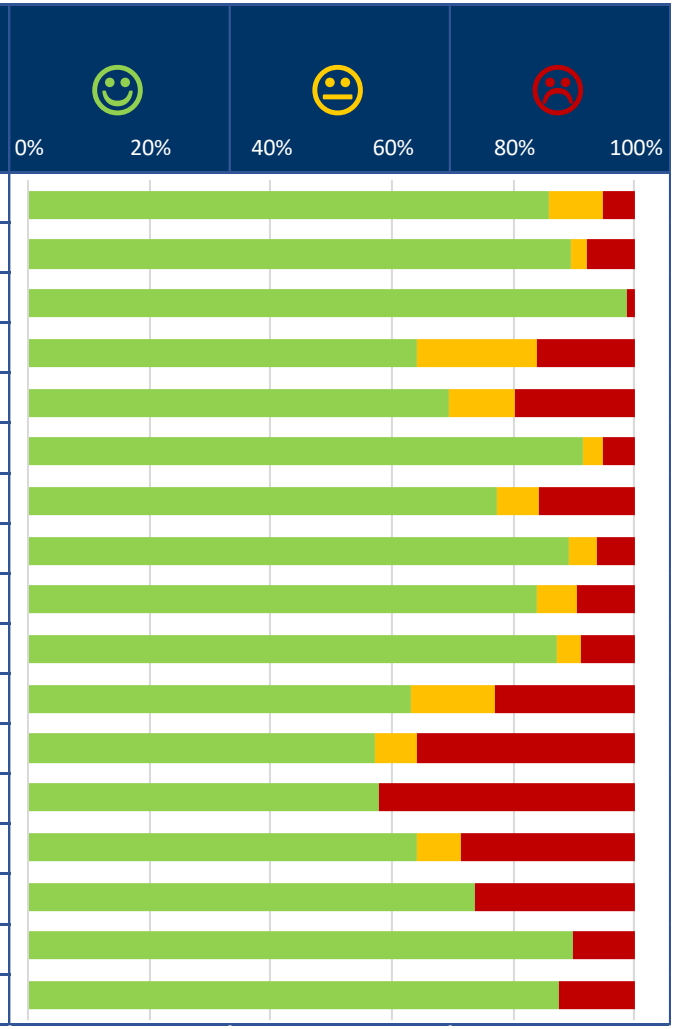

CV* [%]
50%
25%
0%
For information onyl
Avg: 26.3%
calculations via subpopulation
25%
23%
8%
38%
44%
15%
27%
18%
23%
22%
32%
47%
30%
23%
31%
22%
20%
Abamectin B1a
Clopyralid
Copper
Dithianon
DTCs
Ethephon
Folpet
Folpet (sum)
MPP (=aka MPPA)
N-Acetyl glufosinate
Phthalimid
2,4-DNOP (free phenol)
Meptyldinocap
Meptyldinocap (sum, calculated)
Meptyldinocap (sum, follow. hydr.)
Difluoroacetic acid (DFA)
Cyhalothrin (sum)
Mandatory
Optional
Extra

Overall Performance I

COMPULSORY / OPTIONAL / Extra Compounds

EU+EFTA

Compound	No. of Labs (all)	No. of Subpopulation for AV (excl. outliers)	FNs (therein)	Outliers (therein)	AAZ (excl. FNs)	CV* [%]
Abamectin B1a	99		2	1	1.0	24.6%
Clopyralid	77		2	1	0.9	23.4%
Copper	75		0	1	0.2	7.7%
Dithianon	81	42	2	0	1.2	38.1%
DTCs	92		5	5	1.8	43.6%
Ethephon	96		3	2	1.0	14.7%
Folpet	88		8	3	1.2	26.8%
Folpet (sum)	83		2	3	0.8	18.4%
MPP (=aka MPPA)	75		2	2	1.9	22.8%
N-Acetyl glufosinate	79		4	1	1.6	21.9%
Phthalimid	87	17	1	2	3.3	32.4%
2,4-DNOP (free phenol)	14		2	1	2.2	46.9%
Meptyldinocap	19		1	5	24.9	29.6%
Meptyldinocap (sum, calculated)	14		1	3	6.4	23.4%
Meptyldinocap (sum, follow. hydr.)	19		1	3	2.9	30.9%
Difluoroacetic acid (DFA)	10		1	0	0.6	21.7%
Cyhalothrin (sum)	15		1	1	0.8	20.5%



EURL-SRM

Overall Performance II

Rules for Category A:

EU+EFTA

- Analysed for at least 17 out of 19 compulsory pesticides
- Correctly found at least 10 out of 11 compulsory pesticides present in test item

- No FPs among compulsory analytes

	No. of Labs	[%]
	EU/EFTA / (3rd C)	
Category A	50 (3)	41 % (25%)
Category B	73 (9)	59 % (75%)

EURL-SRM

Overall Performance II

Rules for Category A:

EU+EFTA

- Analysed for at least 17 out of 19 compulsory pesticides
- Correctly found at least 10 out of 11 compulsory pesticides present in test item

- No FPs among compulsory analytes

Excluding Cu

	No. of Labs	[%]
	EU/EFTA / (3rd C)	
Category A	56 / (3)	46 % / (25%)
Category B	67 / (9)	54 % / (75%)

Methods used

(according to information provided by participants, which may not be fully accurate)

	QuEChERS-Style	Mini-Luke/S19	EtAc-Mth	QuPPe-Style	Deriv (ethylene)	ALL
2,4-DNOP (free phenol)	100%	0%	0%	0%	0%	100%
Meptyldinocap	100%	0%	0%	0%	0%	100%
Meptyldinocap (sum, calculated)	100%	0%	0%	0%	0%	100%
Meptyldinocap (sum, follow. hydr.)	95%	0%	5%	0%	0%	100%
Gamma Cyhalothrin	95%	0%	5%	0%	0%	100%
Dithianon	93%	2%	2%	2%	0%	100%
Abamectin B1a	93%	2%	3%	2%	0%	100%
Folpet (sum)	89%	6%	6%	0%	0%	100%
Phthalimide	89%	5%	3%	2%	0%	100%
Folpet	88%	6%	5%	0%	0%	100%
Clopyralid	88%	2%	0%	10%	0%	100%
Ethephon	2%	0%	0%	97%	1%	100%
MPP (=aka MPPA)	4%	0%	0%	96%	0%	100%
N-Acetyl glufosinate	2%	0%	0%	98%	0%	100%
Difluoroacetic acid (DFA)	0%	0%	0%	100%	0%	100%

Method used for Dithiocarbamates

Methods used

(according to information provided by participants, which may not be fully accurate)

DTCs

Appoach	No. Labs	% of Labs
LLP (isooctane)	48	47%
Headspace	26	25%
Headspace-SPME	10	10%
Spectroph. (Xanthogenate)	11	11%
Spectroph. (Cu-Acetate)	5	5%
Derivatization + QuEChERS	2	2%
ALL	102	100%

Method used for Copper

Methods used

(according to information provided by participants, which may not be fully accurate)

Cu

Approach	No. Labs	% of labs
ICP-MS	60	71%
ICP-MS (SF)	3	4%
AES	10	12%
FAAS	5	6%
IC-MS/MS	6	7%
IC-Conductivity	1	1%
ALL	85	100%

Use of ILIS

Use of ILIS

(according to information provided by participants, which may not be fully accurate)

More and more labs use ILIS for polar compounds or sensitive compounds

Pesticides	ILIS	Other IS	None	ALL	At what stage is ILIS used ? Beginning	Interm.	Final Aliquot
Dithianon	25%	33%	43%	100%	21		1
Folpet	22%	36%	42%	100%	13		8
Phthalimide	11%	41%	48%	100%	7		3
Abamectin B1a	9%	41%	50%	100%	3		
Clopyralid	4%	40%	56%	100%	3		
2,4-DNOP (free phenol)		60%	40%	100%			
Gamma Cyhalothrin		59%	41%	100%			
Meptyldinocap		59%	41%	100%			
Meptyldinocap (sum, follow. hydr.)		48%	52%	100%			
Ethephon	55%	5%	40%	100%	49	1	9
N-Acetyl glufosinate	47%	11%	41%	100%	35		6
MPP (=aka MPPA)	47%	13%	40%	100%	33		6
Difluoroacetic acid (DFA)		27%	73%	100%			
DTC (expr. as CS2)	1%	16%	83%	100%	1		
Copper	1,2%	58,8%	40%	100%			1

More and more labs using ILIS add it at the beginning

EURL-SRM

Poor performance and Feedback

Poor performance

EU+EFTA

88 EU/EFTA OfLs reported

200 results indicating poor performance (therein 47 FNs/FN* and 7 FPs)

Compulsory Analytes			
abs. z scores > 2		FP	
No. of Labs	No. of Results	No. of Labs	No. of Results
86	166	4	6

Optional Analytes			
abs. z scores > 2		FP	
No. of Labs	No. of Results	No. of Labs	No. of Results
13	24	1	1

Extra Analytes	
abs. z scores > 2	
No. of Labs	No. of Results
3	3

Feedback on Poor Performance

- **51 EU/EFTA OfLs gave feedback for poor performance in 108 cases** (as of 14 June)

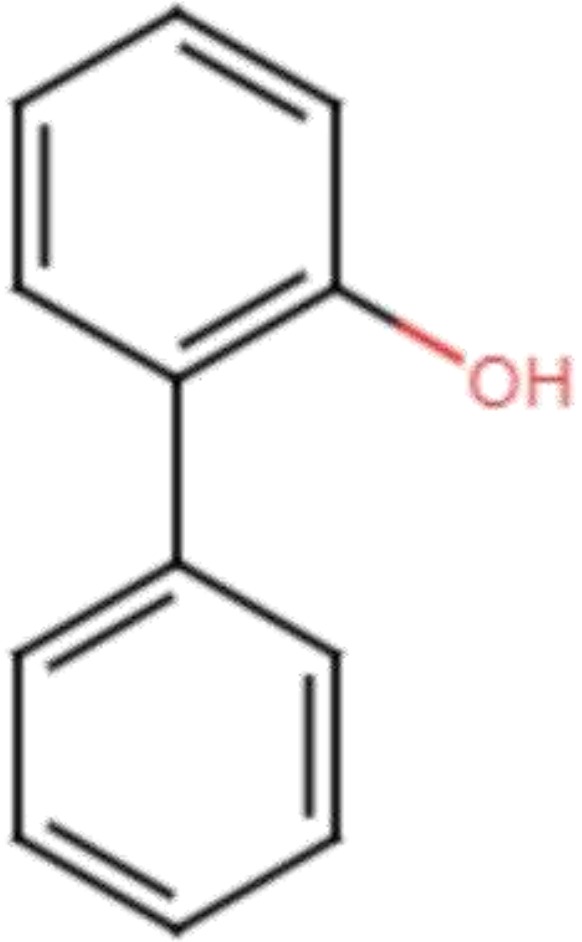
No. cases	Reasons
40	**Analytes losses** (e.g. during transport, sample preparation); therein **13 in case of decomposition of folpet in GC** injection resulting to overestimation of PI
27	**Analytical procedure was inappropriate**; therein **21 cased using GC to determine folpet and/or PI** in the presence of both analytes
23	Others/Miscellaneous
20	**Lack of experience**
12	**Transcription- / documentation-/ communication-/ error**
9	**Calculation error** (e.g. use of wrong factor, to express residue as required in PT; to address dilutions etc.)
8	**Measurement problems** (e.g. poor chromatographic separation, poor sensitivity, signal interfered by matrix)

Feedback on Poor Performance

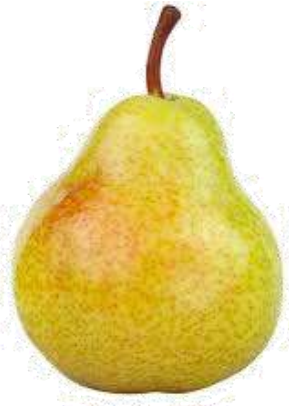
- **51 EU/EFTA OfLs gave feedback for poor performance in 108 cases** (as of 14 June)

No. cases	Reasons
8	**Inappropriate / erroneous calibration approach** (e.g. matrix effects not properly compensated)
7	**Erroneous analytical standard** (e.g. due to degradation, wrong purity, wrong dilution) (One lab reported erroneous purity of purchased avermectibe std. (confirmed by EURL-SRM)
5	**Misinterpretation / Misevaluation** of measurement data
4	**Analytical procedure was appropriate but it was not properly performed** (e.g. important component - e.g. water - was not used, extraction time too short/long)
1	**Result not or not properly corrected for recovery**
1	**Deficient QC-measures** that would have helped to recognize that method generates FNs, FPs or strongly biased results (e.g. no recovery test)

Analysis of OPP (sum)



2-Phenylphenol in Pears



From EFSA Reasoned opinion

EFSA Journal 2017;15(2):4696

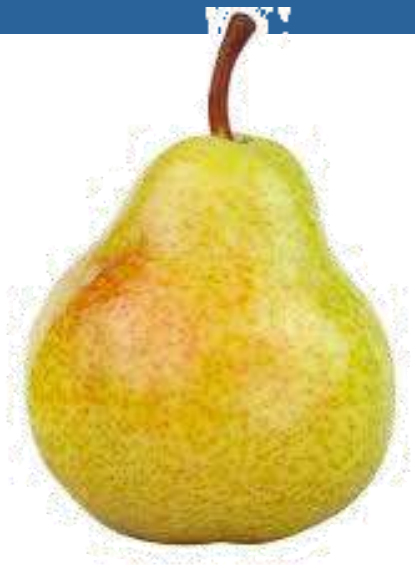
In **pears**, analysed **28 weeks after treatment**, the main residues found in extracts of the different fractions of the fruits were **2-phenylphenol (6% of TRR)** and **its conjugates (74% of TRR). …**

Post-extraction **solids** of peel and pulp were further characterized by hydrolysis steps which **released conjugates of 2-phenylphenol**.

Residue Definition finally Established:

*2-phenylphenol (sum of **2-phenylphenol and its conjugates**, expressed as 2-phenylphenol)*

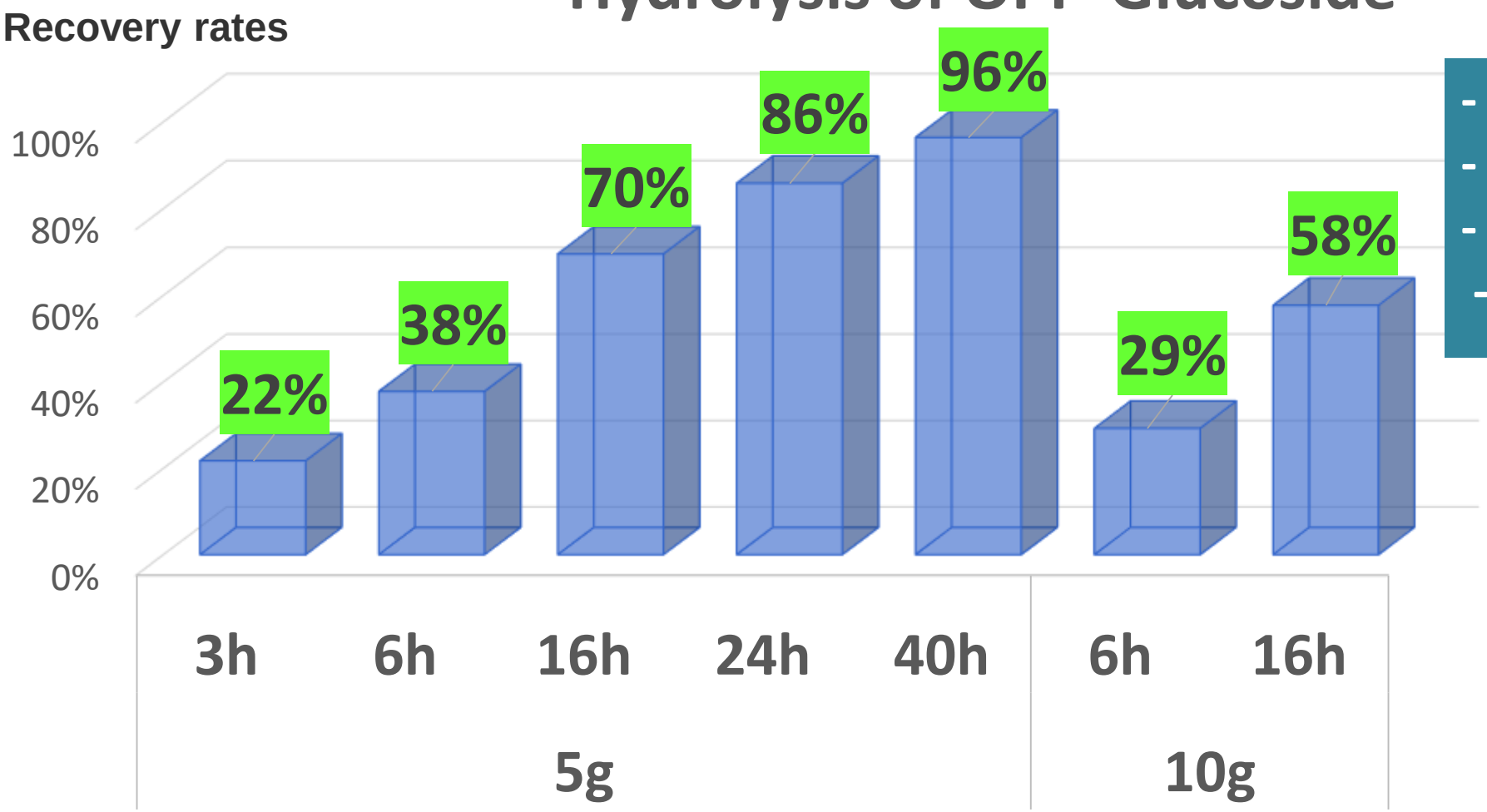
2-Phenylphenol in Pears



Experiment: Treatment of Pears in Lab with OPP

- Pears **dipped in aqueous OPP-Na-salt** solution and stored
- In parallel non-treated pears stored (to use as blank)
- **Storage**: ca. 2 weeks at RT in dark
- **Cryomilling** (treated and blank)
- Extracted via QuEChERS (with and without hydrolysis)
- Matrix-matched calibration
- Additionally use of ILIS

Hydrolysis of OPP-Glucoside

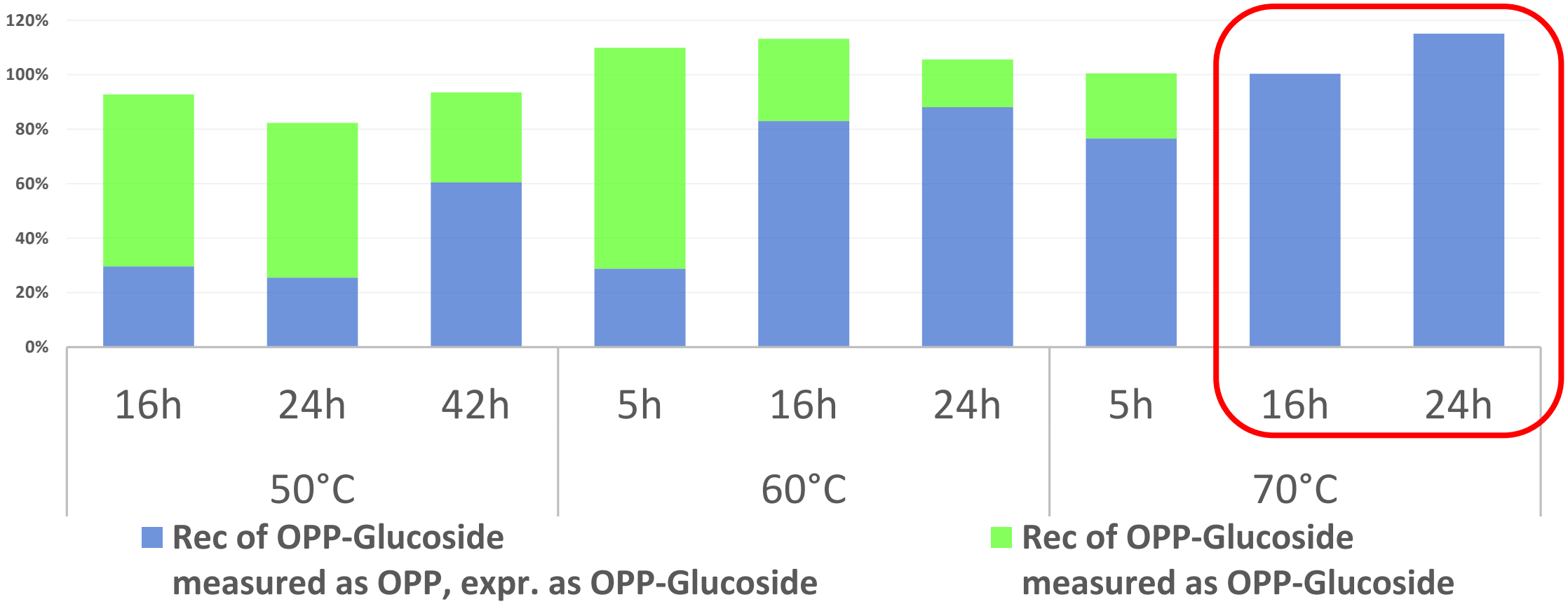


- Spiked as OPP-Glc
- Hydrolyzed w. H_2SO_4
- Measured as OPP
  - Expressed as OPP-Glc

0.5 ppm OPP-Glucoside spiked on **Orange**
Hydrolysis: using 2ml 10N H2SO4 at **60°C**

Reducing sample size improves hydrolysis yields

Acidic Hydrolysis of OPP Glucoside – Very Challenging !!



5g sample spiked OPP-Glucosid. Hydrolysis by adding 2 mL H_2SO_4 10N

Measurement: OPP-Glucoside and OPP via LC-MS/MS

Hydrolysis of OPP Glucoside – Very Challenging !!

5g Matrix + 2 mL H_2SO_4 10N + 1mL water,
16-24h at 70°C
Neutralize with 2 mL NaOH 10 N
Continue with normal QuEChERS

Lab logistics -> Overnight (unattended) Reaction

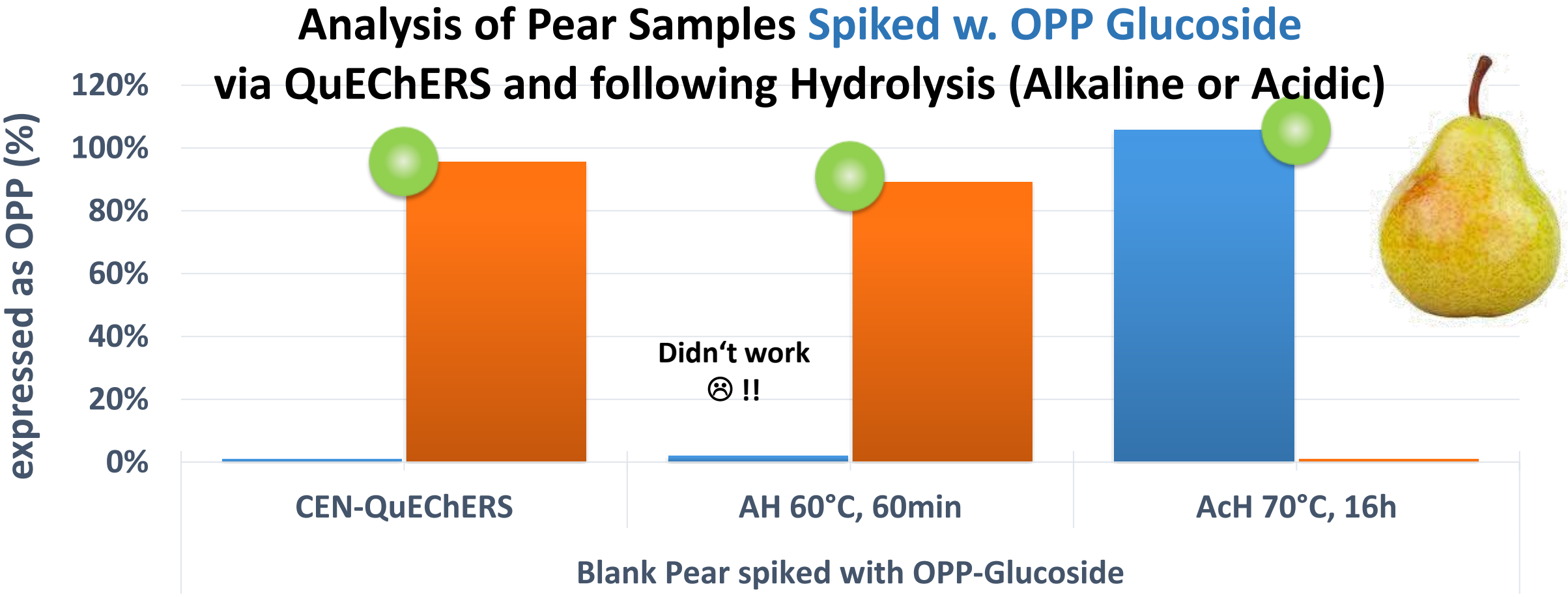
6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
						1h	2h	3h	4h	5h	6h	7h	8h	9h	10h	11h	12h	13h	14h	15h	16h	17h	18h	19h	20h														
							1h	2h	3h	4h	5h	6h	7h	8h	9h	10h	11h	12h	13h	14h	15h	16h	17h	18h	19h	20h													
								1h	2h	3h	4h	5h	6h	7h	8h	9h	10h	11h	12h	13h	14h	15h	16h	17h	18h	19h	20h												
									1h	2h	3h	4h	5h	6h	7h	8h	9h	10h	11h	12h	13h	14h	15h	16h	17h	18h	19h	20h											
										1h	2h	3h	4h	5h	6h	7h	8h	9h	10h	11h	12h	13h	14h	15h	16h	17h	18h	19h	20h										
											1h	2h	3h	4h	5h	6h	7h	8h	9h	10h	11h	12h	13h	14h	15h	16h	17h	18h	19h	20h									
												1h	2h	3h	4h	5h	6h	7h	8h	9h	10h	11h	12h	13h	14h	15h	16h	17h	18h	19h	20h								
													1h	2h	3h	4h	5h	6h	7h	8h	9h	10h	11h	12h	13h	14h	15h	16h	17h	18h	19h	20h							
														1h	2h	3h	4h	5h	6h	7h	8h	9h	10h	11h	12h	13h	14h	15h	16h	17h	18h	19h	20h						

Hour in the day to **end reaction**

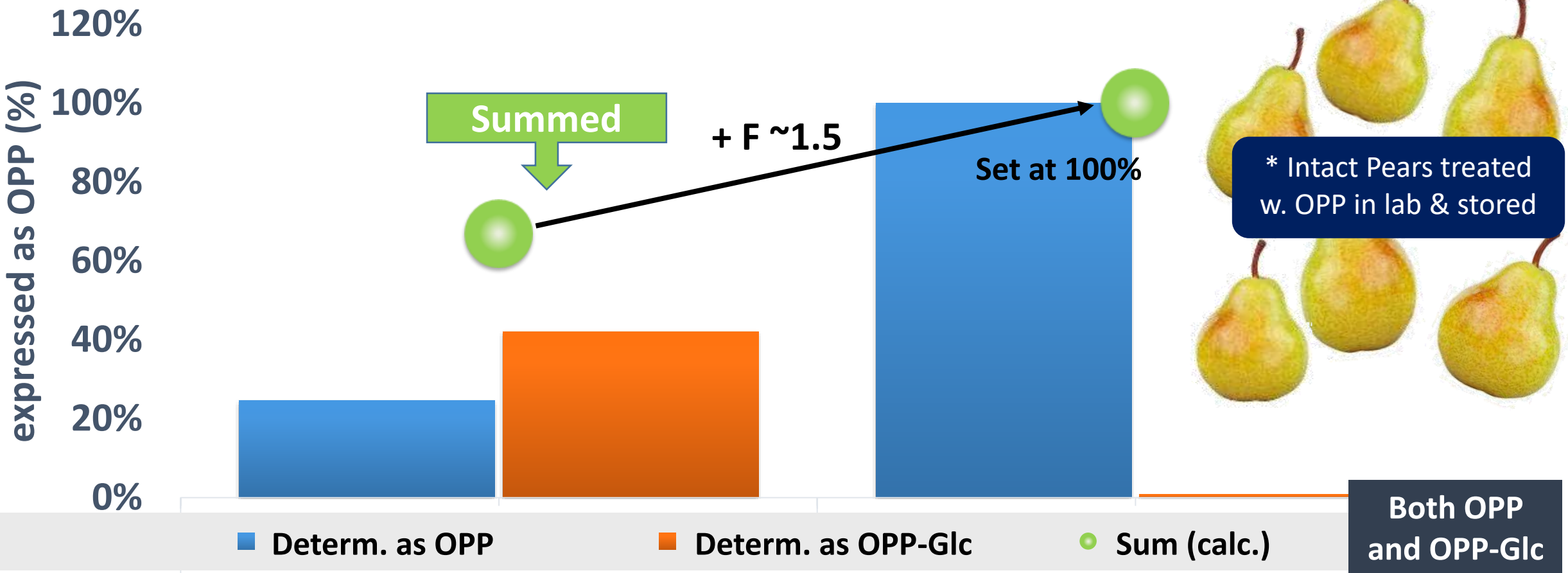
Hour in the day to **start reaction**

Analysis of OPP (sum) following hydrolysis to OPP

Both OPP and OPP-Glc measured by LC-MS/MS



Determination of OPP and OPP-Glucoside in SAMPLE 1* using QuEChERS or QuEChERS with Acidic Hydrolysis (AcH)

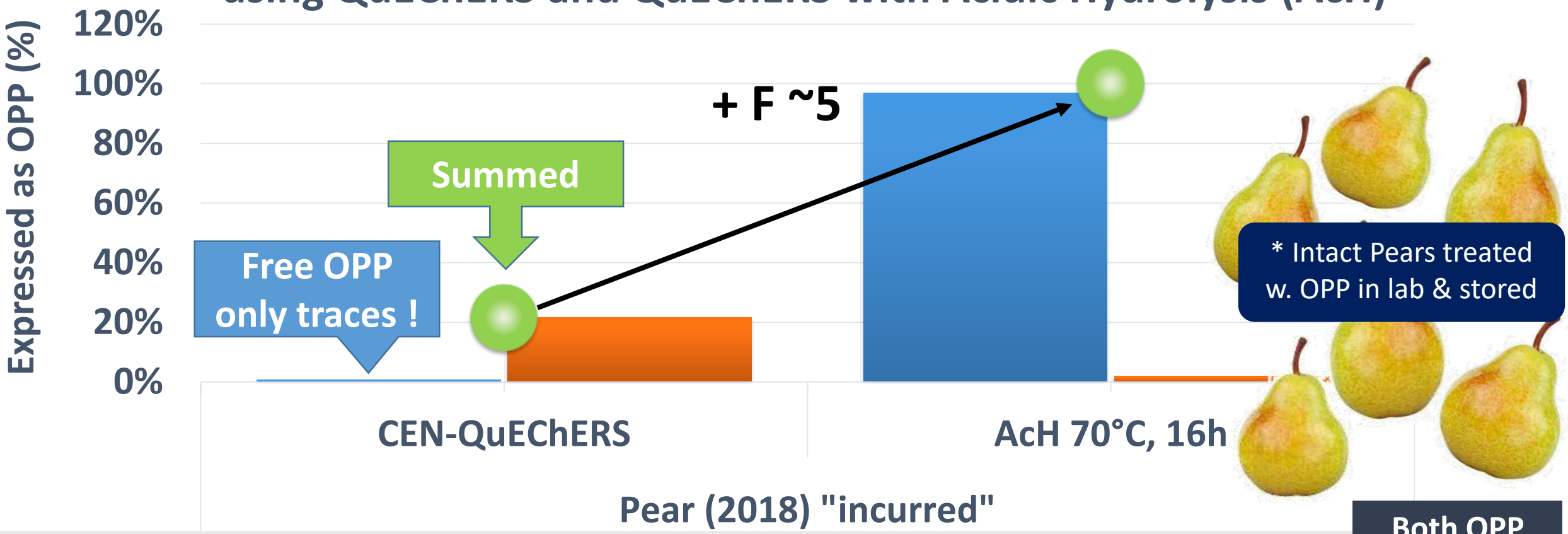


* Intact Pears treated w. OPP in lab & stored

Both OPP and OPP-Glc measured by LC-MS/MS

CONCLUSION: A large share (>75%) of OPP spiked in pears was conjugated. Only a fraction of the hydrolysable conjugates were OPP-Glucoside.

Determination of OPP and OPP-Glucoside in SAMPLE 2* using QuEChERS and QuEChERS with Acidic Hydrolysis (AcH)



* Intact Pears treated w. OPP in lab & stored

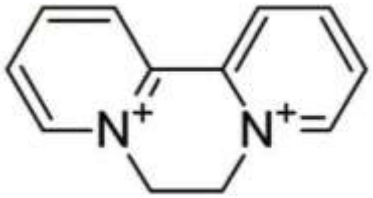
Both OPP and OPP-Glc measured by LC-MS/MS

CONCLUSION: Almost all the OPP spiked in pears was conjugated.
Only a very small fraction of the hydrolysable conjugates were present as OPP-Glucoside.

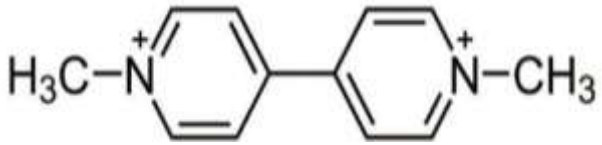
PQ / DQ

Analysis of Diquat (DQ) and Paraquat (PQ)

- Both are non-selektive herbicides
- Both are banned in the EU … but are still widely used elswhere (e.g. as crop-desiccants (e.g. on potatoes, oilseeds, cereals)



Diquat (DQ)



Paraquat (PQ)

Analysis of Diquat (DQ) and Paraquat (PQ)

- EU-MRLs mostly at LOQ with some exeptions

Vázquez C (2015)

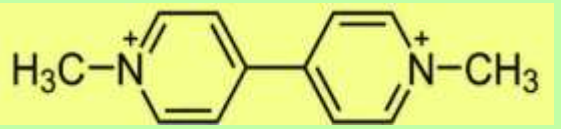
e.g.:

- **PARAQUAT**
  - **Rice**: 0.05 ppm

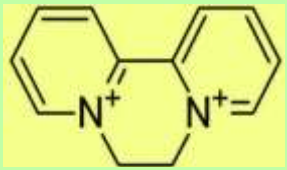
- **DIQUAT**
  - **Oats**: 2 ppm
  - **Potatoes**: 0.1 ppm
  - **Oil seeds:** Linseed 5 ppm, Rapeseed: 1.5 ppm, Sunflower seed 0.9 ppm, Soy 0.3 ppm, Oat 2 ppm
  - **Pulses:** 0.2 ppm (Peas 0.3 ppm),
  - **Tree nuts:** 0.2 ppm
  - **Tree fruits:** Citrus, Pome fruit, Stone fruit …: 0.02 ppm
  - **Other fruits:** Strawberries: 0.05 ppm; Bananas 0.02 ppm

CHALLENGES IN THE ANALYSIS OF PQ and DQ:

MRM-Ion-Ratios Variable Depending on Matrix



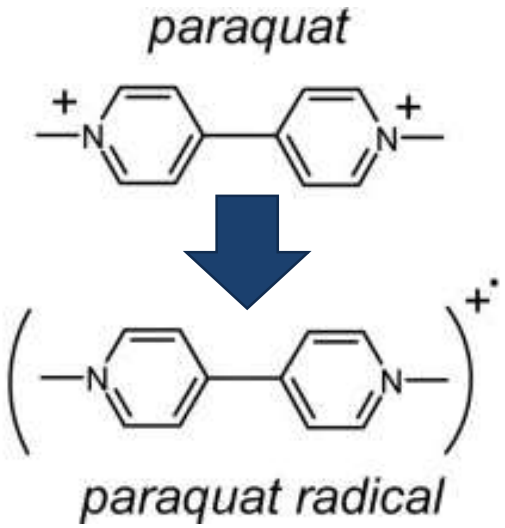
Paraquat (PQ)



Diquat (DQ)

DQ and PQ form **various precursor ions**:

- **Dications $[M]^{2+}$**
- **Radical cations $[M]^{+*}$**
- **Deprotonated cations $[M\text{-}H^{+}]^{+}$**

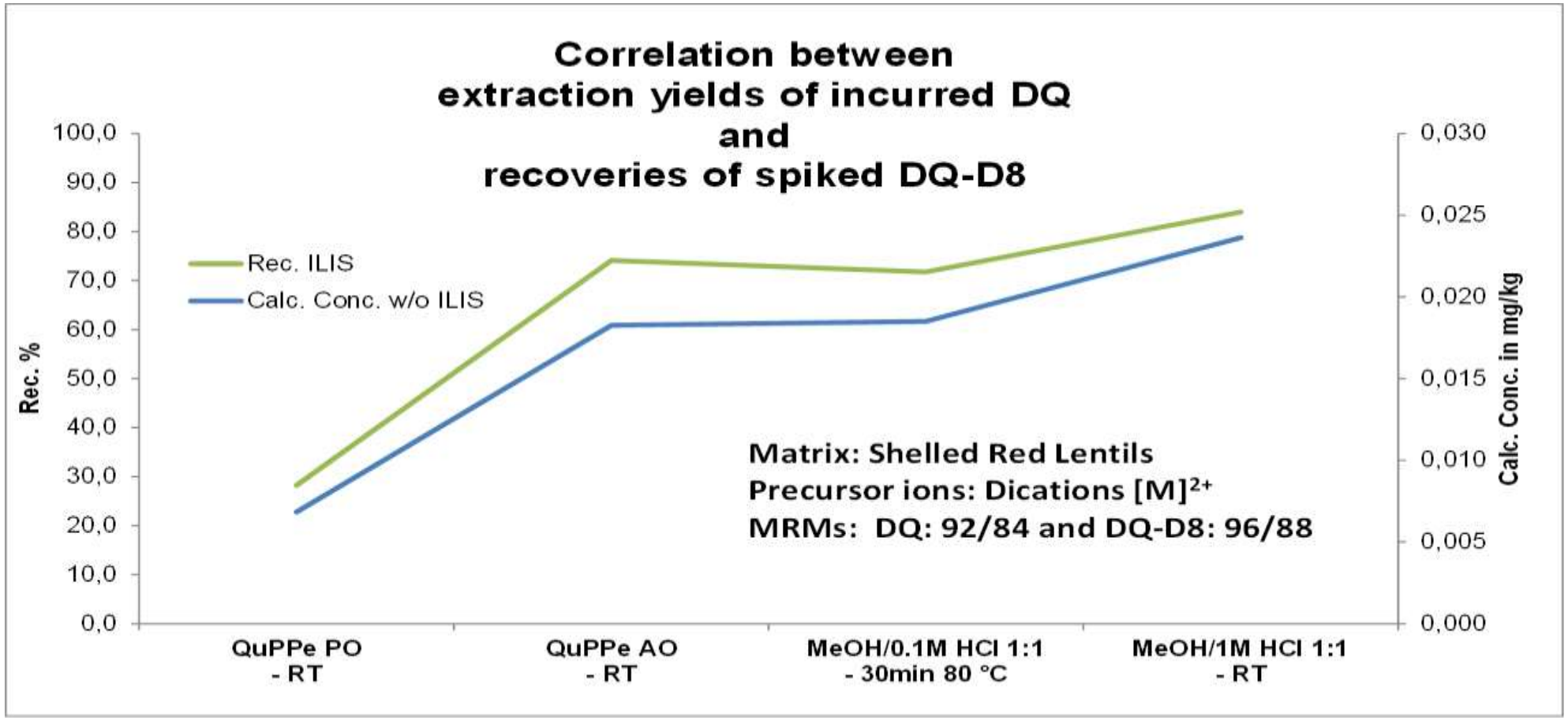


Share of different precursor ions depends on:

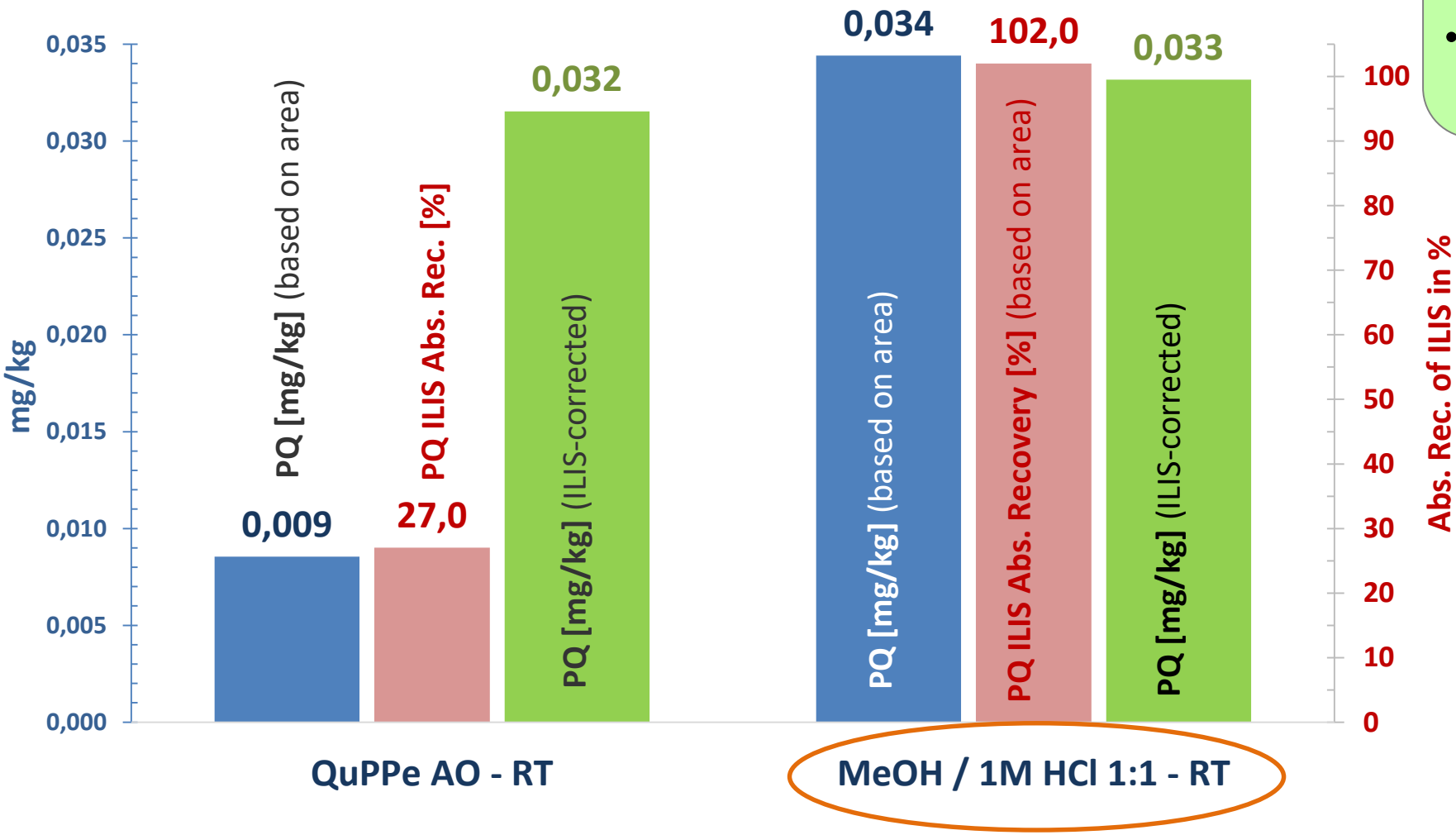
- **Composition of mobile phase** during elution **(incl. co-eluting matrix)**
- Design and condition of the **LC-MS/MS interface**

QuPPe: Diquat and Paraquat – Extractability

- Yields of incurred residues correlate well with the recoveries of spiked DQ/PQ
  → incurred residues and spiked residues are subject to the same equilibria



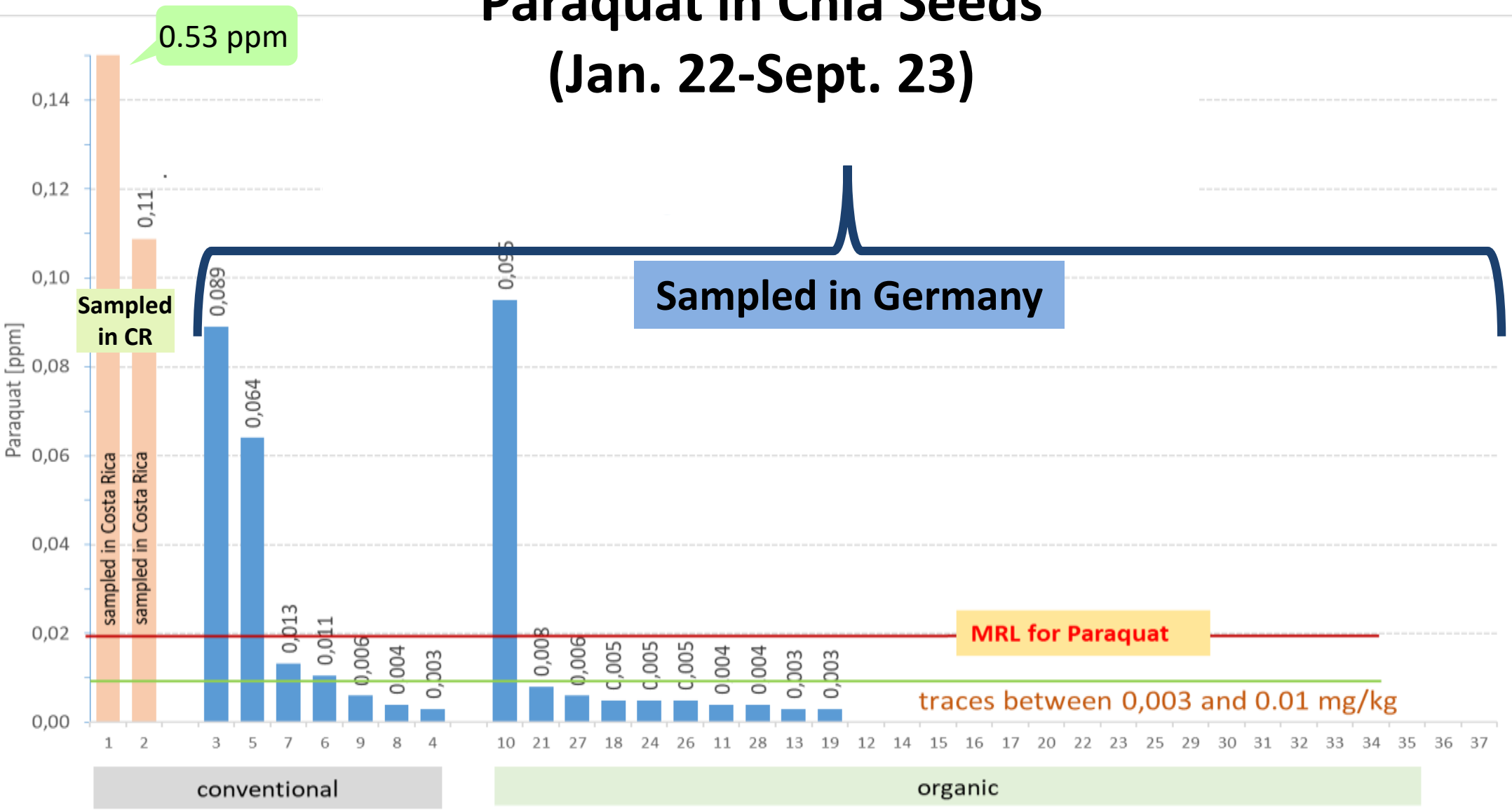
Black Pepper with Incurred Residues of Paraquat



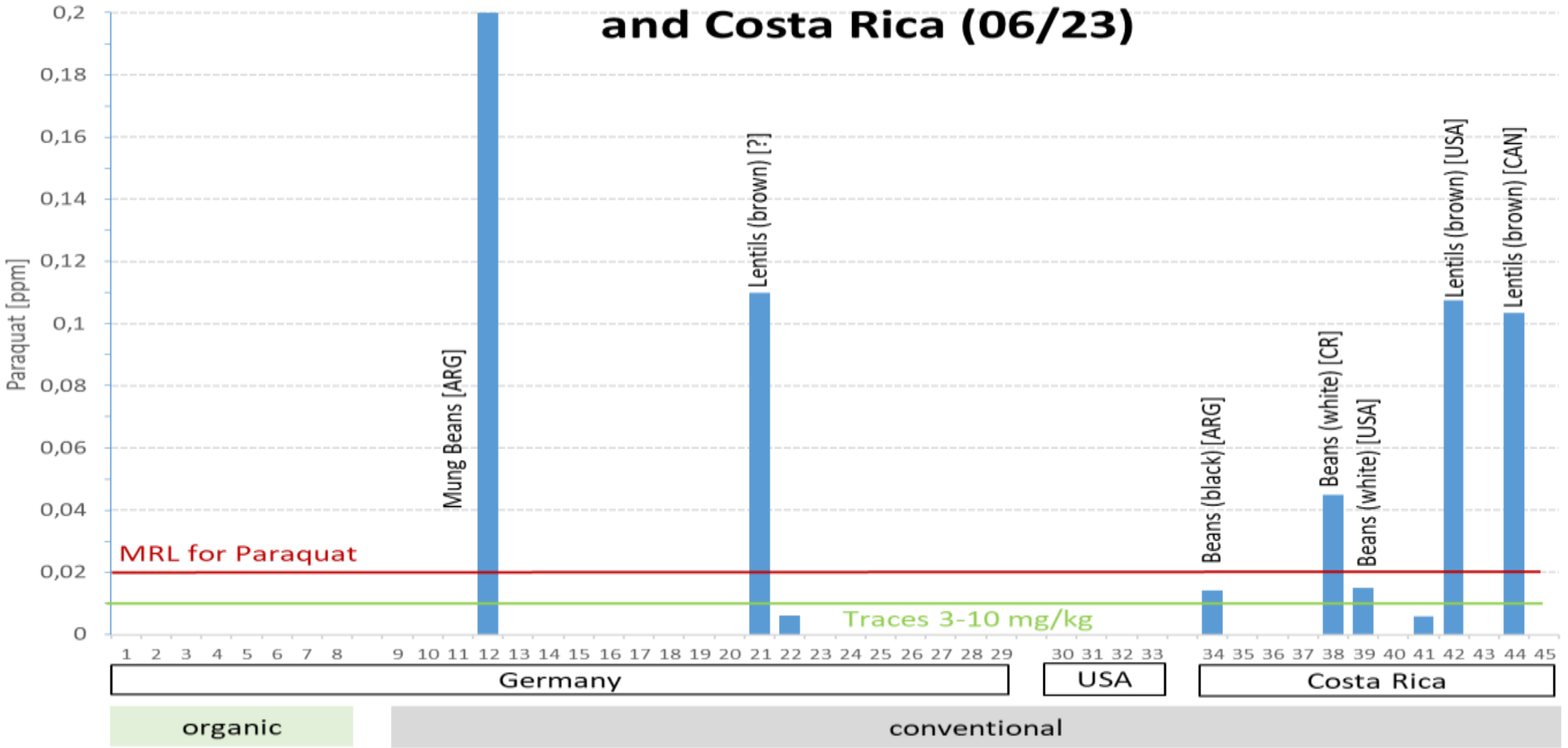
Message:

- **1% HCl was sufficient for quantitative recovery (of ILIS)**
- **ILIS-based correction worked well even in normal QuPPe !!**

Paraquat in Chia Seeds (Jan. 22-Sept. 23)



Paraquat in Pulses collected from the markets in Germany (01/23 - 09/23), USA (08/23) and Costa Rica (06/23)



Monitoring extraction efficiency of PQ/ DQ based on ILIS recoveries
Samples analyzed for Diquat and Paraquat (05/22 - 04/24)

Matrix	No. of samples
Beans	62
Chan	2
Chia	47
Chickpeas	15
Coffee	1
Corn	3
Lentils	**31**
Linseed (flax)	**18**
Moringa	1
Mustard	2
Peanut	11
Peas	11
Potato	**11**
Quinoa	1
Rye	2
Sesame	20
Soybeans	3
Spelt	2
Spices	47
Sunflower	4
Sweet Potato	8
Tapiaoca	1
Wheat	8
TOTAL	**311**

Extraction Conditions currently employed by EURL-SRM:

- **Solvent: 10 mL 1 M HCl / MeOH 1/1**

(+ 10 ml water for dry commodities)

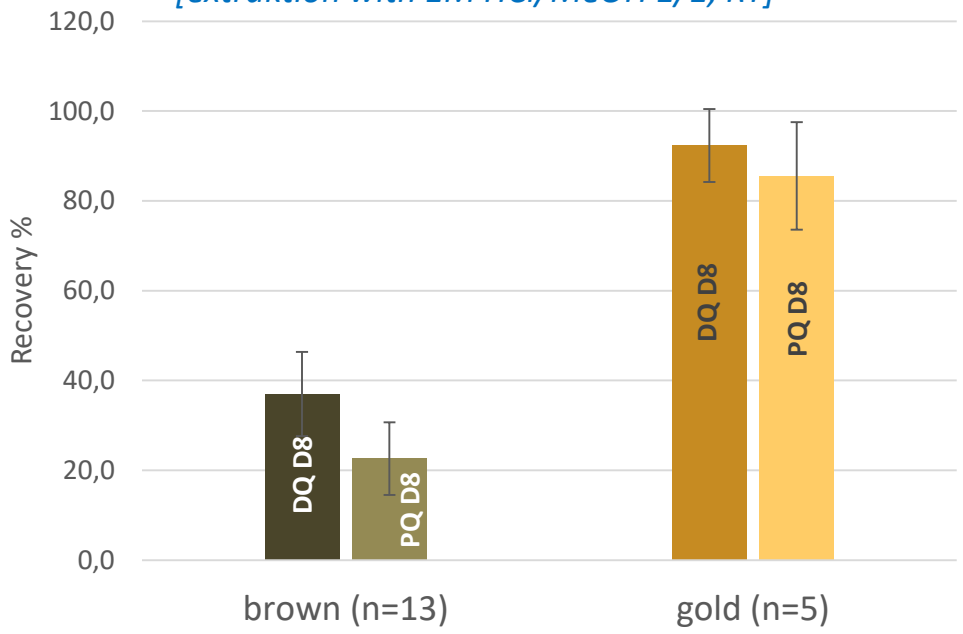
(= 0,25 M HCl in water/MeOH 75/25 in final extract)

- **Extraction temperature:** RT

- **ILIS:** DQ D8 and PQ D8

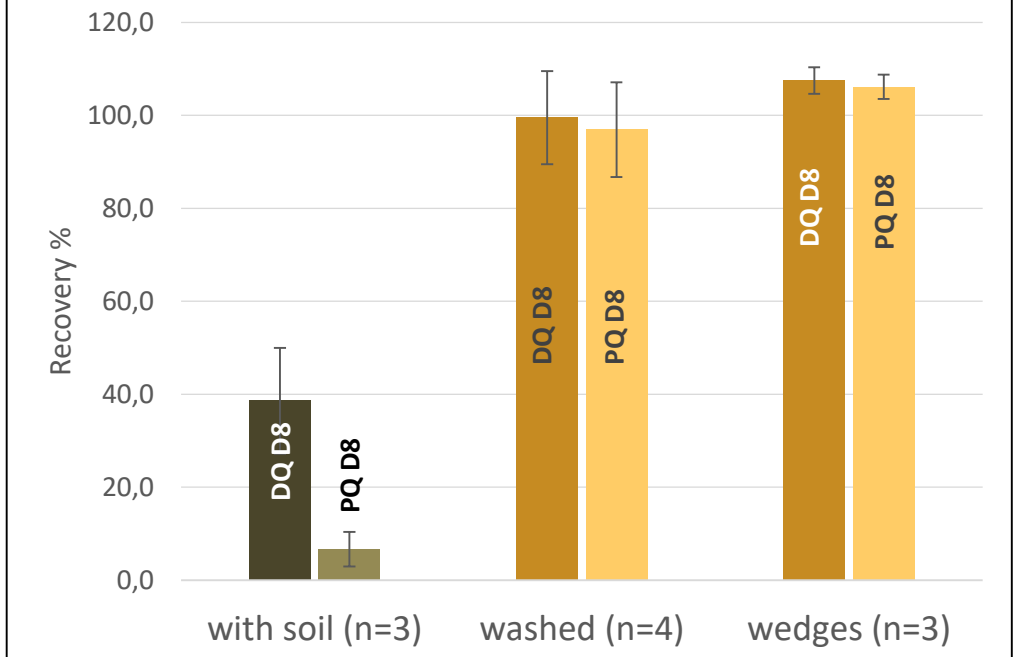
Recovery ILIS in Linseed

[extraktion with 1M HCl/MeOH 1/1, RT]

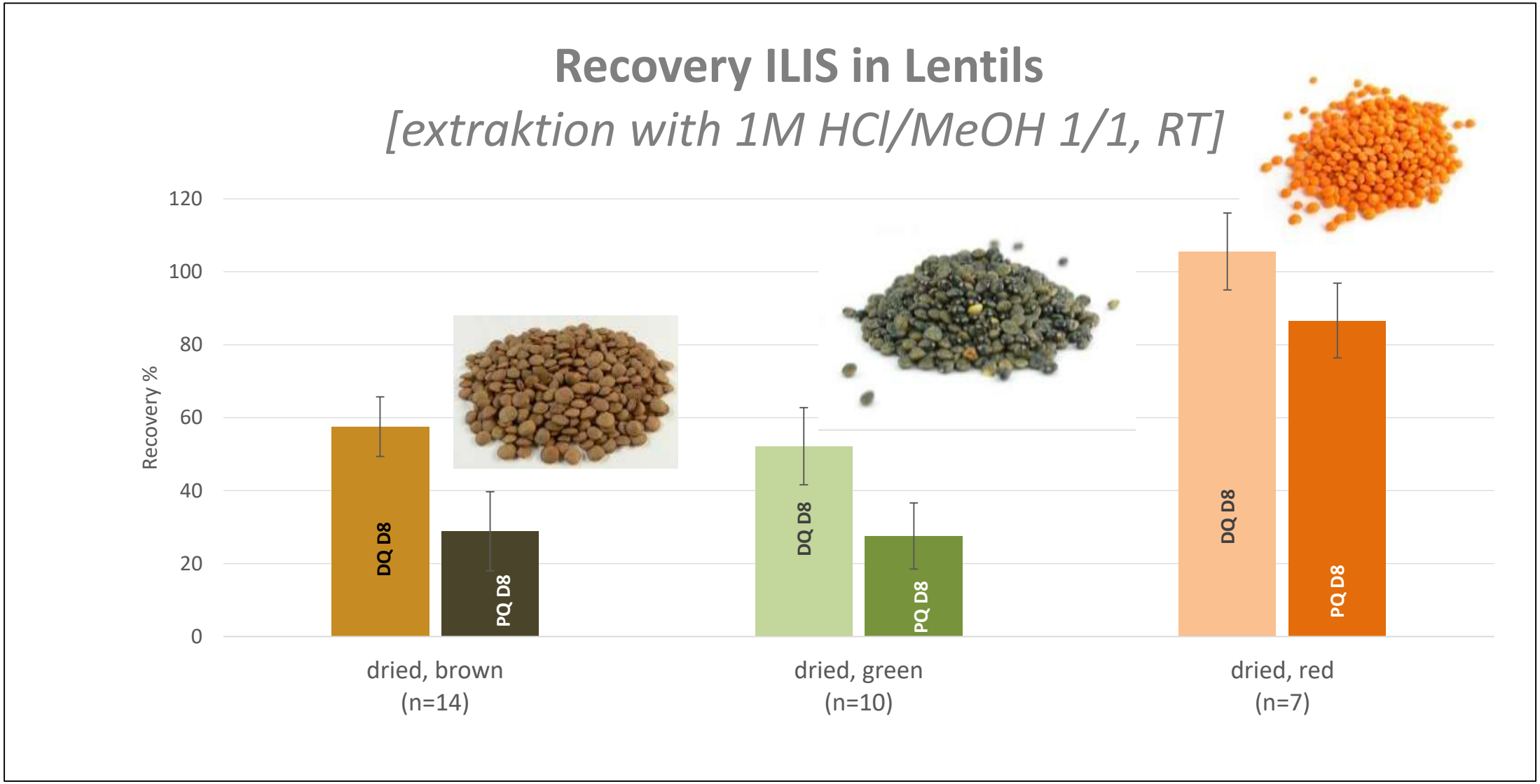


Recovery ILIS in Potato

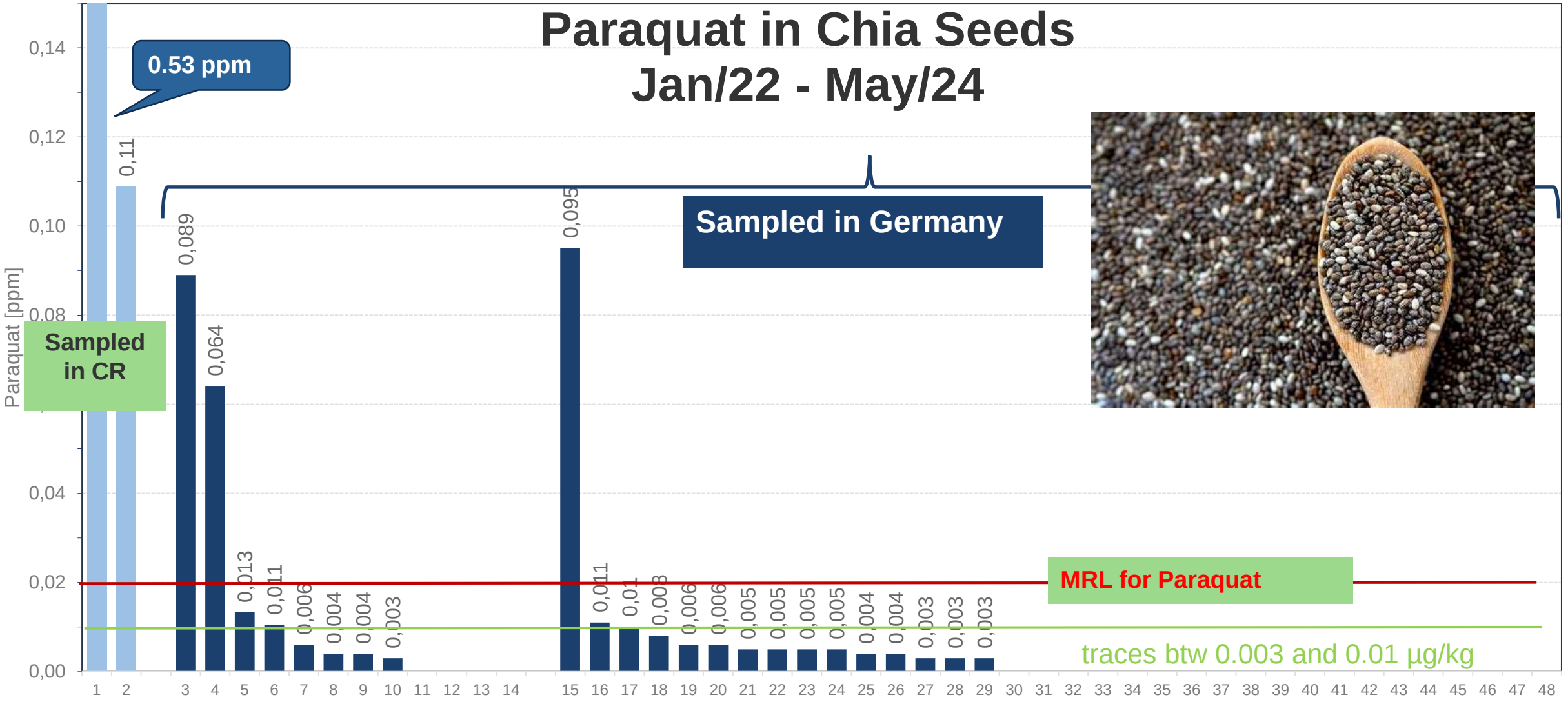
[extraktion with 1M HCl/MeOH 1/1, RT]



Extraction Efficiency – Recovery ILIS Lentils

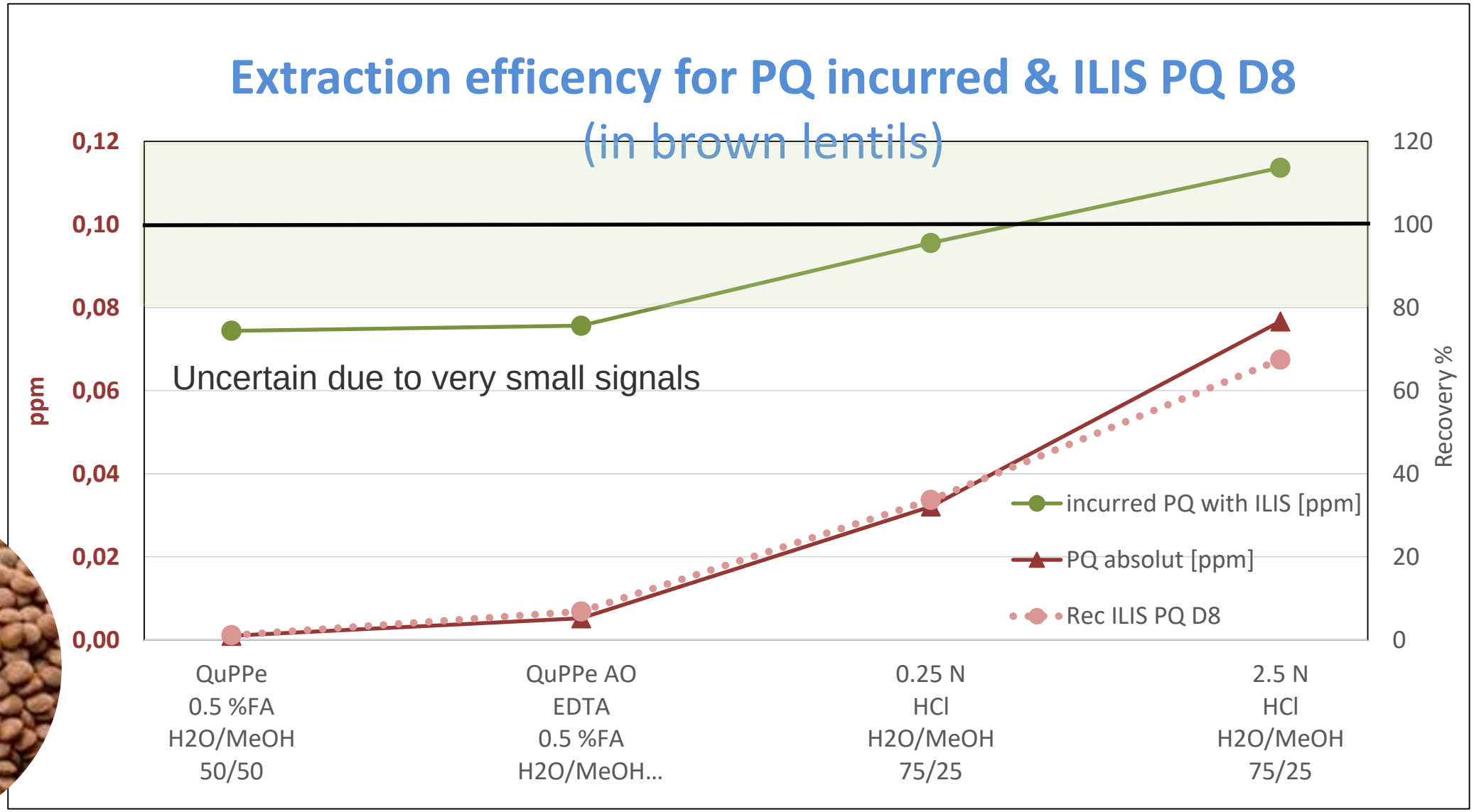


Paraquat in Chia Seeds
Jan/22 - May/24



Extraction efficency for PQ incurred & ILIS PQ D8

(in brown lentils)

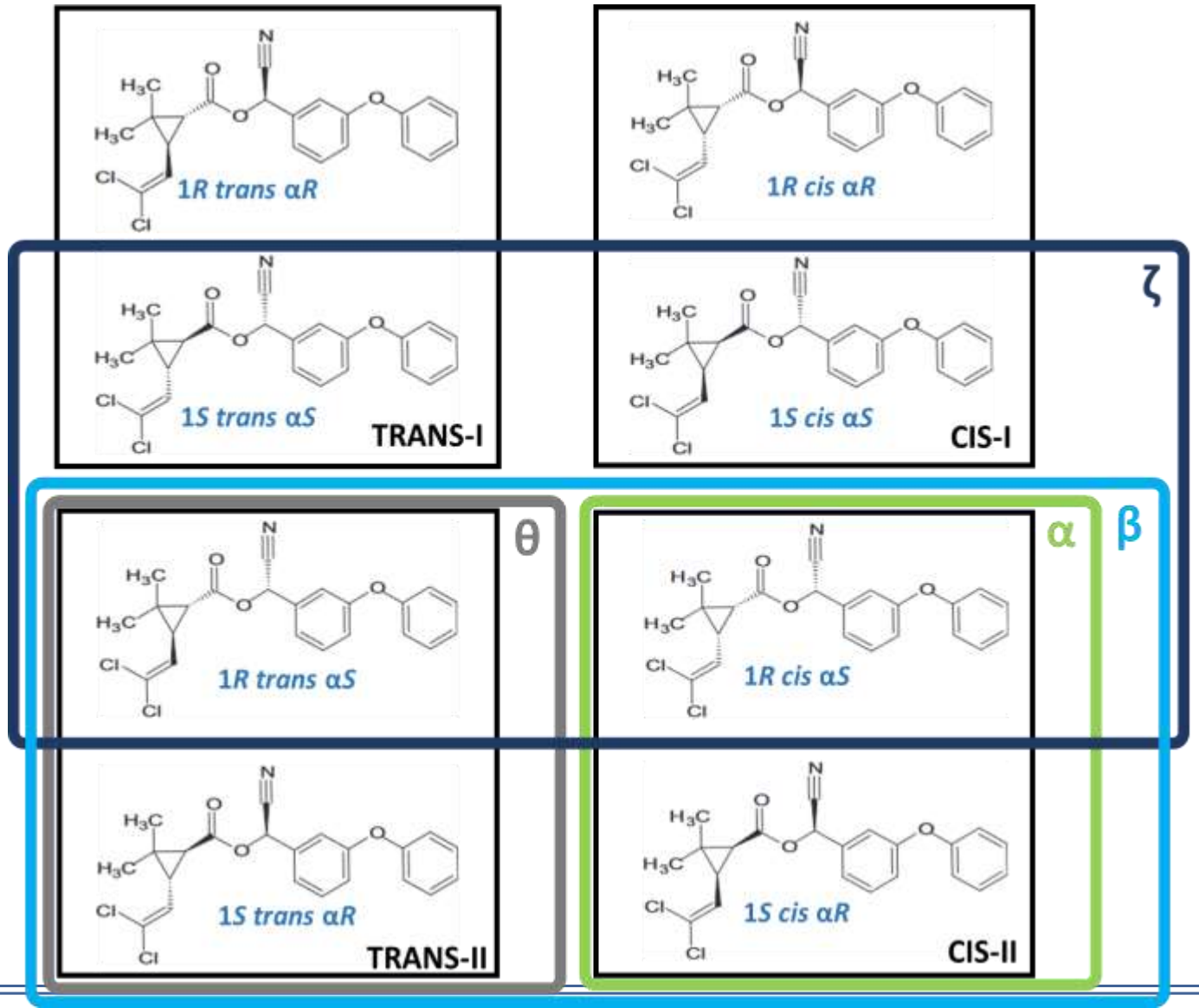


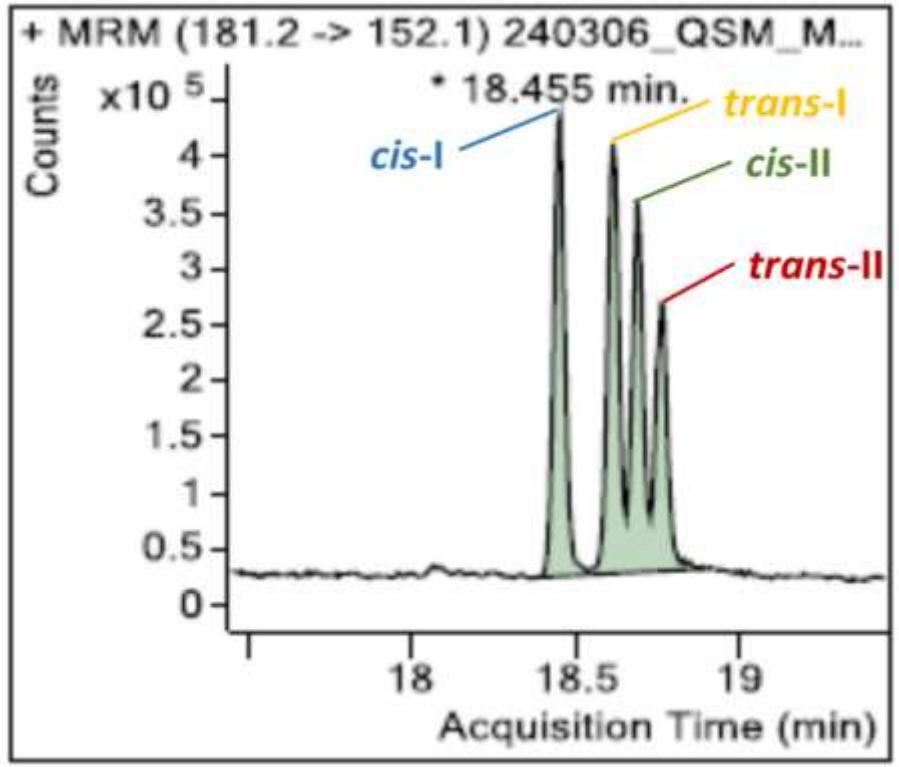
Paraquat in Pulses

collected from markets in
in Germany (01/23 - 05/24),
Costa Rica (06/23), USA (8/23) & Australia (01/24)

Cypermethrin
Alpha- Cypermethrin

Composition of Active Substances (Isomer Mixtures)

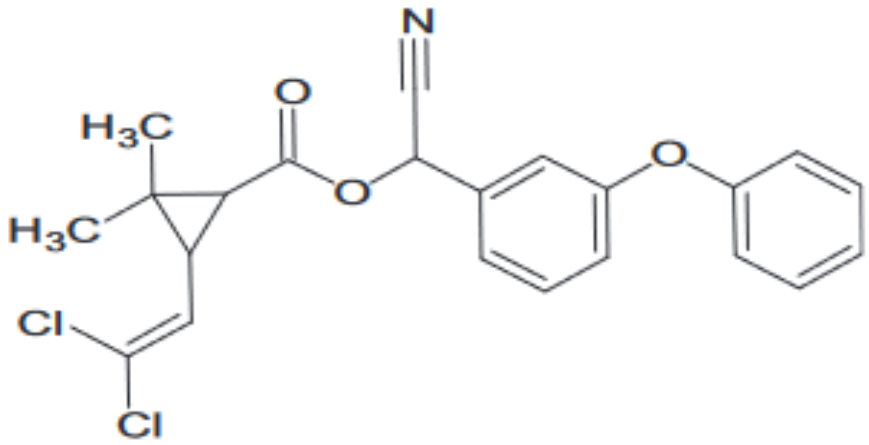




GC-MS/MS – Cypermethrin - (m/z 181/152)

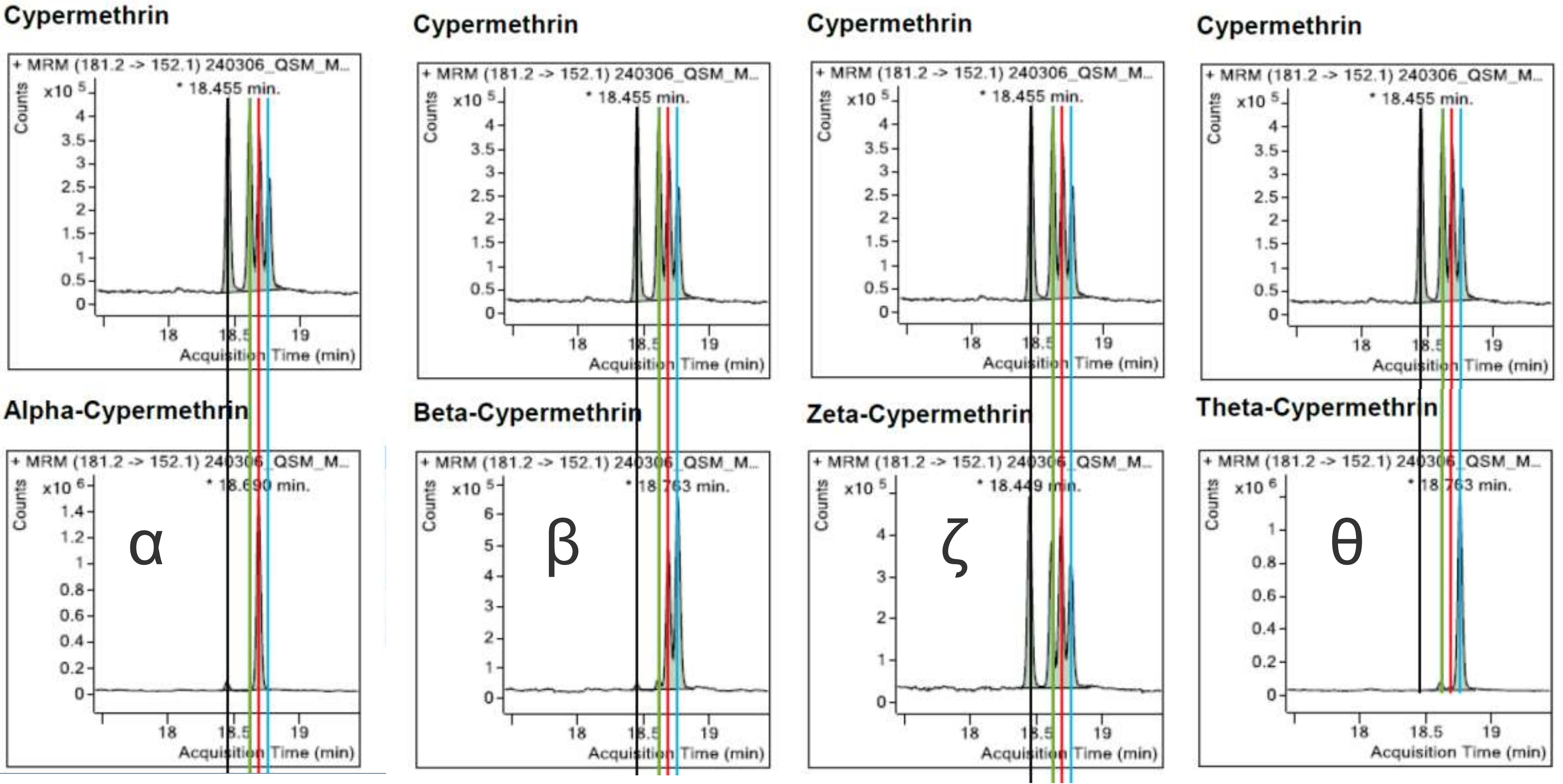
General Info:

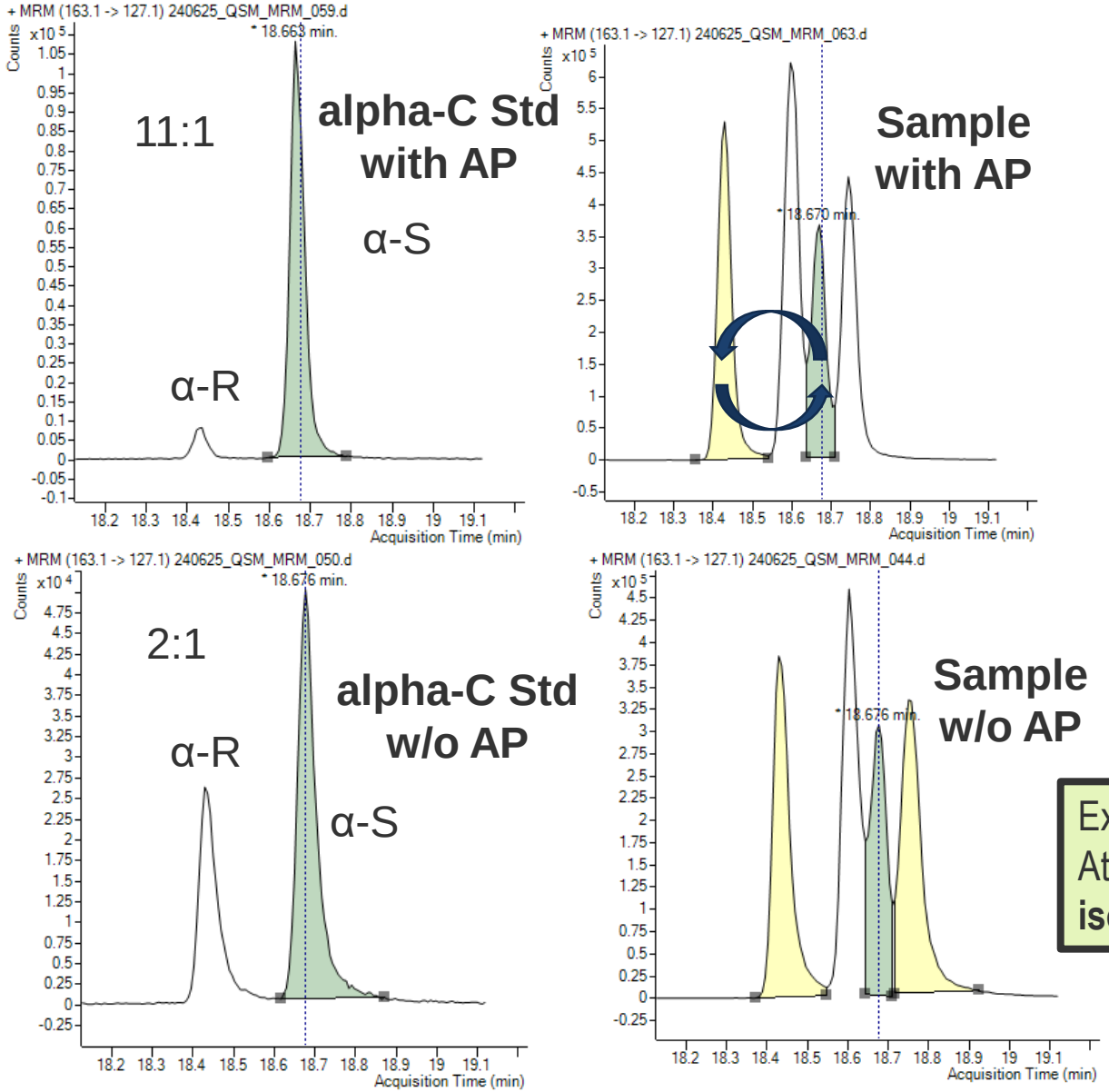
- Cypermethrin: 3 chiral ventres ☛ **8 isomers (4 enantiomeric pairs)**
- Conventional (non-enantioselective) Chr/phy, 4 peaks
- **α-cypermethrin** (=alphamethrin) composed of enantiom. pair "1*R cis* α-*S*" / "1*S cis* α-*R*" (***cis*-II pair**) at racemic composition
- Toxicology:
  - Highest mammalian toxicity: 1*R cis* and α-*S*-configurations (50% of **α**-cyp.; 11 % of cyp.)
  - ARfD : α-Cyp. 0.00125 vs. Cyp: 0.005 mg/kg bw
  - ADI: α-Cyp. 0.00125 vs. Cyp: 0.005 mg/kg bw/day.
- EU-Approval:
  - Cypermethrin: still approved
  - Alpha-cypermethrin (till June 2021)
  - zeta-cypermethrin (till December 2020)



Peak 1	"Cis-I": 1R, 3R αR (=1R cis αR) + 1S, 3S αS (=1S cis αS)
Peak 2	„Trans-I": 1R, 3S αR (=1R trans αR) + 1S, 3R αS (=1S trans αS)
Peak 3	„Cis-II": 1R, 3R αS (=1R cis αS) + 1S, 3S αR (=1S cis αR)
Peak 4	„Trans-II": 1R, 3S αS (=1R trans αS) + 1S, 3R αR (=1S trans αR)

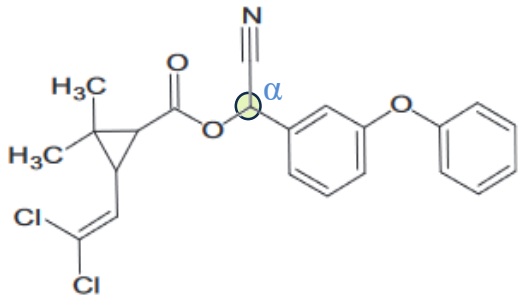
GC-MS/MS





Analysis via GC

In hot GC-injector **epimerization** on α-Carbon



Extent of isomerisation depends on …

- **Injection conditions**, e.g. injection mode, temp.
- **Status of Liner**
- Amount & type of co-extractants (i.e. **matrix-type**)
- Presence of **Analyte Protectants** (“APs”)

Experience w. Deltamethrin: **Isomerization is bidirectional (α-S←→α-R).**
At a **similar isomeric composition** between sample extracts and calibr. Std., **isomerization-related errors will equalize** accurate quantification is possible.

Thank You for Your Attention

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