

5th

LATIN AMERICAN PESTICIDE RESIDUE WORKSHOP

Food and Environment

European Union proficiency tests in fruits and vegetables. Main results obtained during the last 10 years

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EURL-FV




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LAPRW2015

Overview

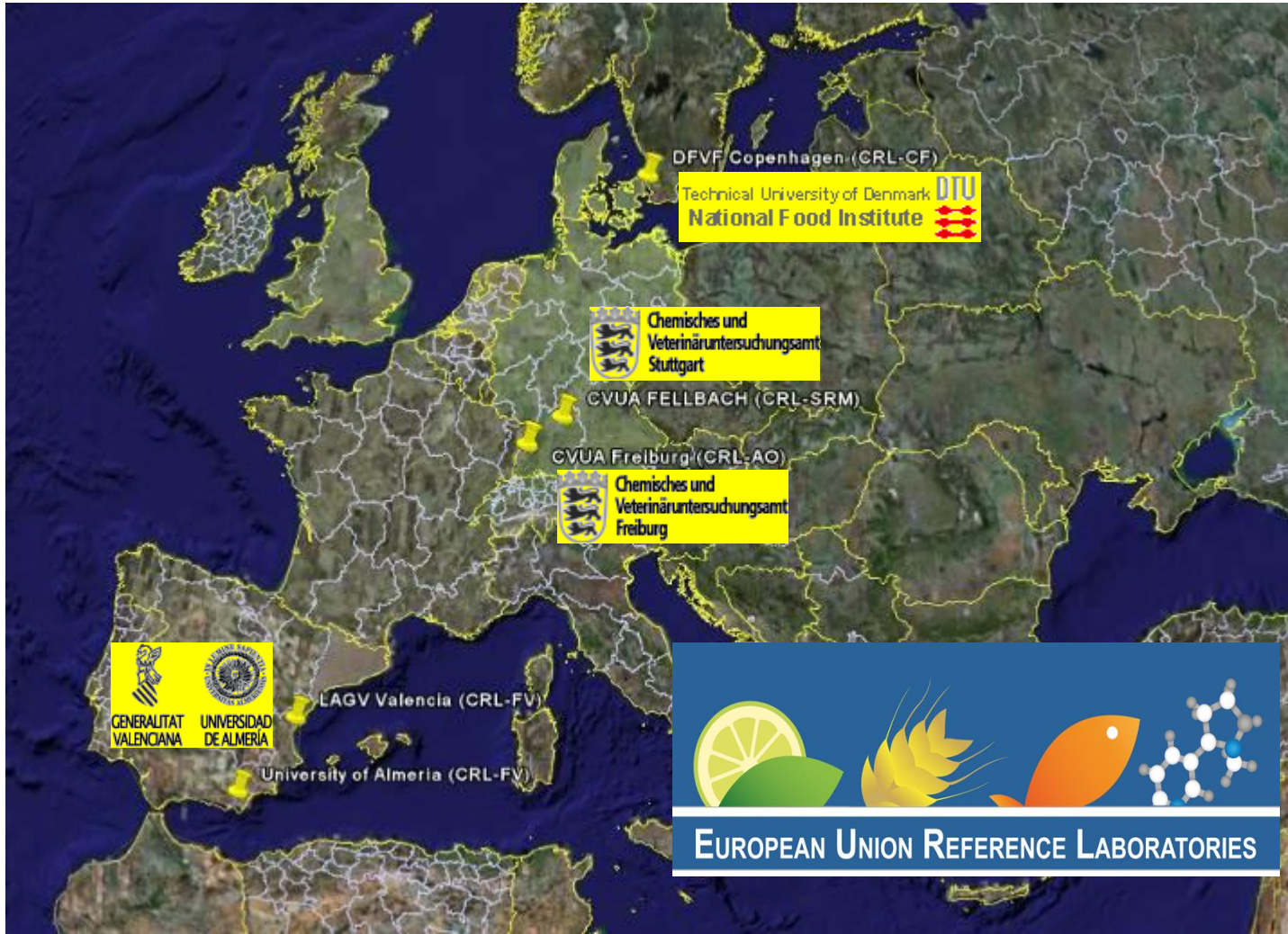
1. Management, organization and preparation of test samples.
2. Evaluation of the results
3. Main Results obtained
4. Instrumentation
5. Specific cases of relevance
6. Conclusions

A large, faint watermark of the EURL logo and the European Union flag's stars is centered in the background.

1. Management, organization and preparation of test samples



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EURL Scientific Activities

European Union Proficiency Tests EUPTs

Proficiency tests are carried out on an annual basis in order to continuously improve the quality, accuracy and comparability of the residue data reported by EU Member States to the European Union, as well as by other Member States, within the framework of the EU multi-annual coordinated control programme and national monitoring programmes.

European Union Proficiency Tests

EUPTs

Organised

EURLs

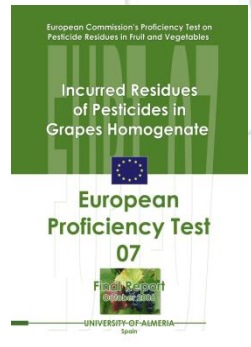
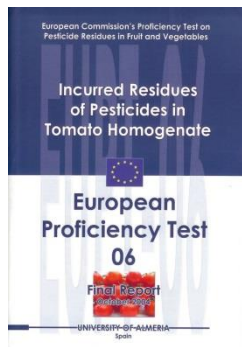
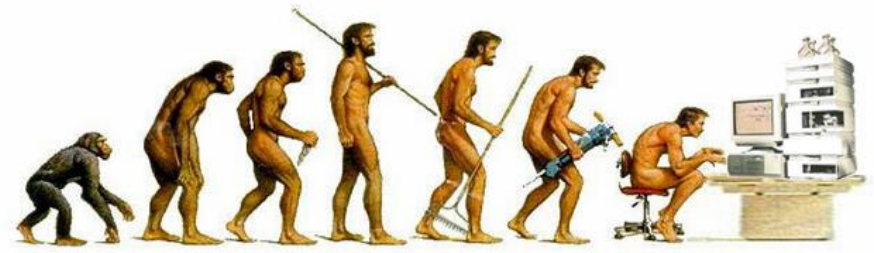


All laboratories analysing samples for the official control of pesticide residues, which shall participate in the European Union Proficiency Tests (EUPTs) for pesticide residues organised by the European Union

Proficiency Tests - History

1995-2004

- 5 PTs on MRM in FV



Proficiency Tests - History

ISO/IEC 17043




EURL
European Commission Proficiency Test FV-12



EURL
European Commission Proficiency Test FV-13



EURL-FV
European Commission Proficiency Test FV-14



EURL-FV
European Union Proficiency Test FV-15




EURL
European Proficiency Test FV-16



EURL
European Proficiency Test FV-17



EURL
European Proficiency Test FV-SM-02



EURL
European Proficiency Test FV-SM-03



EURL-FV
European Proficiency Test FV-SM-04



EURL-FV
European Union Proficiency Test FV-SM-05



EURL
European Proficiency Test FV-SM-06



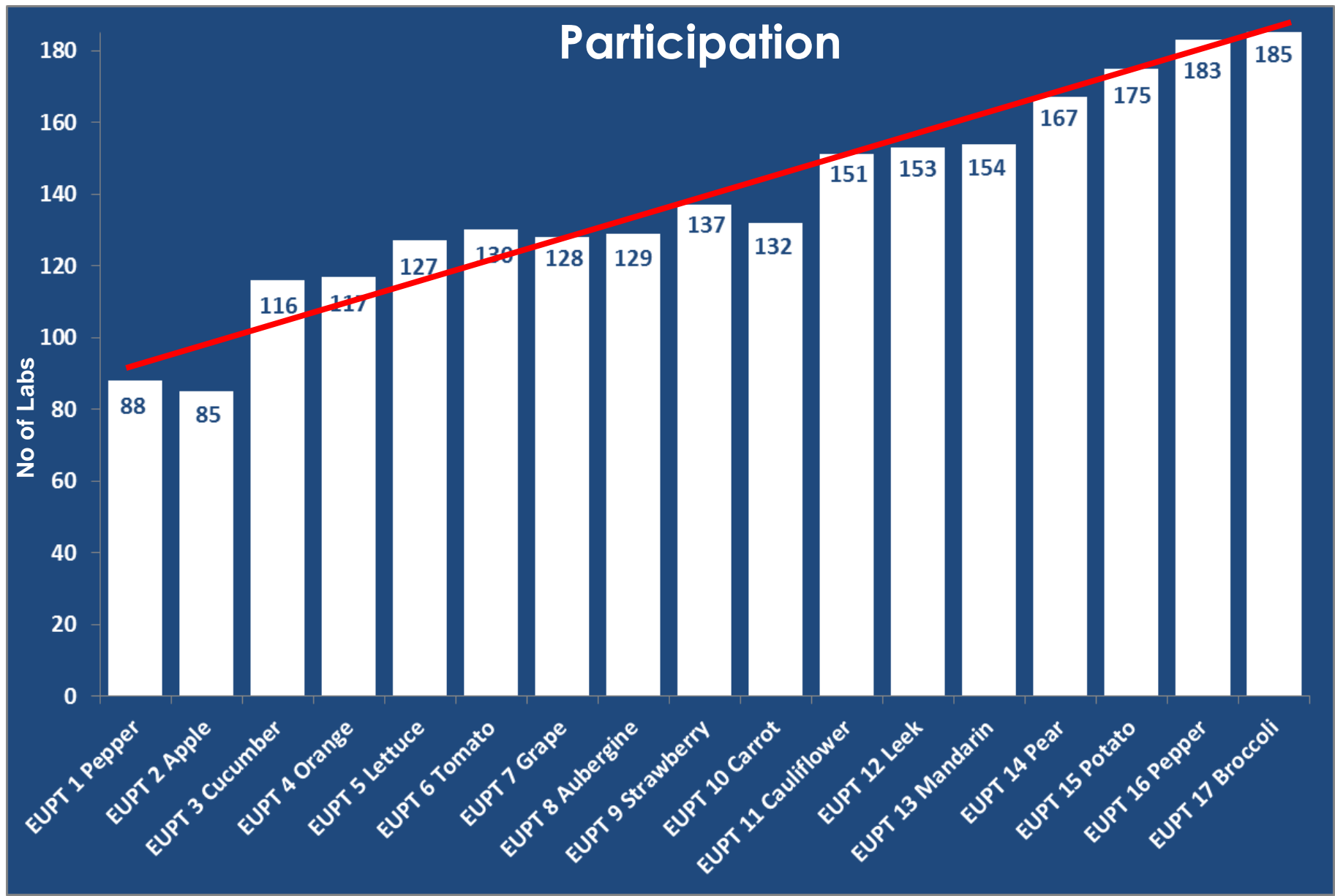
EURL
European Proficiency Test FV-SM-07




EURL
U-RT-FV16



EURL
I-RT-FV16



Participant countries-EU



Participant countries-Other countries (18)



Participant countries-Latin American countries (7)



ORGANISATION-EURL-FV



Samples and Protocol



Results



Reports



INFORMATION

Lab 1



Lab 2



Lab 3



Lab 4



Lab 5



EUPT-FV17- TARGET PESTICIDE LIST



Pesticide	MRRL (mg/Kg)
3-hydroxy-carbofuran	0.01
Acephate	0.01
Acetamiprid	0.01
Acrinathrin	0.01
Aldicarb	0.01
Aldicarb Sulfone	0.01
Aldicarb Sulfoxide	0.01
Azinphos-methyl	0.01
Azoxystrobin	0.01
Benfuracarb	0.01
Benomyl	0.01
Bifenthrin	0.01
Bitertanol	0.01

EUPT-FV1 to EUPT-FV17 in numbers

EUPT N°	Matrices	N° of Participants	N° of Possible Pesticides	N° of pesticides evaluated in test item
1	Pepper	88	33	6
2	Apple	85	41	6
3	Cucumber	116	48	14
4	Orange	117	57	14
5	Lettuce	127	57	15
6	Tomato	130	57	13
7	Grape	128	65	16
8	Aubergine	129	68	16
9	Strawberry	137	82	19
10	Carrot	132	113	18
11	Cauliflower	151	128	21
12	Leek	153	144	17
13	Mandarin	154	144	19
14	Pear	167	175	18
15	Potato	175	175	18
16	Pepper	183	175	22
17	Broccoli	185	183	11

107 Pesticides Used to Treat the Sample in last ten EUPT-FVs

Acephate	Difenoconazole	Kresoxim-methyl	Pirimicarb
Acetamiprid	Diflubenzuron	Lambda-Cyhalothrin	Pirimphos-methyl
Acrinathrin	Dimethoate	Linuron	Prochloraz
Aldicarb(sum)	Diphenilamine	Malathion	Procydimone
Amitraz (DMPF&DMF)	Dithiocarbamates(CS2)	Mecarbam	Propoxur
Azinphos-methyl	Endosulfan	Metalaxyl	Propyzamide
Azoxystrobin	EPN	Metamidophos	Prothiofos
Bifenthrin	Fenamiphos	Methidathion	Pyraclostrobin
Boscalid	Fenamiphos sulfone	Methiocarb sum	Pyridaben
Bromopropylate	Fenamiphos sulfoxide	Methiocarb	Pyrimethanil
Bupirimate	Ethion	Methomyl	Pyriproxifen
Buprofezin	Fenhexamid	Methoxyfenozone	Quinoxifen
Cadusafos	Fenitrothion	Methyl-Tiophanate	Quintozene
Captan	Fenpropathrin	Mevinphos	Spinosad
Carbaryl	Fludioxinil	Monocrotophos	Spirodiclofen
Carbendazim	Flufenoxuron	Myclobutanil	Tebuconazole
Carbofuran sum	Fluopicolide	Omethoate	Tetraconazole
Chlorpropham	Flutolanil	Ortophenilphenol	Thiabendazole
Chlorpyrifos	Folpet	Oxamyl	Thiacloprid
Chlorpyrifos-methyl	Fosthiazate	Oxydemeton-methyl	Tolclofos-methyl
Chlothalonil	Hexythiazox	Parathion	Tolyfluanid
Cypermethrin	Imazalil	Penconazole	Triadimenol
Cyprodinil	Imidacloprid	Pencycuron	Triazophos
Delthamethrin	Indoxacarb	Pendimethalin	Trifloxystrobin
Diazinon	Iprodione	Permethrin	Triflumuron
Dichlofluanid	Iprovalicarb	Phosalone	Vinclozolin
Dicofol degradation	Isofenphos-methyl	Phosmet	

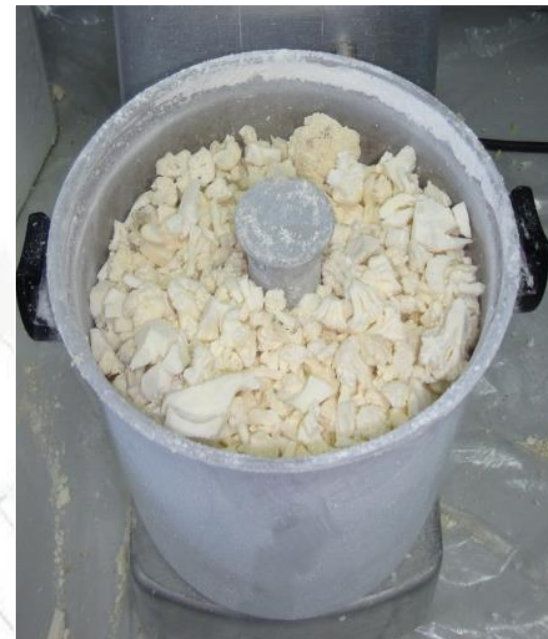
Growing of the test item



Plant treatment



Preparation of the test item



Preparation of the test item-Shipment to the participants



2. Evaluation of the results



Z-scores

$$z_i = (x_i - x_i^*) / \text{FFP-s}_i$$

x_i Result reported by the participant laboratory, or the MRRL for those laboratories that didn't detect the presence of the pesticide in the sample.

x_i^* Assigned value

FFP-s_i Standard deviation for each pesticide (= 0,25 multiplied by the assigned value)

$$|z| \leq 2$$

Acceptable

$$2 < |z| < 3$$

Questionable

$$|z| \geq 3$$

Unacceptable

Category A and B classification

- Category A laboratories
 - detect at least 90% of the pesticides present in the sample.
 - report no false positives.
- The rest are in Category B

Combined z-scores (average of squared z-scores)

$$AZ^2 = \frac{\sum_{i=1}^n z_i^2}{n}$$

n = number of z-scores to be considered in the calculation

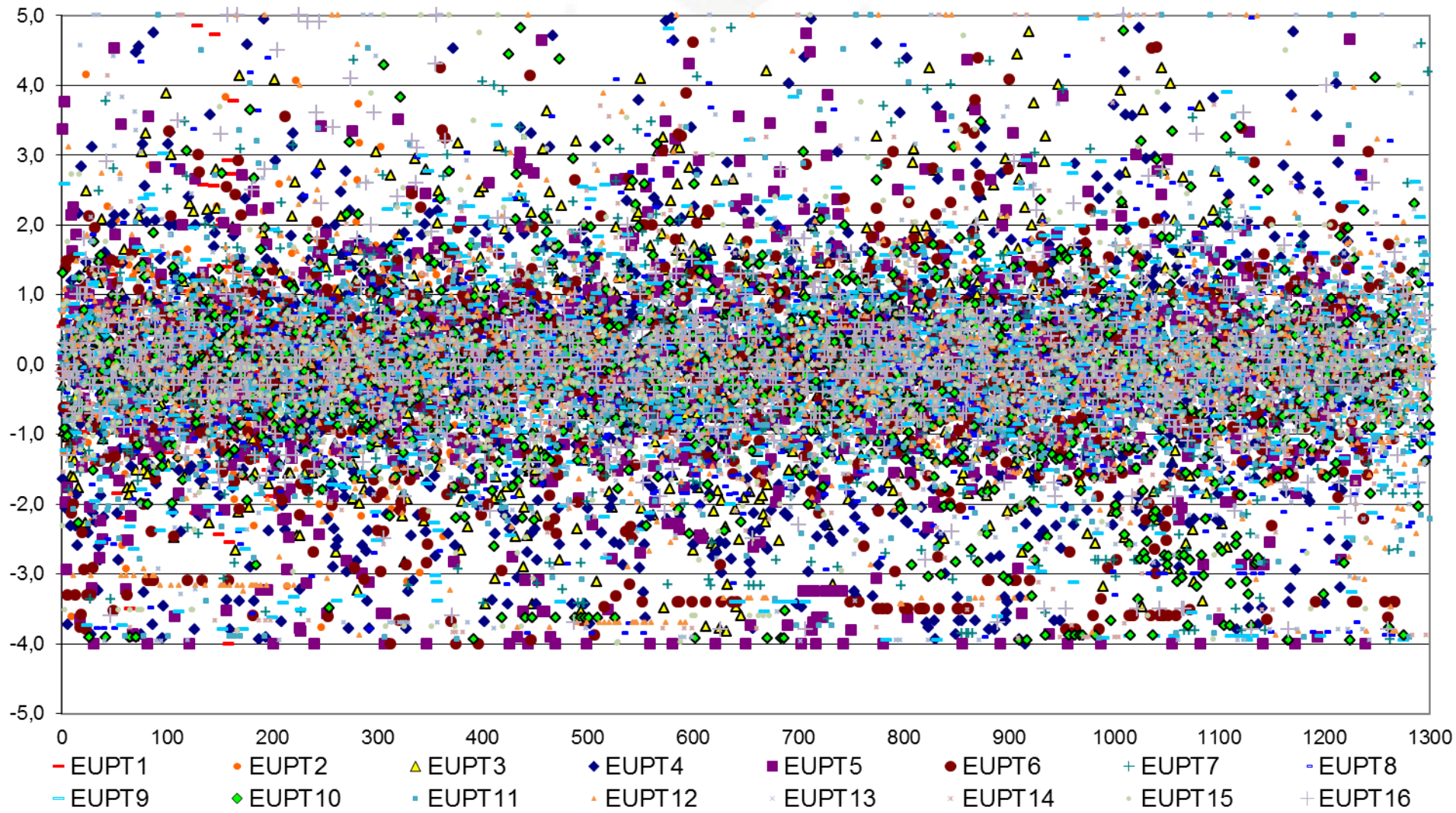
$AZ^2 \leq 2$	Good
$2 < AZ^2 \leq 3$	Satisfactory
$AZ^2 > 3$	Unsatisfactory

3. Main Results obtained

EURL

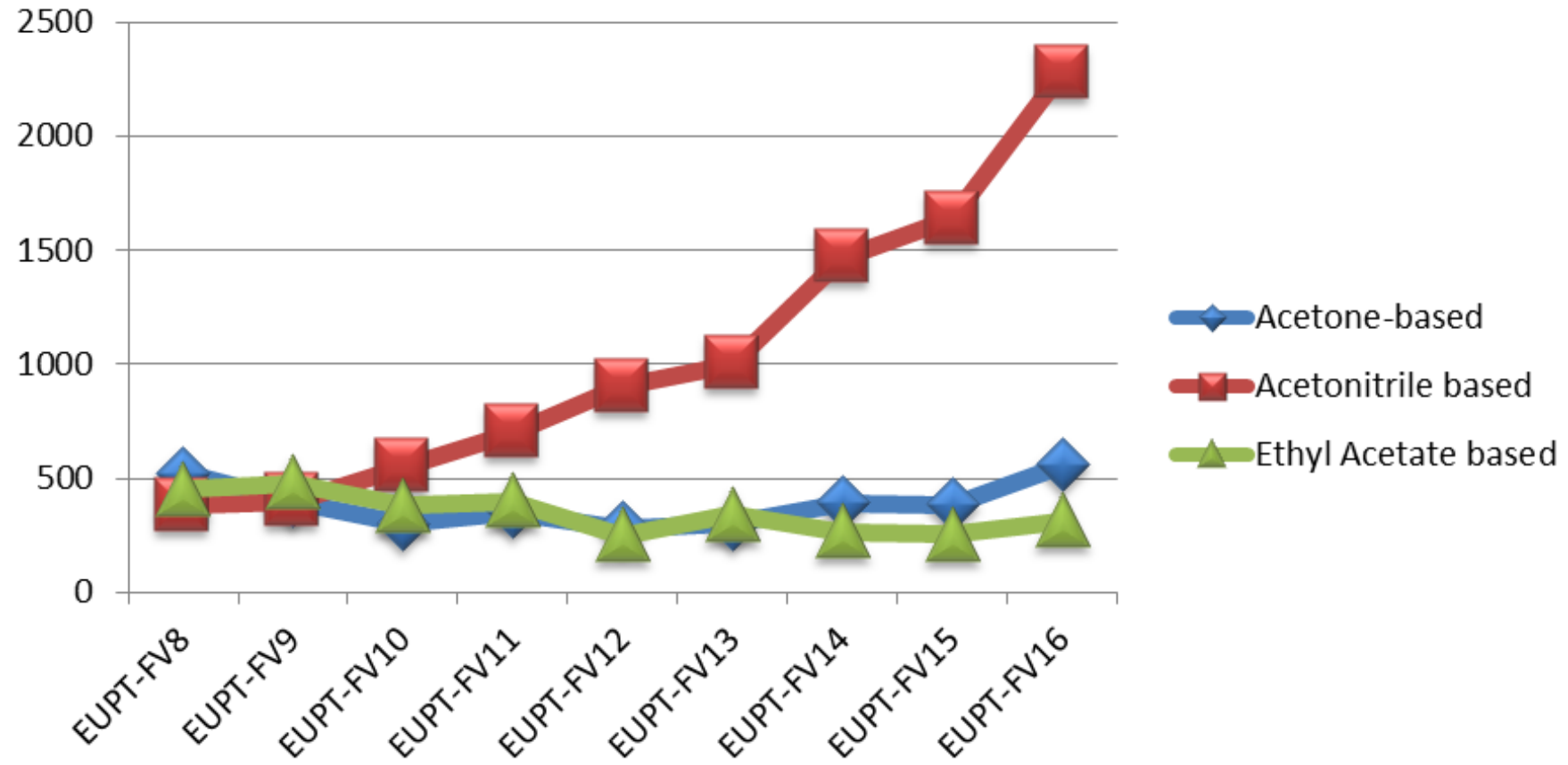
Summary of Results

16 EUPTs z-Score Results (27128)



Extraction methods

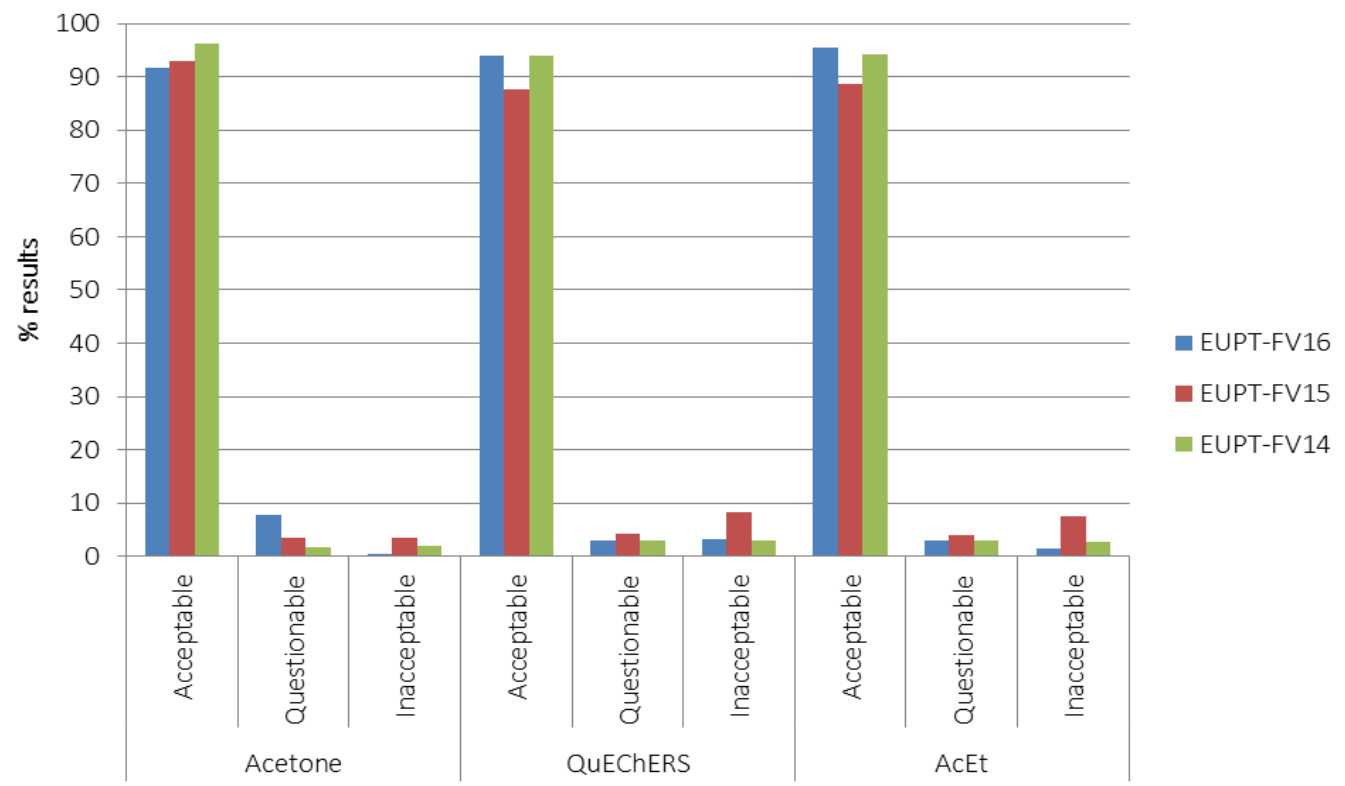
Number of results reported by extraction method



Extraction methods

Classification of z-scores by extraction method

	Acetone			QuEChERS			AcEt		
	Acceptable	Questionable	Inacceptable	Acceptable	Questionable	Inacceptable	Acceptable	Questionable	Inacceptable
EUPT-FV16	91,7	7,7	0,6	93,9	2,9	3,2	95,5	2,9	1,6
EUPT-FV15	93,0	3,4	3,6	87,7	4,2	8,2	88,6	3,9	7,5
EUPT-FV14	96,2	1,8	2	93,9	3,1	3	94,3	3	2,7



Extraction methods

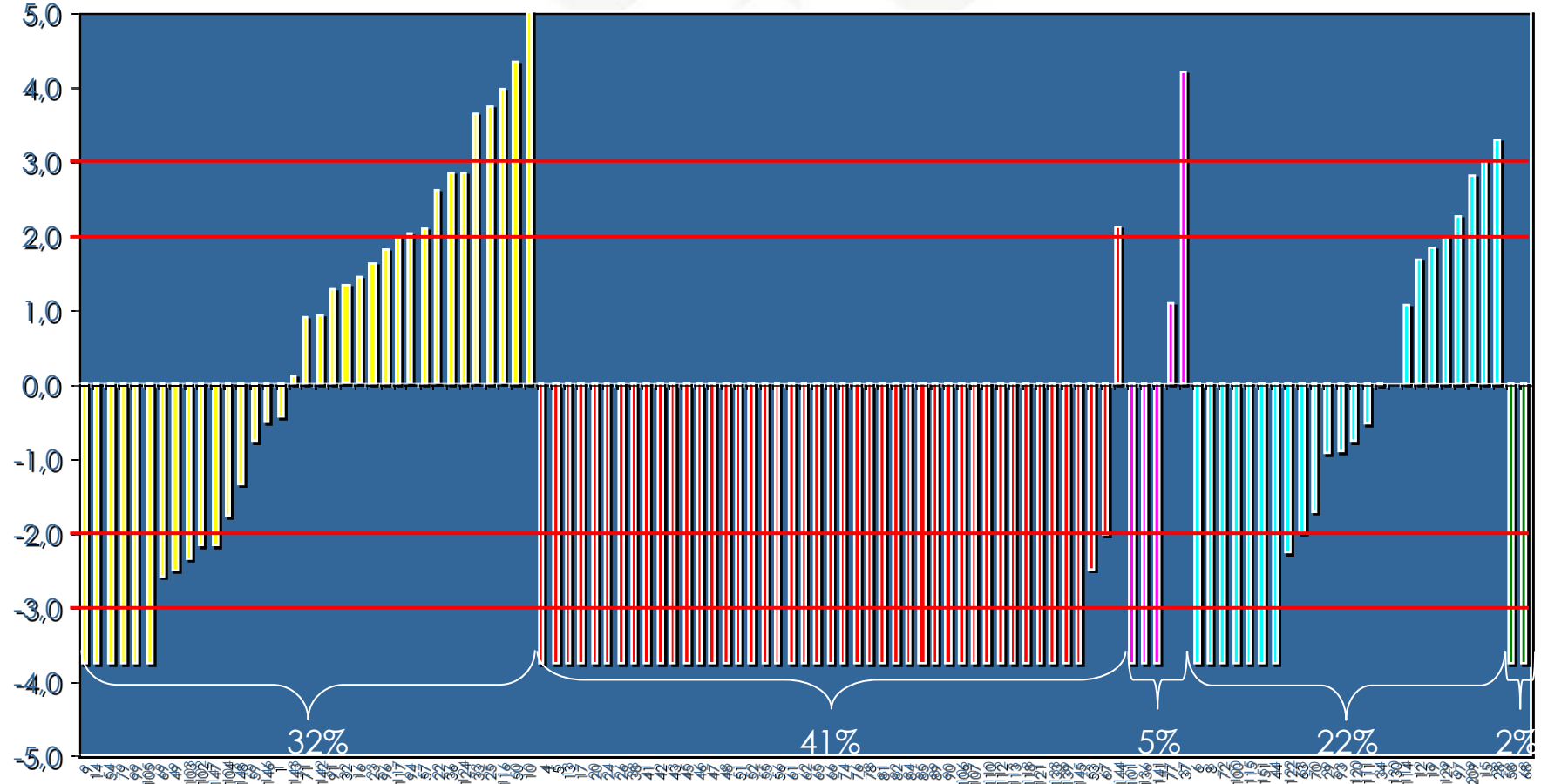
EUPT-FV12 - Leek



35% of Reported Results
 40% of False Negative Results
 25% of Not Analysed Results

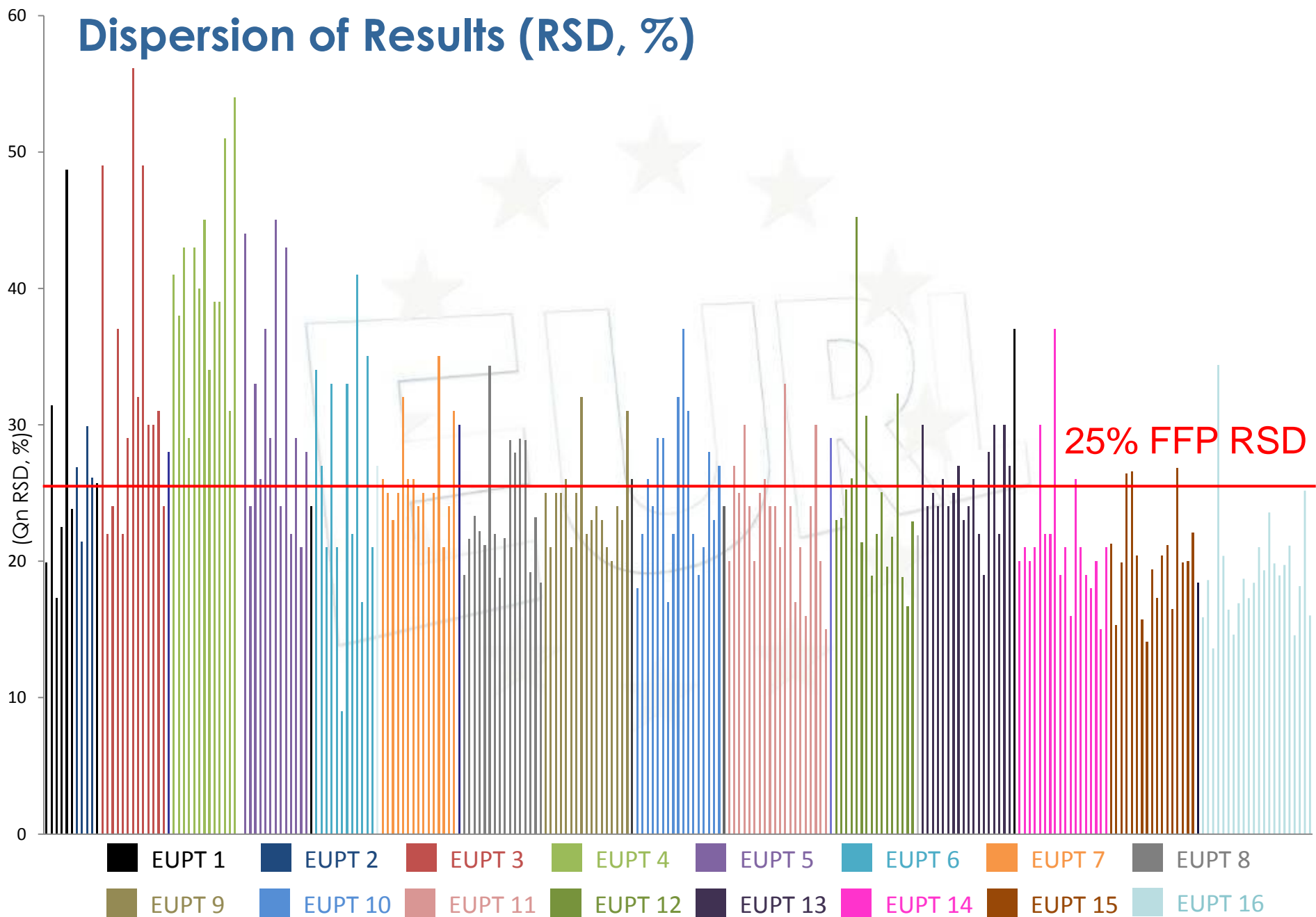
$|z| \leq 2$ Acceptable
 $2 < |z| \leq 3$ Questionable
 $3 < |z|$ Unacceptable

Chlorothalonil



- Acetone
- Acetonitrile
- Dichloromethane
- Ethyl Acetate
- Methanol

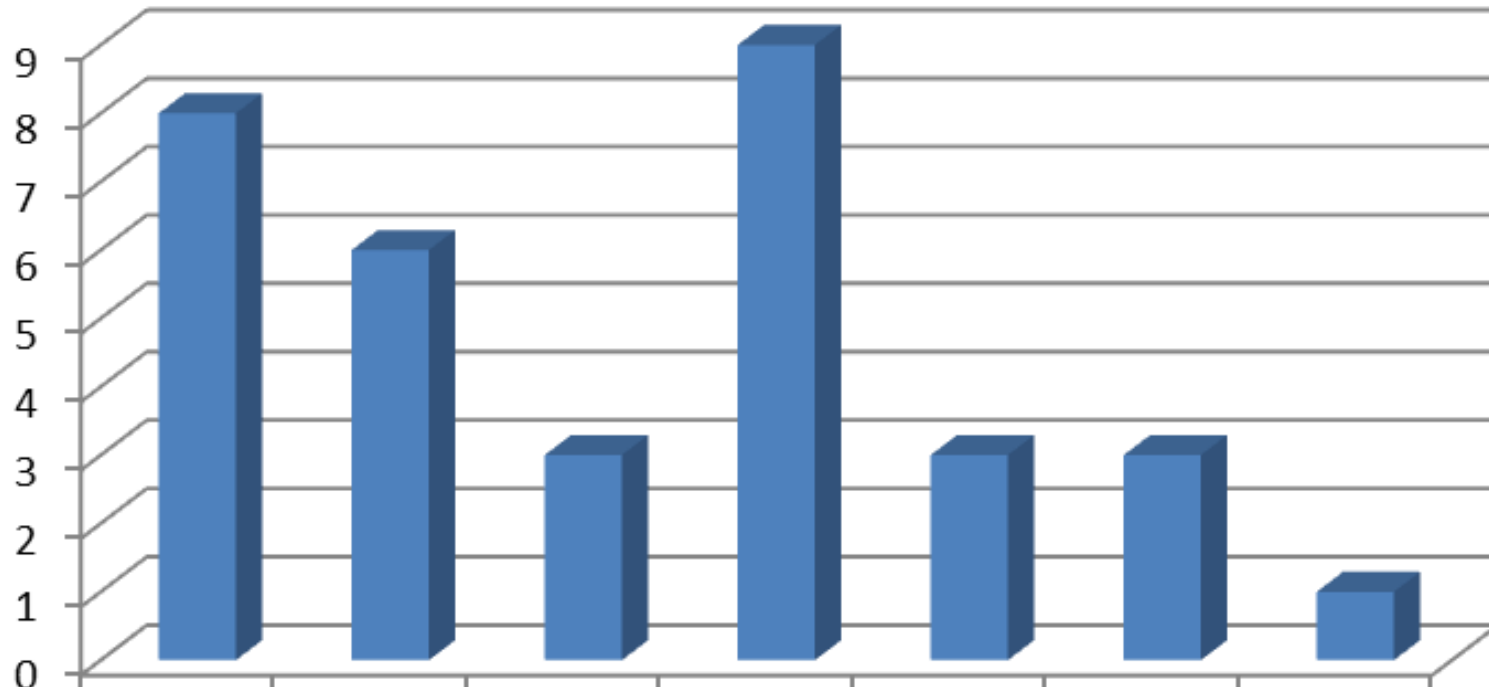
Dispersion of Results (RSD, %)



Dispersion of Results (RSD, %)

Number of Pesticides with $Q_n > 25\%$

No.



FV10



FV11



FV12



FV13



FV14



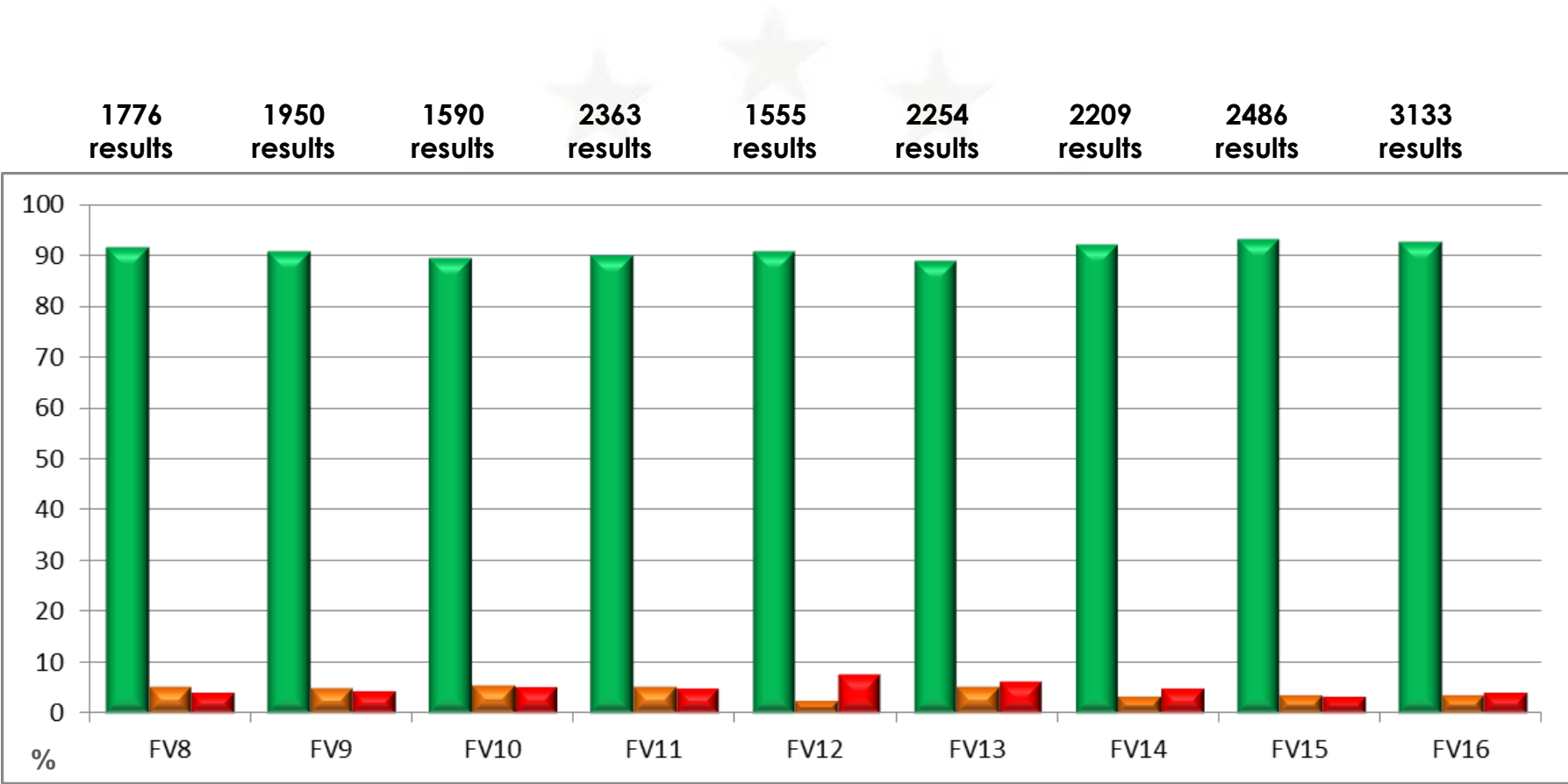
FV15



FV16



Classification of z-scores

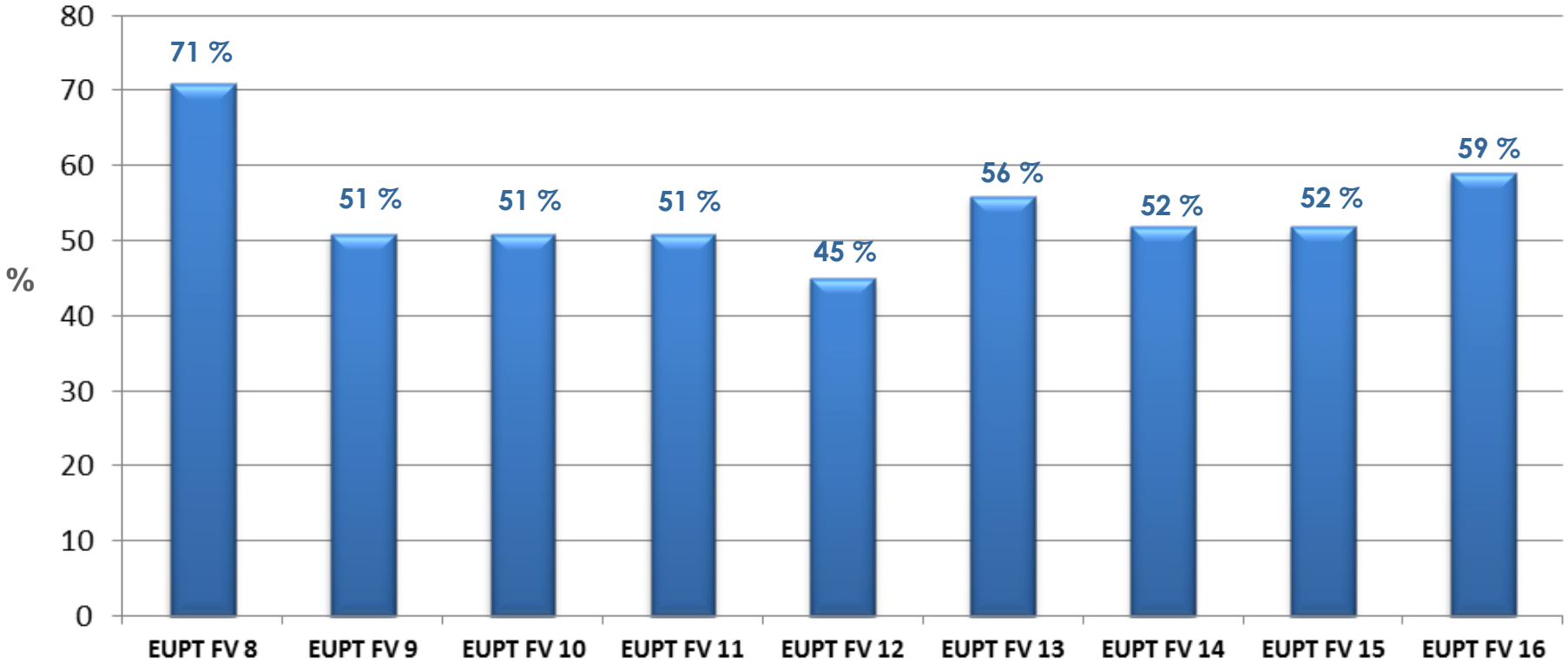


Acceptable

Questionable

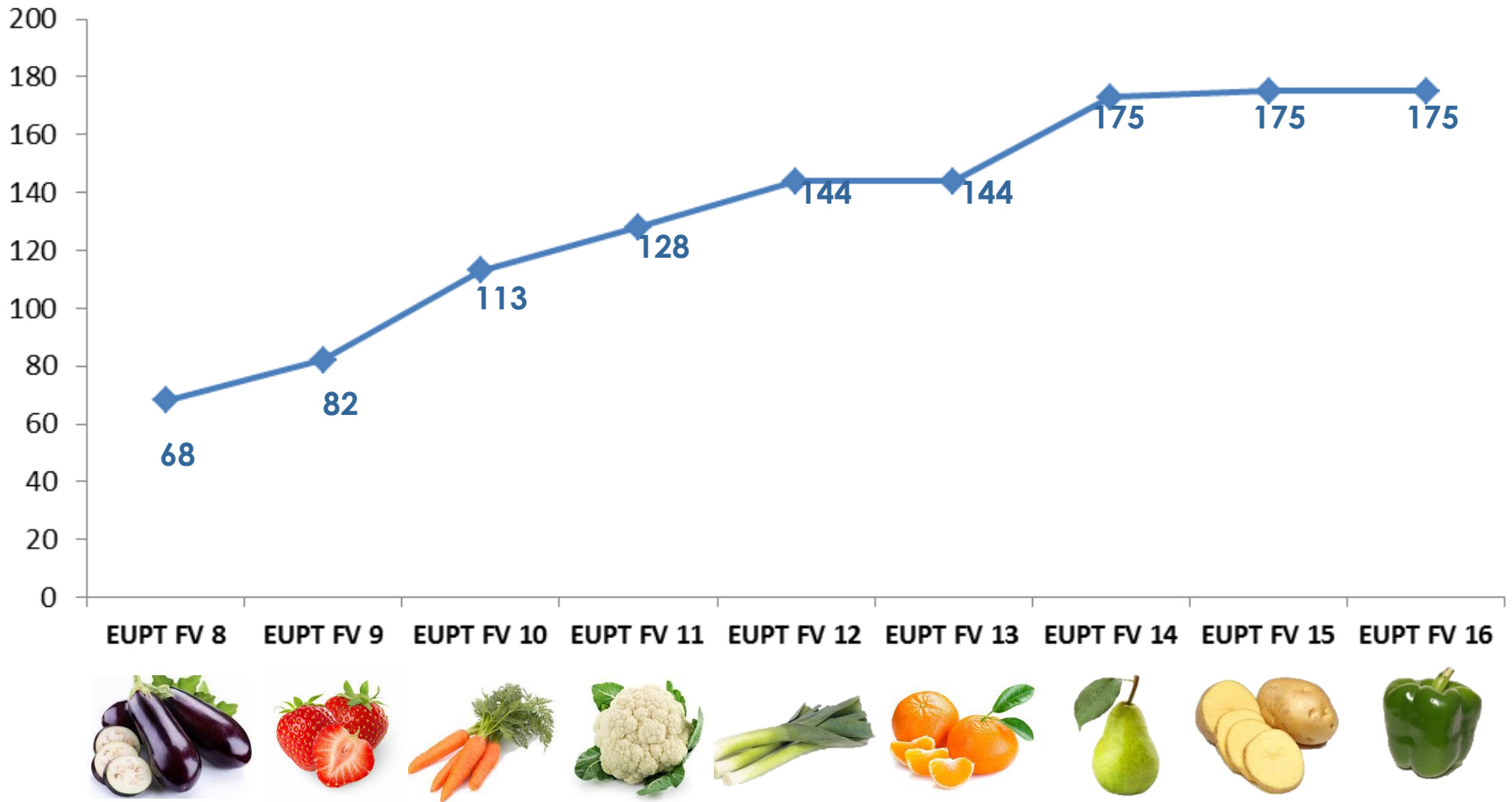
Unacceptable

Laboratories in Category A



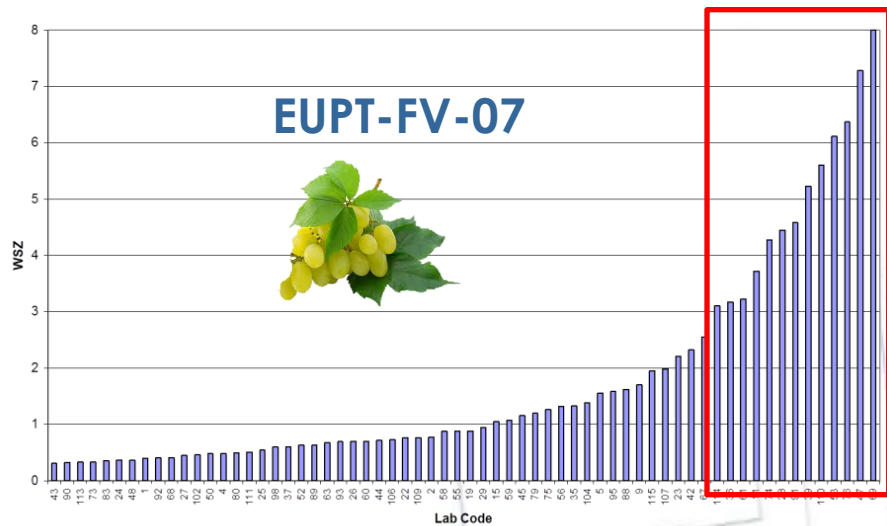
Laboratories in Category A

Number of pesticides in target list

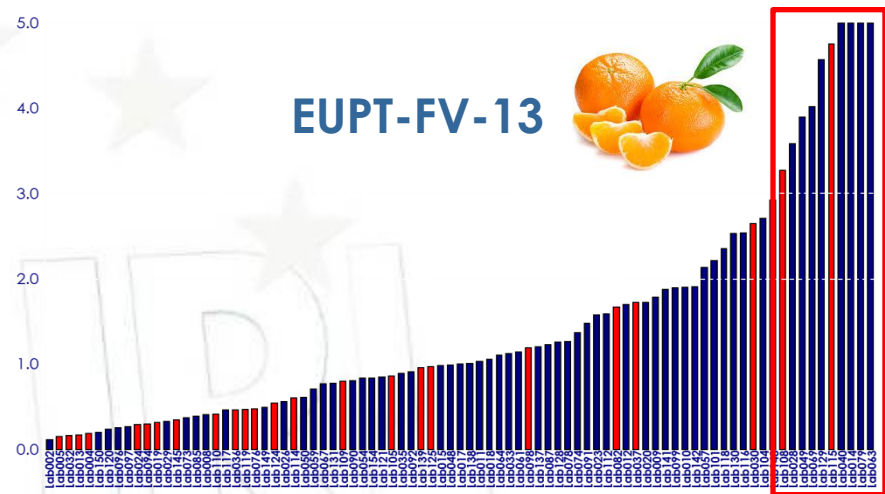


Classification of combined z-scores (only Labs Cat A)

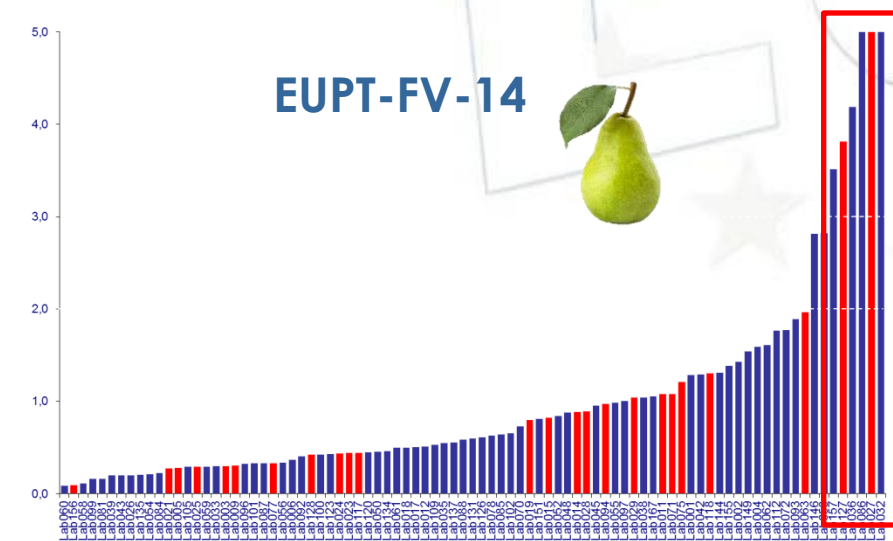
EUPT-FV-07



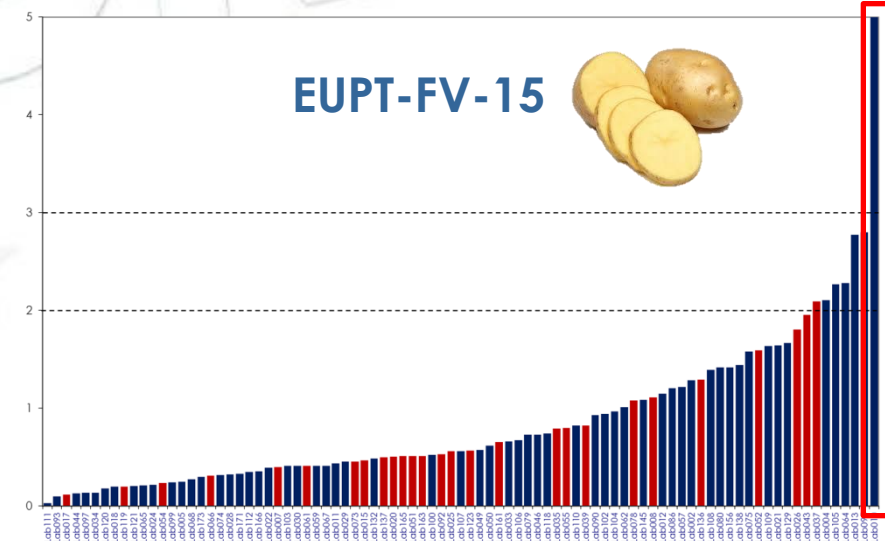
EUPT-FV-13



EUPT-FV-14

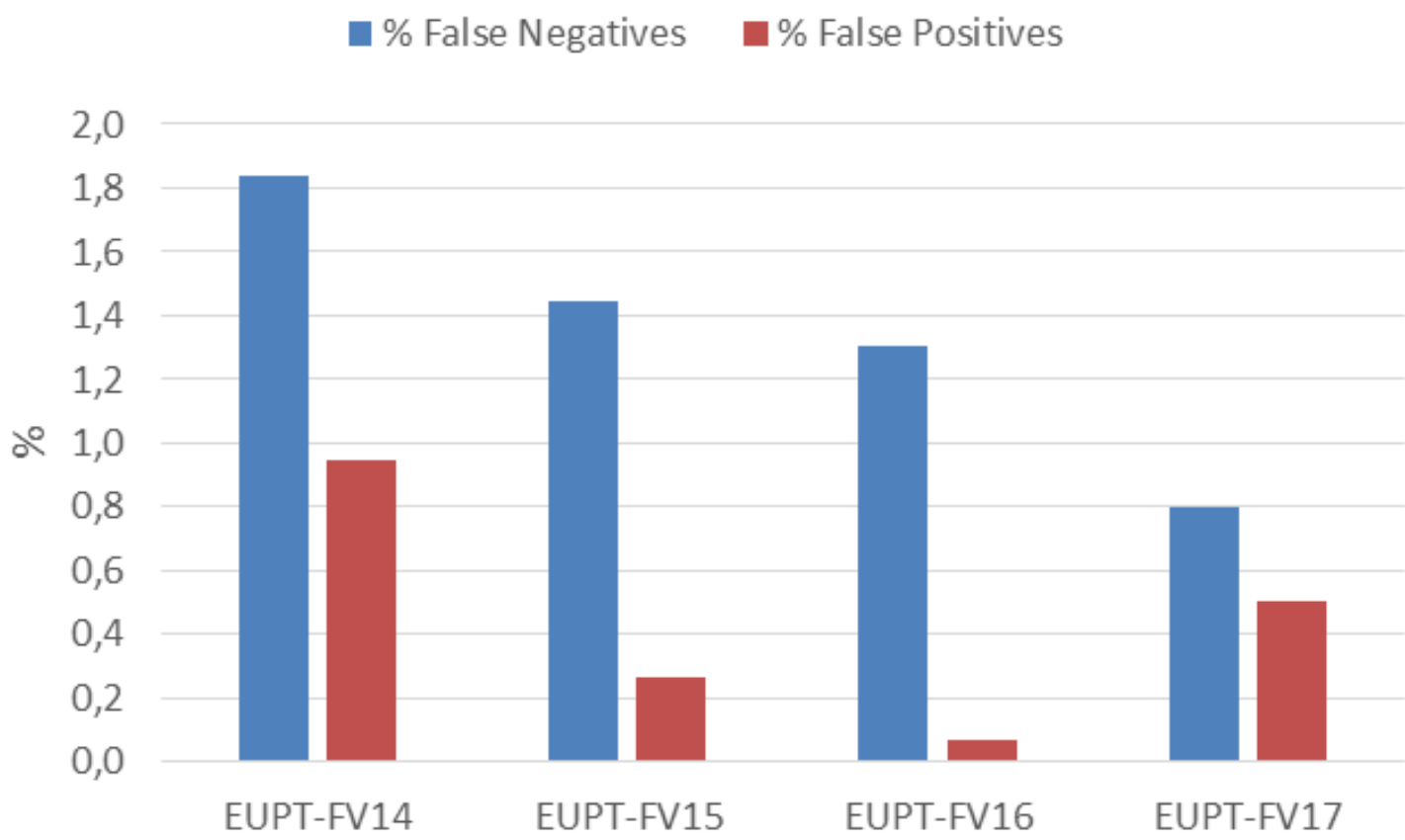


EUPT-FV-15



False Negatives and Positives

Percentage of False Positives and Negatives



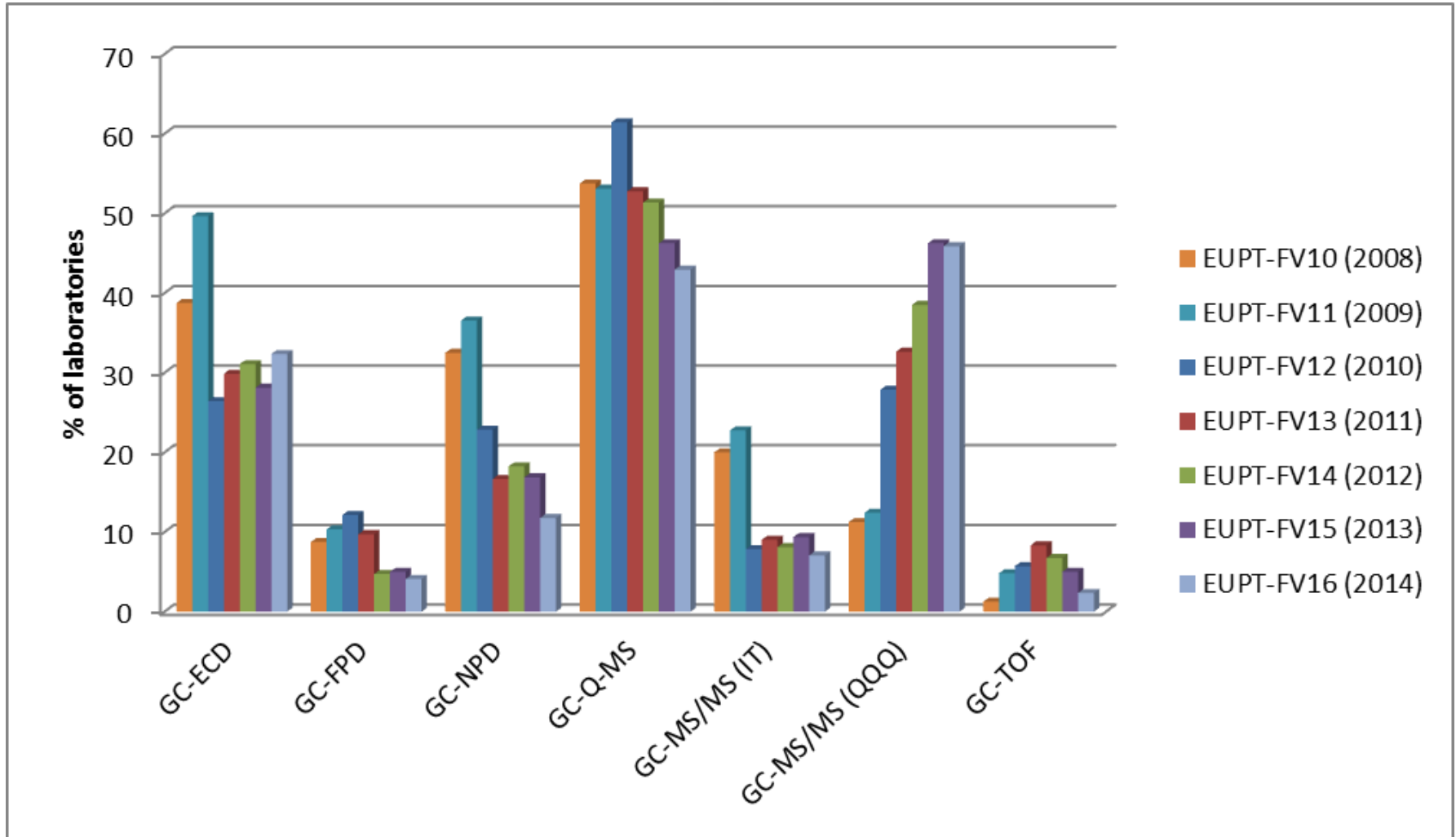


4. Instrumentation

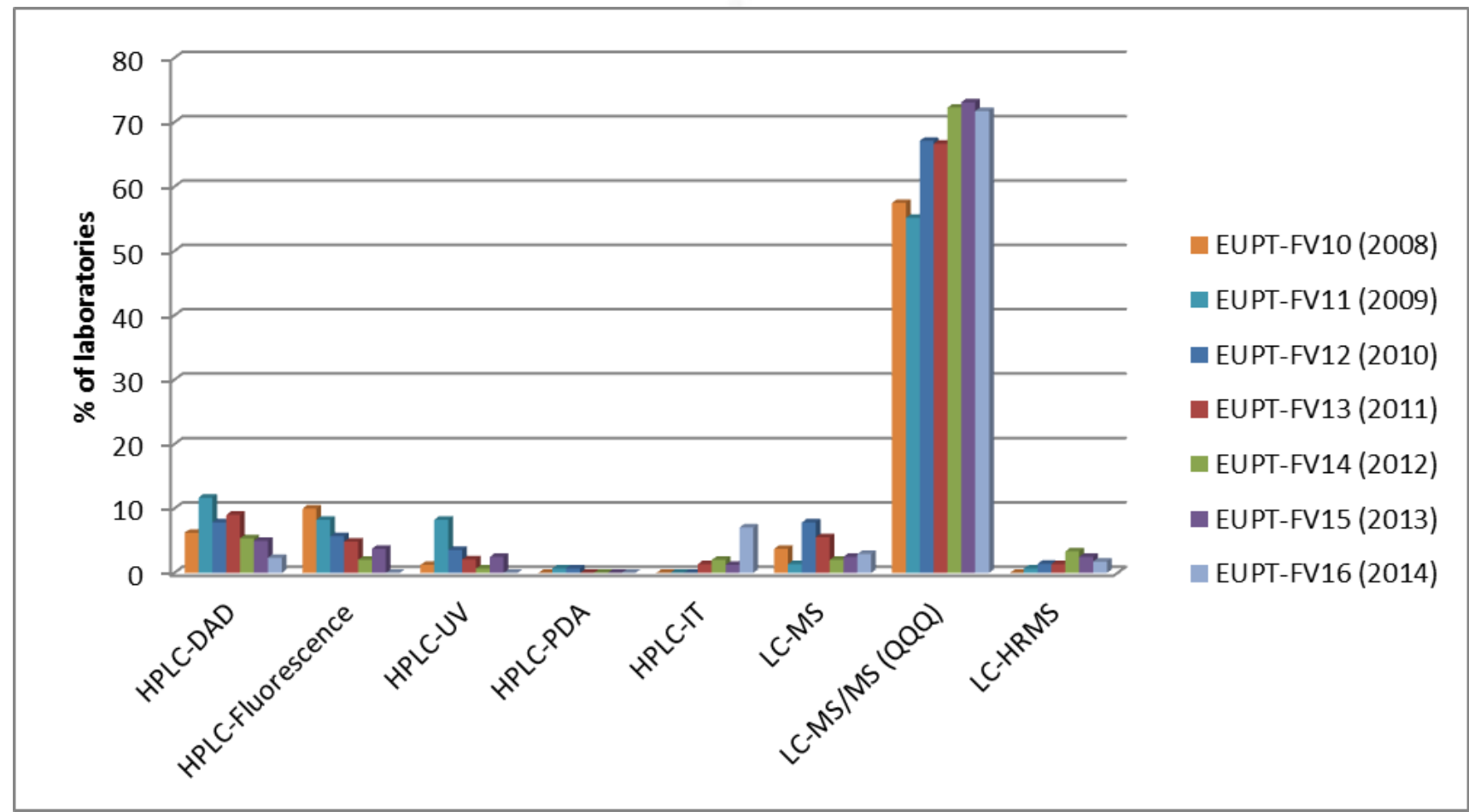
EUPT No.	Matrices	% of Chromatographic Techniques used	
		GC	LC
1	Pepper	100*	0
2	Apple	77*	23*
3	Cucumber	89*	13*
4	Orange	96*	4*
5	Lettuce	96*	4*
6	Tomato	87	13
7	Grape	76	24
8	Aubergine	79	21
9	Strawberry	80	20
10	Carrot	66	34
11	Cauliflower	64	36
12	Leek	63	37
13	Mandarin	53	47
14	Pear	51	49
15	Potato	44	56
16	Pepper	57	43
17	Broccoli	61	39

* More than 90% of the detectors used were 'classical detectors': ECD, NPD, UV...

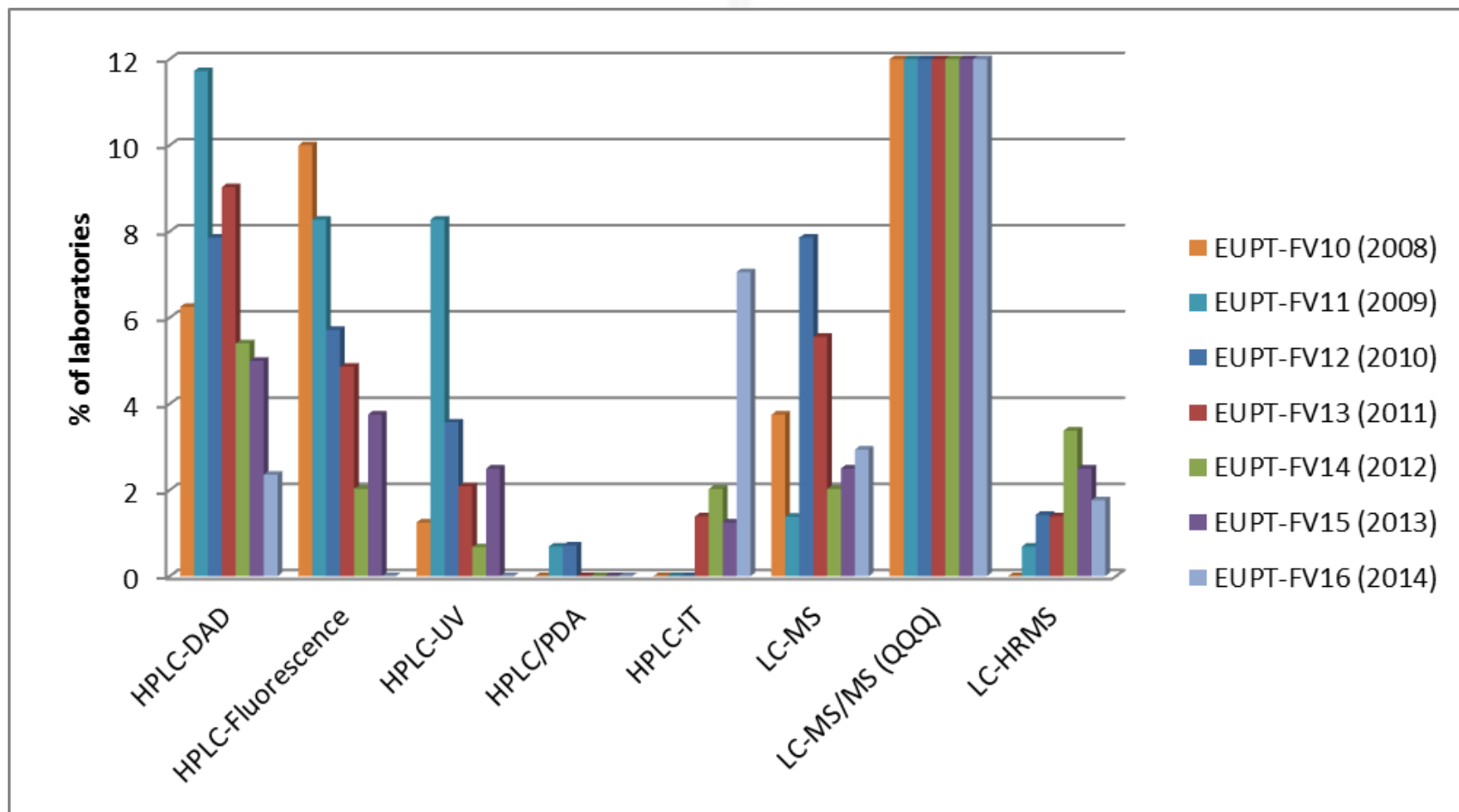
Gas chromatography



Liquid chromatography



Liquid chromatography-zoom



5. Specific cases of relevance

EURL

EUPT-FV10



The carrot sample was treated with methiocarb and methiocarb sulfone

The residue definition is:

Methiocarb:

(Sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone expressed as methiocarb)

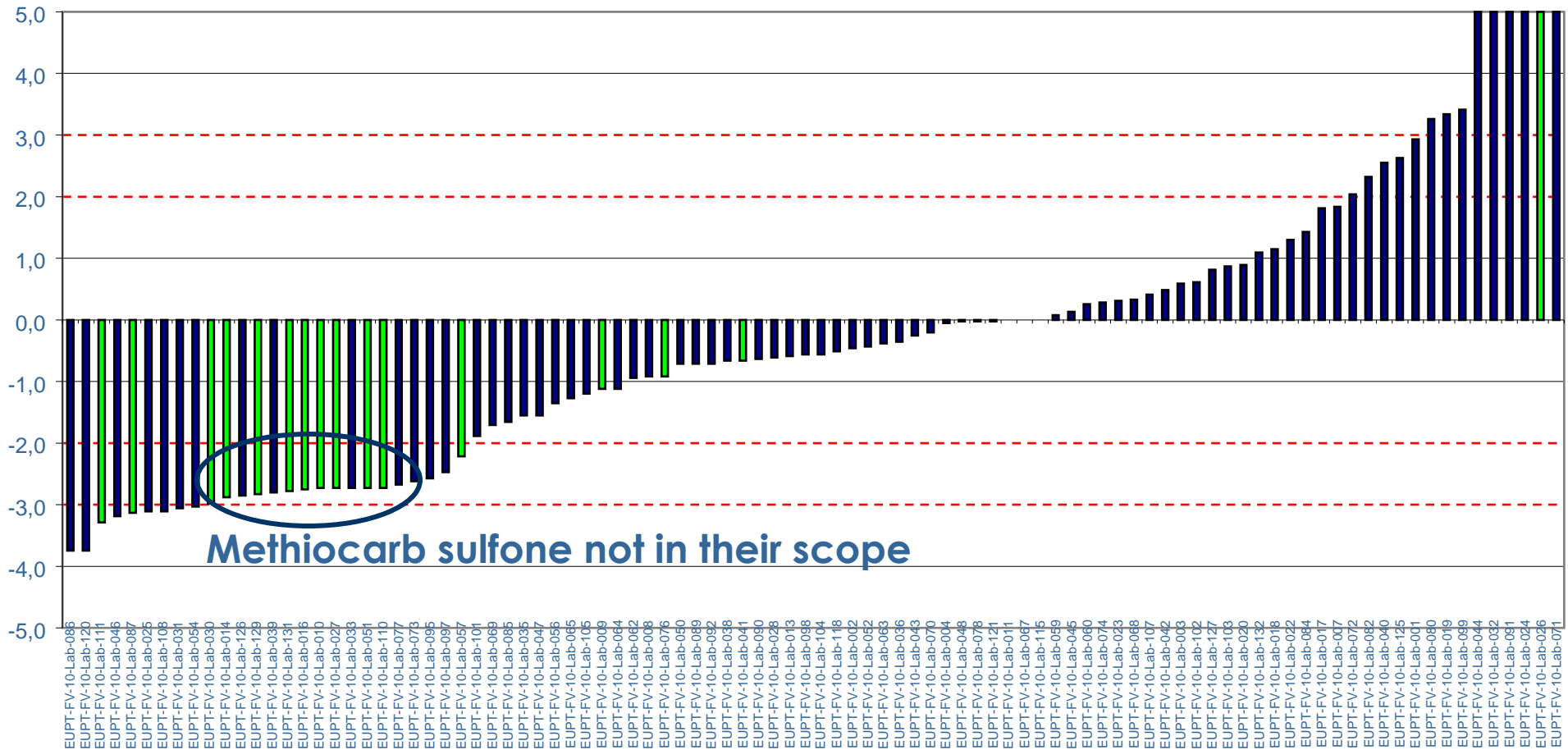
Correction Factor

$$\begin{aligned}
 \text{Methiocarb Sum} &= C_{\text{Methiocarb}} + 0.934 * C_{\text{M. Sulfoxide}} + 0.876 * C_{\text{M. Sulfone}} = \\
 &= (0.043 + 0.934*0.052+ 0.876*0.067) = 0.150 \text{ mg/Kg}
 \end{aligned}$$

Methiocarb Sum

59% Acceptable
 23% Questionable
 18% Unacceptable

- GC
- LC
- GC and LC

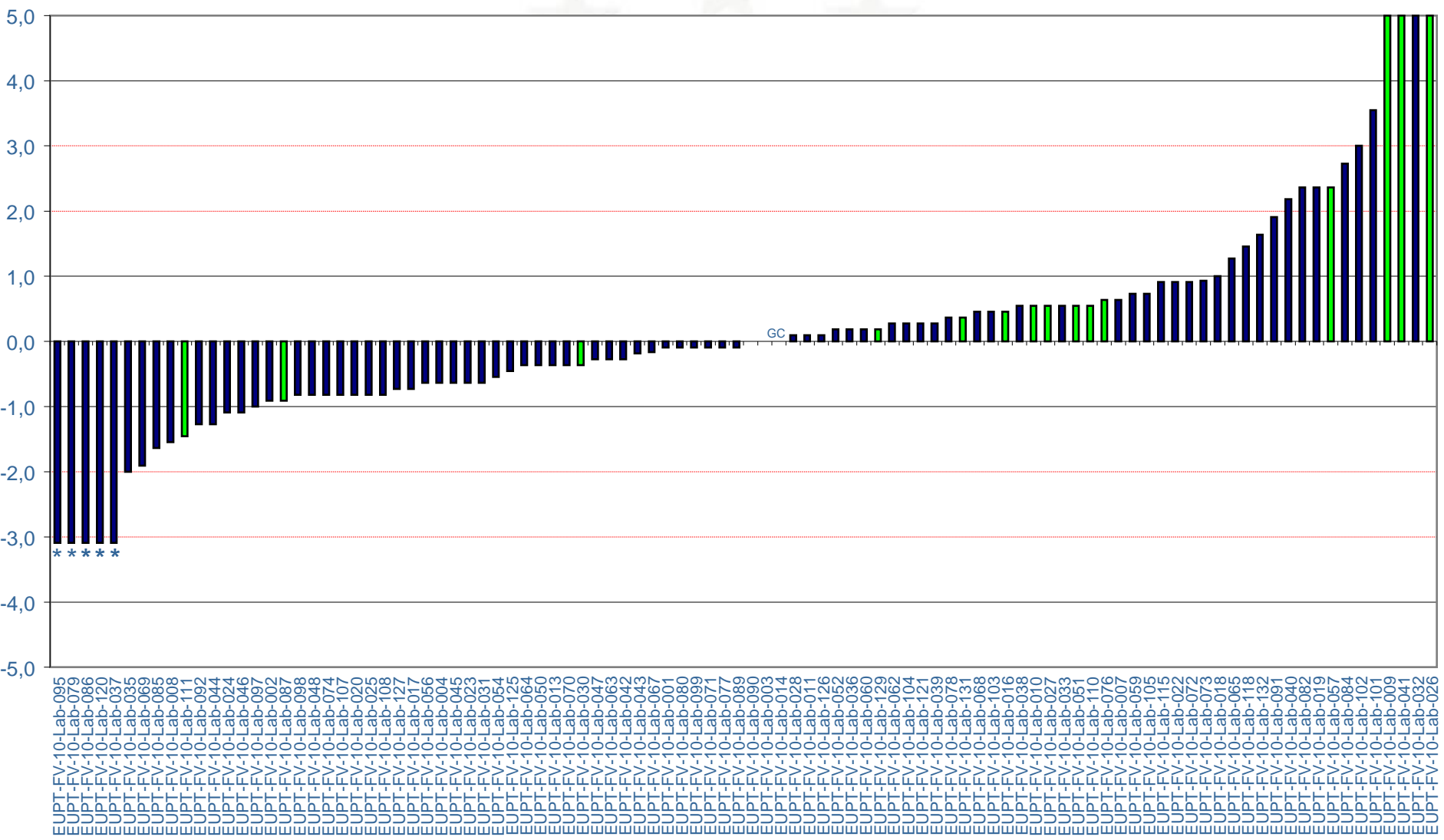


Methiocarb sulfone not in their scope

84% Acceptable
 5% Questionable
 11% Unacceptable

Methiocarb Only

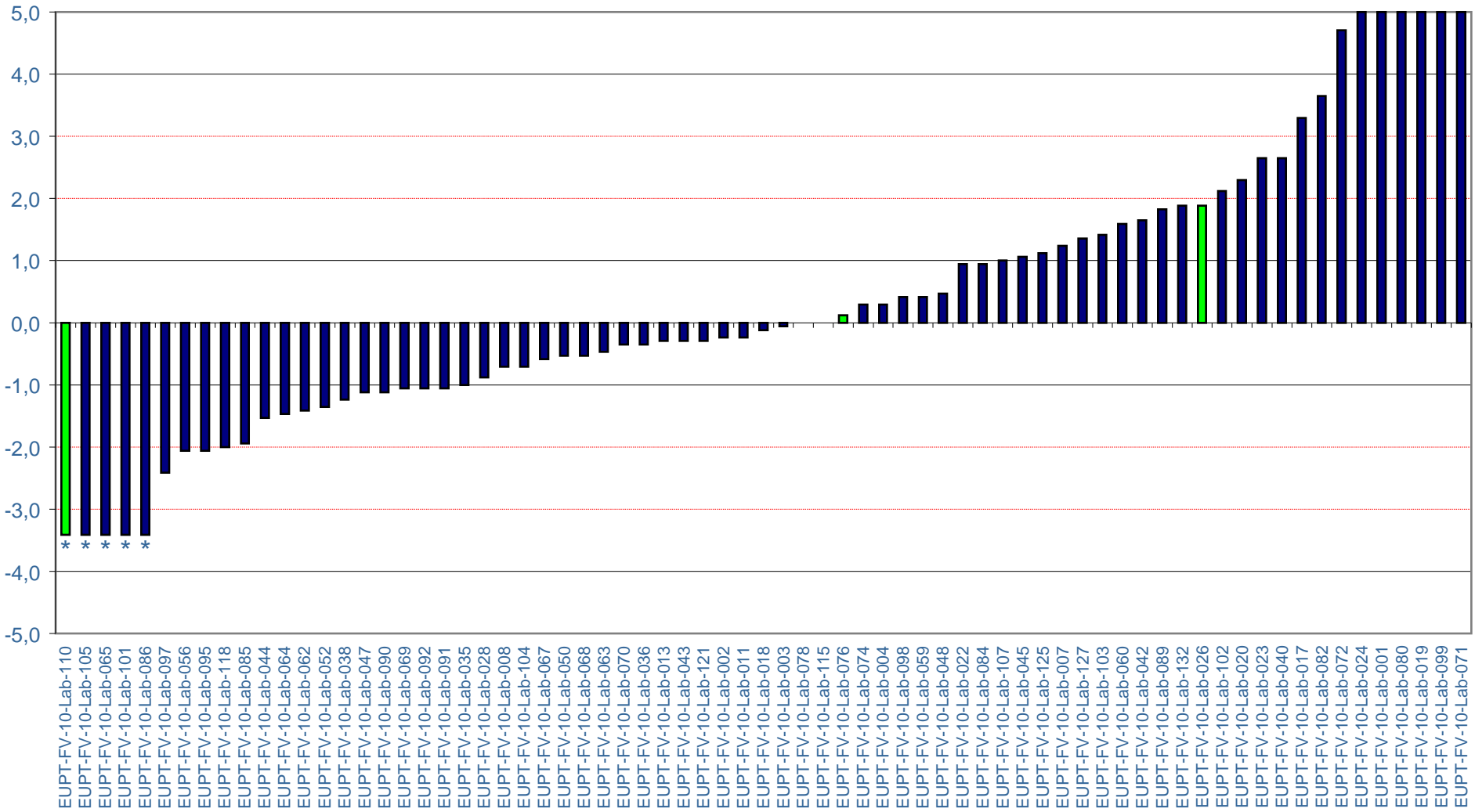
- GC
- LC
- GC and LC



Methiocarb sulfone

69% Acceptable
 11% Questionable
 20% Unacceptable

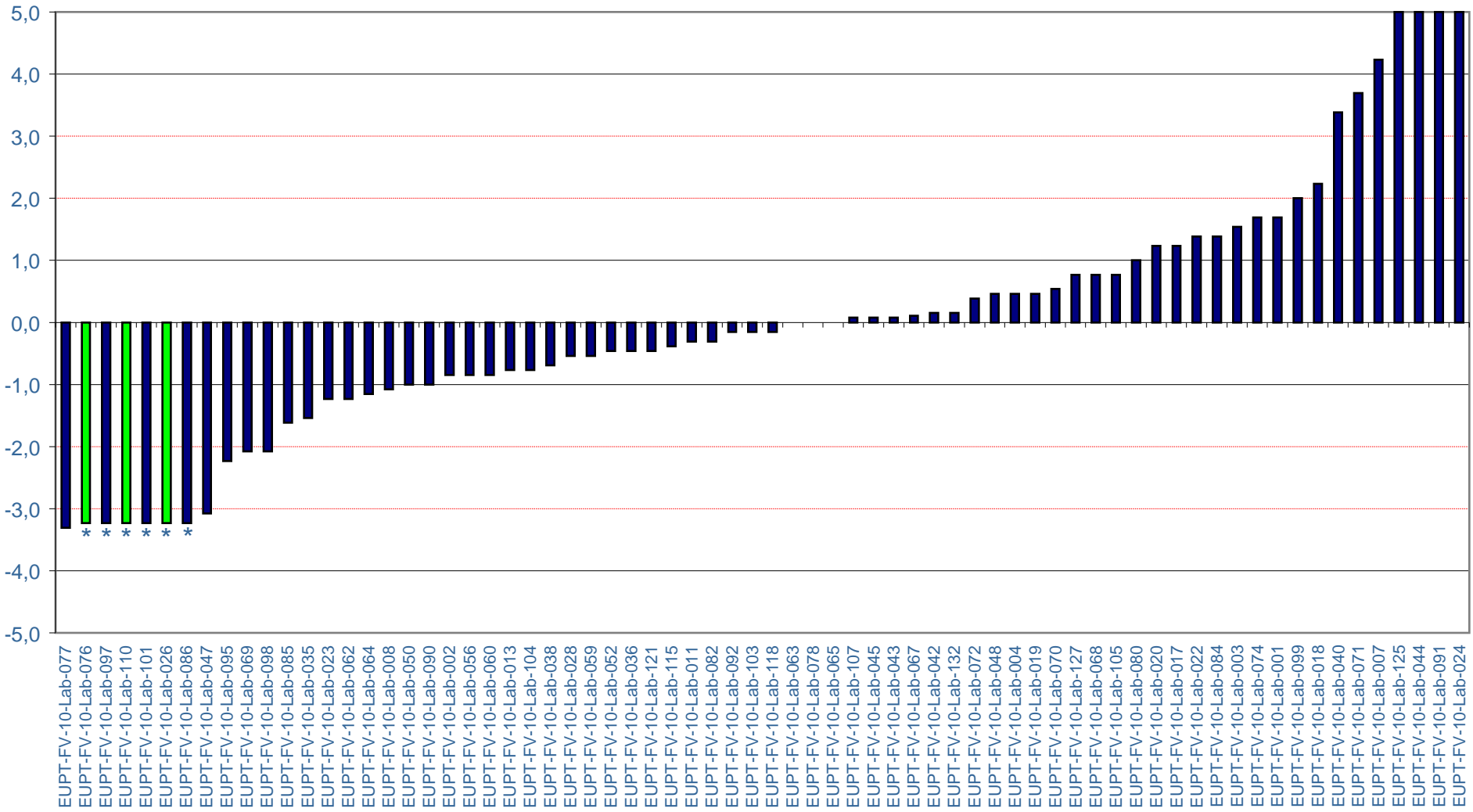
- GC
- LC
- GC and LC



74% Acceptable
 4% Questionable
 22% Unacceptable

Methiocarb sulfoxide

- GC
- LC
- GC and LC



Evolution of the laboratories performance throughout the years

Common Pesticides

New in EUPT-FV14 Target List

Spirodiclofen

Present in EUPT-FV14 and EUPT-FV15 Test Item

	% of Reported Results	% of False Negative results
EUPT-FV-14	58	3
EUPT-FV-15	66	1

	% of z-scores		
	Acceptable	Questionable	Unacceptable
EUPT-FV-14	89	2.0	9.0
EUPT-FV-15	91	4.5	4.5

Evolution of the laboratories performance throughout the years

Common Pesticides

Thiabendazole

	% of z-scores		
	Acceptable	Questionable	Unacceptable
EUPT-FV-13	83	8	8
EUPT-FV-14	97	1	2
EUPT-FV-15	95	3	1

Evolution of the laboratories performance throughout the years

Common Pesticides

Iprodione

	% of z-scores		
	Acceptable	Questionable	Unacceptable
EUPT-FV-07	85	3	11
EUPT-FV-09	86	4	10
EUPT-FV-14	93	2	5

Conclusions

- Proficiency Tests are an efficient evaluation system of the performance of the laboratories along the time. They are one of the best sources of information for the labs to improve their methodologies and quality control system by detecting systemic errors.
- Throughout the years the results of the PTs have improved, although the laboratories should put their efforts into increasing the number of pesticides in their scope. This improvement is related with the introduction of new updated LC and GC triple quadrupoles.
- The introduction of new pesticides in the target list provides an incentive for the laboratories to expand their scope.



**Special thanks to all the EUPT-FV
participants**



**for their efforts and wonderful
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in reporting information and results



Special Thanks to the EUPT-Panel



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Tuija Pihlström
Amadeo R. Fernández-Alba



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THANK YOU FOR YOUR
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