



ASSESSMENT OF PERFORMANCE OF LABORATORIES IN DETERMINING ACTIVE INGREDIENT CONTENT IN DIFFERENT FORMULATIONS.



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TOPICS

- ❖ INTRODUCTION
- ❖ ORGANISATION
- ❖ RESULTS
- ❖ CONCLUSION



INTRODUCTION

Analysis of pesticides is a challenge for analysts because they need to monitor specification of pesticide formulations available for farmer agricultural applications.

The monitoring programs are very important to check the quality of pesticide formulations and to control the spurious product available in the marketplace. As consequence, the assessment of performance of laboratories by regular participation in the proficiency test (PT) program is very important component of laboratory quality assurance.

The PT participation provide independent evidence that laboratory quality procedure, test methods and other operation are under control.

INTRODUCTION

During the 2018 and 2019, the National Institute of Health organized two PT on the determination of active ingredient in commercial plant protection products.

The activity planned in the framework of the collaboration with Health Ministry and National Institute of Health.

Due to the national monitoring program are in compliance with the European monitoring program it useful to enlarge the invitation to European member state laboratories that works in this issue.



INTRODUCTION

During 2018 and 2019, seven samples were analysed

- ▶ 2018 - three different commercial products were obtained from DuPont Manufacturer

The products contain:

- ▶ Cymoxanyl 20% (WP)
- ▶ Methomyl 20% (SL)
- ▶ Oxamyl 5% (GR)

- ▶ 2019 - four different commercial products were obtained from Adama, Newpharm and Syngenta

The products contain:

- ▶ Dimethomorph 6% (WP)
- ▶ Amisulbron 5% (WG)
- ▶ Propiconazole 25% (EC)
- ▶ Pirimiphos-methyl 5% (Liquid)

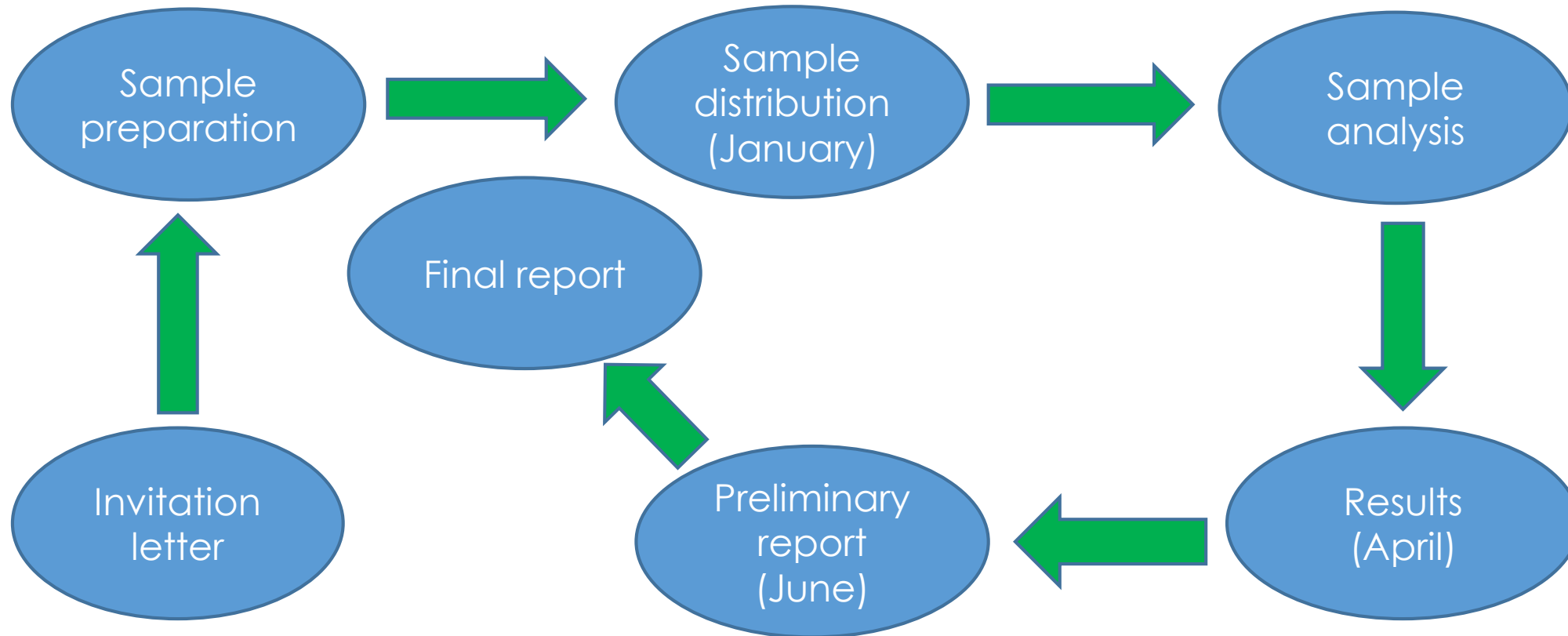
INTRODUCTION

The Italian National Institute of Health laboratory is not accreditate as promoter for PTs.
Anyway, we follow the guidelines:

- ❖ ISO/IEC 17043:2010 (E)
- ❖ ISO 13528: 2015
- ❖ Protocol of Association of American Pesticide control officials (AAPCO)



ORGANISATION





ORGANISATION

All relevant Italian laboratories and European Laboratories were invited to participate in the Italian Proficiency test on PPPs.

The invitation letter was send to 9 Italian laboratories and to 17 European laboratories.

All laboratories agreed to participate in the test.

The shipment of the test items planned to start on January.

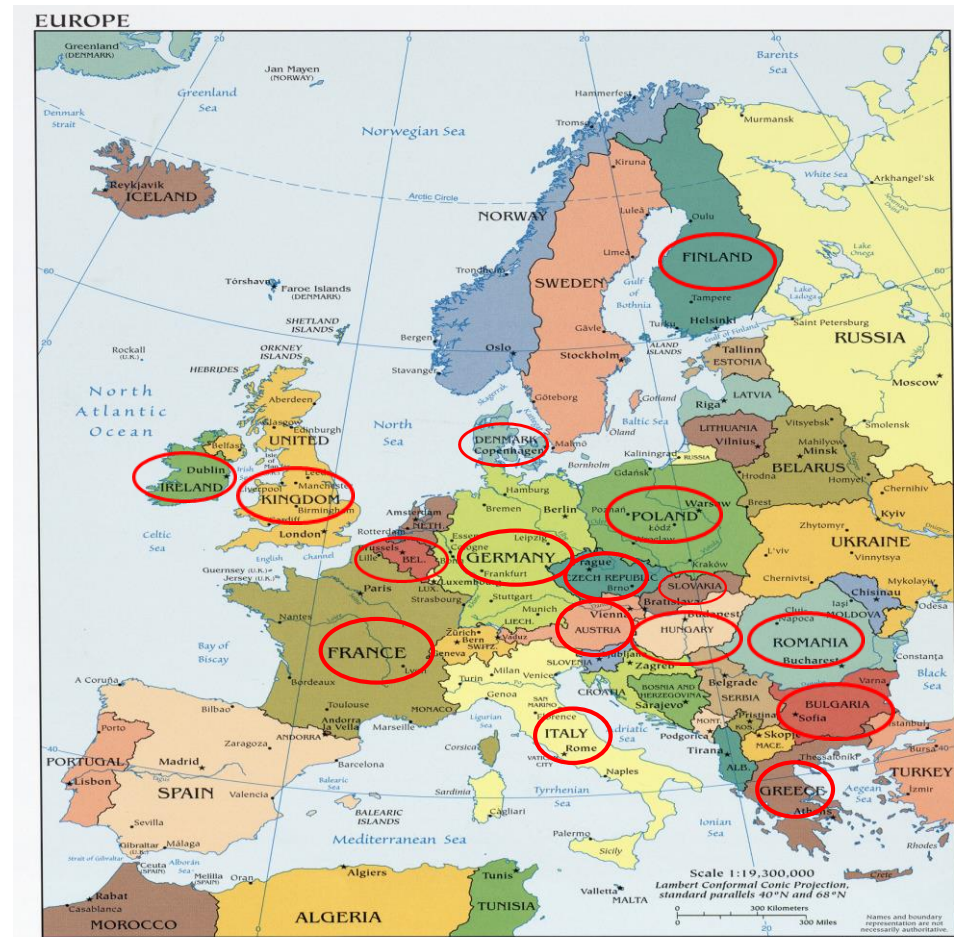
Submission of results and method information done by April.

ORGANISATION

European Countries were:

Austria
Belgium (2 lab)
Bulgaria
Czech Republic
Denmarks
Finland
France
Germany
Greece
Hungary
Italy (9 lab)
Ireland
Poland
Romania
Slovakia
United Kingdom

63° Annual CIPAC meeting – Braunschweig 18th June, 2019



ORGANISATION

Before the shipment:

- ✓ all samples were stored at ambient temperature (25°C)
- ✓ each sample was mixed, mechanically
- ✓ nothing was added to the samples
- ✓ homogeneity and stability tests were performed



ORGANISATION

- ✓ The samples were shipped by courier and at the same time a form was sent to the laboratories (it includes results and information on the analytical methods)
- ✓ The results were elaborate and statistically evaluate





RESULTS

OMOGENEITY TEST

Ten bottle were randomly chosen and analysed in duplicate in two different days.

Considering that sigma PT is unknown the statistical significant difference between PT items used was evaluated with the analysis of variance T-Test at $\alpha=0.05$, if the data series are more than two will need the Fisher Test. The T-test shows a significativity level (P) higher than 0.05 for each active substance. It is possible to say the samples are not different one each other, they are homogeneity.





RESULTS

	Cymoxanil		Methomyl		Oxamyl	
	a*	b*	a*	b*	a*	b*
1	19,36	19,41	18,86	19,51	4,64	5,05
2	19,14	19,36	18,50	18,75	4,86	4,79
3	19,08	19,49	19,11	18,82	4,70	5,01
4	19,34	19,27	19,02	19,63	5,38	4,96
5	19,27	19,28	18,96	19,81	4,91	5,29
6	19,28	18,50	17,06	17,69	5,28	4,98
7	19,49	19,32	18,54	18,81	5,40	5,07
8	19,37	19,47	19,23	18,60	5,53	5,11
9	18,96	18,96	18,62	19,31	5,08	5,34
10	19,32	19,44	18,60	19,57	5,13	5,20
Mean	19,26		18,85		5,09	
Std Dev.	0,236		0,644		0,240	
t**	0,905		1,427		0,100	
P***	0,377		0,171		0,922	
Homogeneity	YES		YES		YES	

*a,b = replicates of the same sample

t** = T of Student Test

P*** = significativity level



RESULTS

	Amisulbrom		Dimethomorph		Pirimiphos-Methyl		Propiconazole	
	a*	b*	a*	b*	a*	b*	a*	b*
1	5,23	5,24	6,48	6,58	5,02	5,19	25,5	24,3
2	5,19	5,23	6,66	6,59	5,03	5,18	23,2	22,2
3	5,12	5,22	6,52	6,39	5,11	5,60	22,2	23,5
4	5,24	5,22	6,60	6,52	4,95	5,02	23,3	23,9
5	5,18	5,24	6,48	6,49	5,23	5,49	24,6	24,5
6	5,18	5,17	6,53	6,41	5,38	5,16	25,1	24,8
7	5,27	5,14	6,44	6,55	5,31	5,43	23,6	24,9
8	5,27	5,06	6,40	6,40	5,00	5,08	24,8	25,1
9	5,14	5,23	6,30	6,43	4,91	5,09	25,2	24,8
10	5,24	5,24	6,57	6,60	5,13	5,12	24,8	25,4
Mean	5,20		6,50		5,17		24,3	
Std Dev.	0,055		0,092		0,186		0,994	
t**	0,281		0,046		1,618		0,26	
P***	0,782		0,963		0,123		0,798	
Homogeinity	YES		YES		YES		YES	

*a,b = replicates of the same sample

t** = T of Student Test

P*** = significativity level

RESULTS

STABILITY TEST

The stability test was performed using two bottles randomly chosen, which were analysed in duplicate in two occasions and each occasion twice.

- ▶ Day 1 – at the beginning of the PT.
- ▶ Day 2 – at the end of the PT.

Stability test was judged acceptable as the percentage difference of concentration, for each active substance was found less than 10%. Any significant decrease in the pesticide concentration was showed during the PT.

The following tables shows the results for each substances



RESULTS

CYMOXANIL 18 th January					CYMOXANIL 3 rd May				
	day 1		day 2			day 1		day 2	
	inj 1	inj 2	inj 1	inj 2		inj 1	inj 2	inj 1	inj 2
Sample 1	19,8	20,0	19,7	19,6	Sample 1	19,2	19,0	20,0	19,8
Sample 2	19,9	19,8	19,8	19,6	Sample 2	18,9	19,3	19,9	19,9
Mean	19,9		19,7		Mean	19,1		19,9	
Std Dev.	0,10		0,10		Std Dev.	0,18		0,08	
Mean of 2 days	19,8				Mean of 2 days	19,5			
Std Dev. Of 2 days	0,14				Std Dev. Of 2 days	0,57			
Deviation (ref 1st Analysis %)				-1,39					
[(M2-M1)/M1]*100									
Deviation (ref to the declared label %)				-1,81					
[(SM-20)/20]*100									
Stabiliy Mean (SM)		19,6			Declared Label			20	
Stability Std Dev		0,19			CV %			0,99	

RESULTS

METHOMYL 18 th Jan					METHOMYL 3 rd May				
	day 1		day 2			day 1		day 2	
	inj 1	inj 2	inj 1	inj 2		inj 1	inj 2	inj 1	inj 2
Sample 1	19,1	19,1	19,2	19,3	Sample 1	18,5	18,9	19,3	19,0
Sample 2	19	18,9	19,4	19,2	Sample 2	18,8	18,6	19,0	19,2
Mean	19,0		19,3		Mean	18,7		19,1	
Std Dev.	0,10		0,10		Std Dev.	0,18		0,15	
Mean of 2 days	19,2				Mean of 2 days	18,9			
Std Dev. Of 2 days	0,18				Std Dev. Of 2 days	0,30			
Deviation (ref 1st Analysis %)				-1,26					
[(M2-M1)/M1]*100									
Deviation (ref to the declared label %)				-4,84					
[(SM-20)/20]*100									
Stabiliy Mean (SM)		19,0			Declared Label		20		
Stability Std Dev		0,17			CV %		0,88		



RESULTS

OXAMYL 18 th Jan					OXAMYL 3 rd May				
	day 1		day 2			day 1		day 2	
	inj 1	inj 2	inj 1	inj 2		inj 1	inj 2	inj 1	inj 2
Sample 1	5,20	5,19	5,31	5,32	Sample 1	5,33	5,31	5,29	5,31
Sample 2	5,43	5,40	5,30	5,33	Sample 2	5,30	5,34	5,30	5,31
Mean	5,31		5,32		Mean	5,32		5,30	
Std Dev.	0,13		0,01		Std Dev.	0,02		0,01	
Mean of 2 days	5,31				Mean of 2 days	5,31			
Std Dev. Of 2 days	0,01				Std Dev. Of 2 days	0,01			
Deviation (ref 1st Analysis %)				0,02					
[(M2-M1)/M1]*100									
Deviation (ref to the declared label %)				6,21					
[(SM-5)/5]*100									
Stabiliy Mean (SM)		5,31			Declared Label			5	
Stability Std Dev		0,00			CV %			0,02	



RESULTS

AMISULBROM December 2018					AMISULBROM June 2019				
	day 1		day 2			day 1		day 2	
	inj 1	inj 2	inj 1	inj 2		inj 1	inj 2	inj 1	inj 2
Sample 1	5,03	5,03	5,53	5,56	Sample 1	4,57	4,59	5,64	5,64
Sample 2	5,29	5,28	5,1	5,07	Sample 2	4,58	4,58	5,1	5,08
Mean	5,16		5,32		Mean	4,58		5,365	
Std Dev.	0,147		0,266		Std Dev.	0,008		0,318	
Mean of 2 days	5,24				Mean of 2 days	4,97			
Std Dev. Of 2 days	0,207				Std Dev. Of 2 days	0,163			
Deviation (ref 1st Analysis %)				3,054					
[(M2-M1)/M1]*100									
Deviation (ref to the declared label %)				2,088					
[(SM-5)/5]*100									
Stabiliy Mean (SM)		5,10			Declared Label		5,00		
Stability Std Dev		0,185			CV %		3,621		



RESULTS

DIMETOMORPH Nov 2018					DIMETHOMORPH June 2019				
	day 1		day 2			day 1		day 2	
	inj 1	inj 2	inj 1	inj 2		inj 1	inj 2	inj 1	inj 2
Sample 1	6,35	6,3	5,84	5,86	Sample 1	6,23	6,14	6,33	6,15
Sample 2	6,42	6,4	6,43	6,43	Sample 2	6,29	6,56	6,26	6,09
Mean	6,37		6,14		Mean	6,31		6,21	
Std Dev.	0,054		0,335		Std Dev.	0,181		0,108	
Mean of 2 days	6,25				Mean of 2 days	6,26			
Std Dev. Of 2 days	0,194				Std Dev. Of 2 days	0,144			
Deviation (ref 1st Analysis %)				-3,57					
[(M2-M1)/M1]*100									
Deviation (ref to the declared label %)				4,25					
[(SM-6)/6]*100									
Stabiliy Mean (SM)		6,26			Declared Label		6,00		
Stability Std Dev		0,169			CV %		2,71		



RESULTS

PIRIMIPHOS METHYL November 2018					PIRIMIPHOS METHYL June 2019				
	day 1		day 2			day 1		day 2	
	inj 1	inj 2	inj 1	inj 2		inj 1	inj 2	inj 1	inj 2
Sample 1	4,92	5,21	5,56	5,2	Sample 1	3,67	4,1	4,26	3,54
Sample 2	5,04	4,9	5,07	5,44	Sample 2	3,60		4,60	4,18
Mean	5,02		5,32		Mean	3,885		4,15	
Std Dev.	0,142		0,223		Std Dev.	0,271		0,443	
Mean of 2 days	5,17				Mean of 2 days	4,02			
Std Dev. Of 2 days	0,183				Std Dev. Of 2 days	0,357			
Deviation (ref 1st Analysis %)				5,98					
[(M2-M1)/M1]*100									
Deviation (ref to the declared label %)				-8,175					
[(SM-5)/5]*100									
Stabiliy Mean (SM)		4,59			Declared Label		5		
Stability Std Dev		0,123			CV %		2,68		



RESULTS

PROPICONAZOLE December 2018					PROPICONAZOLE June 2019				
	day 1		day 2			day 1		day 2	
	inj 1	inj 2	inj 1	inj 2		inj 1	inj 2	inj 1	inj 2
Sample 1	23,4	23,5	23,3	23,2	Sample 1	22,2	21,6	27,0	26,6
Sample 2	23,2	22,3	22,7	22,5	Sample 2	25,3	25,4	25,3	25,6
Mean	23,10		22,93		Mean	23,63		26,13	
Std Dev.	0,548		0,386		Std Dev.	2,007		0,806	
Mean of 2 days	23,01				Mean of 2 days	24,88			
Std Dev. Of 2 days	0,467				Std Dev. Of 2 days	1,406			
Deviation (ref 1st Analysis %)				-0,758					
[(M2-M1)/M1]*100									
Deviation (ref to the declared label %)				-4,225					
[(SM-25)/25]*100									
Stabiliy Mean (SM)		23,94			Declared Label		25		
Stability Std Dev		0,937			CV %		3,912		

RESULTS

The robust estimate of the standard deviation used was the MAD_E value.

To obtain the MAD_E ,

Calculate Median Absolute Deviation (MAD) from the sample median:

$$MAD = median (|X_i - median (X_i)|_{i=1,2,...,n})$$

Calculate MAD_E :

$$MAD_E = K \times MAD$$

For normally distributed data, $K = 1,483$.

$$MAD_E = 1,483 \times MAD$$

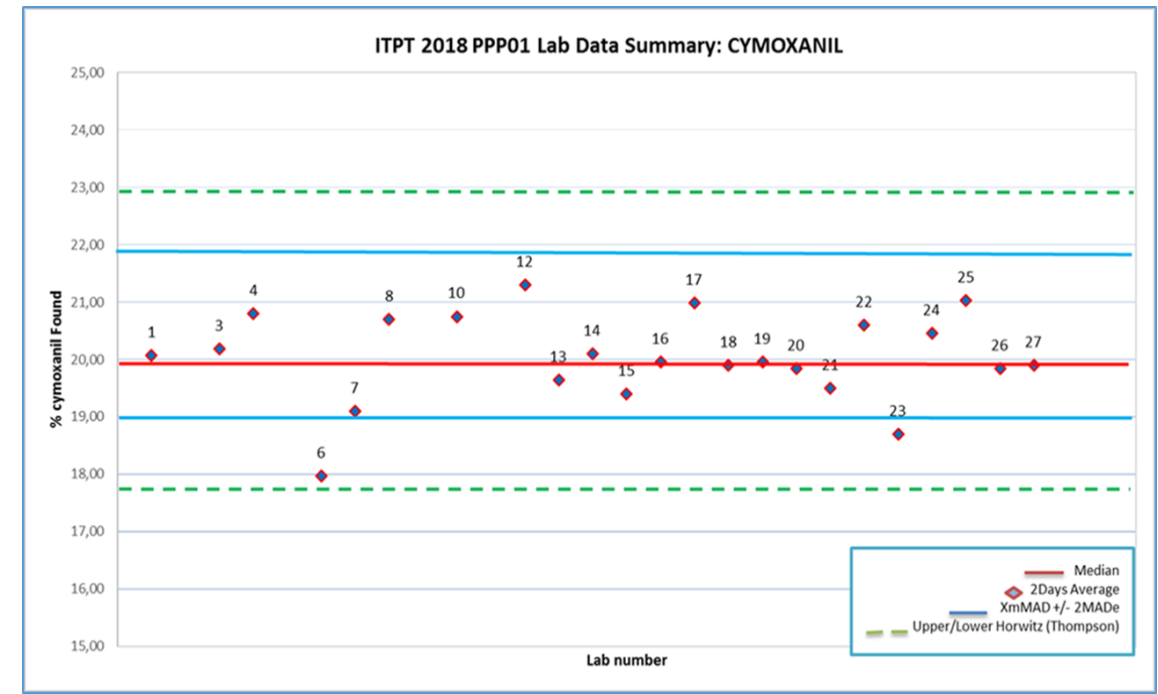
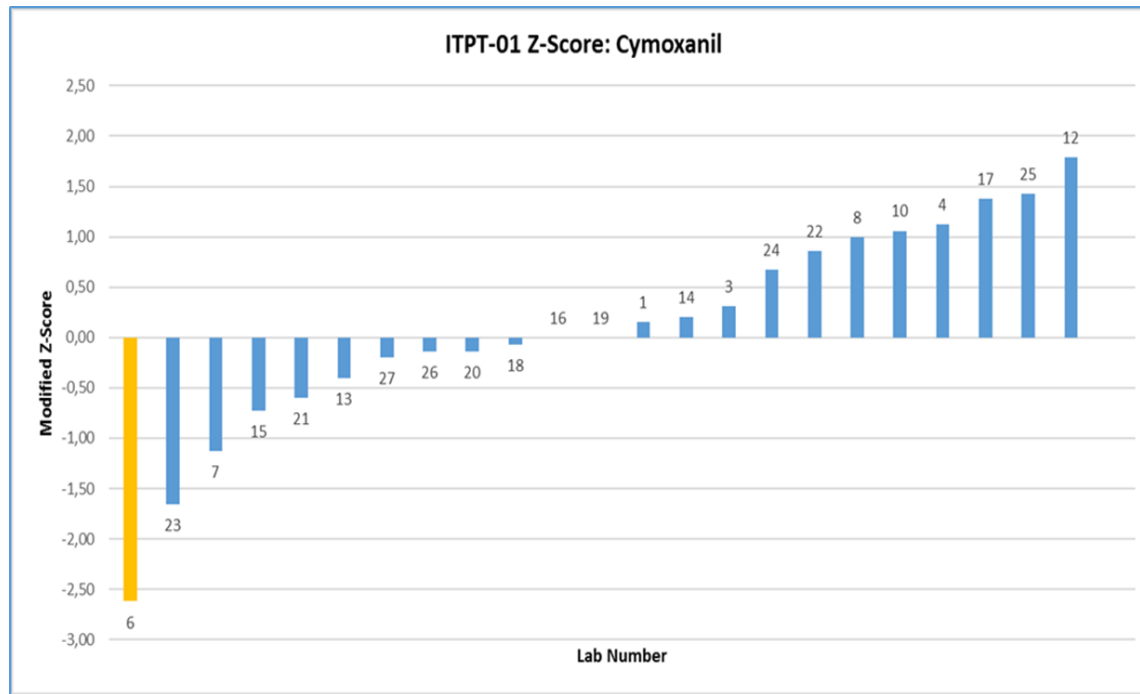
Calculation of Modified Z-scores

Modified Z-scores (Z_i) for each laboratory were calculated as:

$$Z_i = 0,6745 \times (X_i - median) / MAD$$

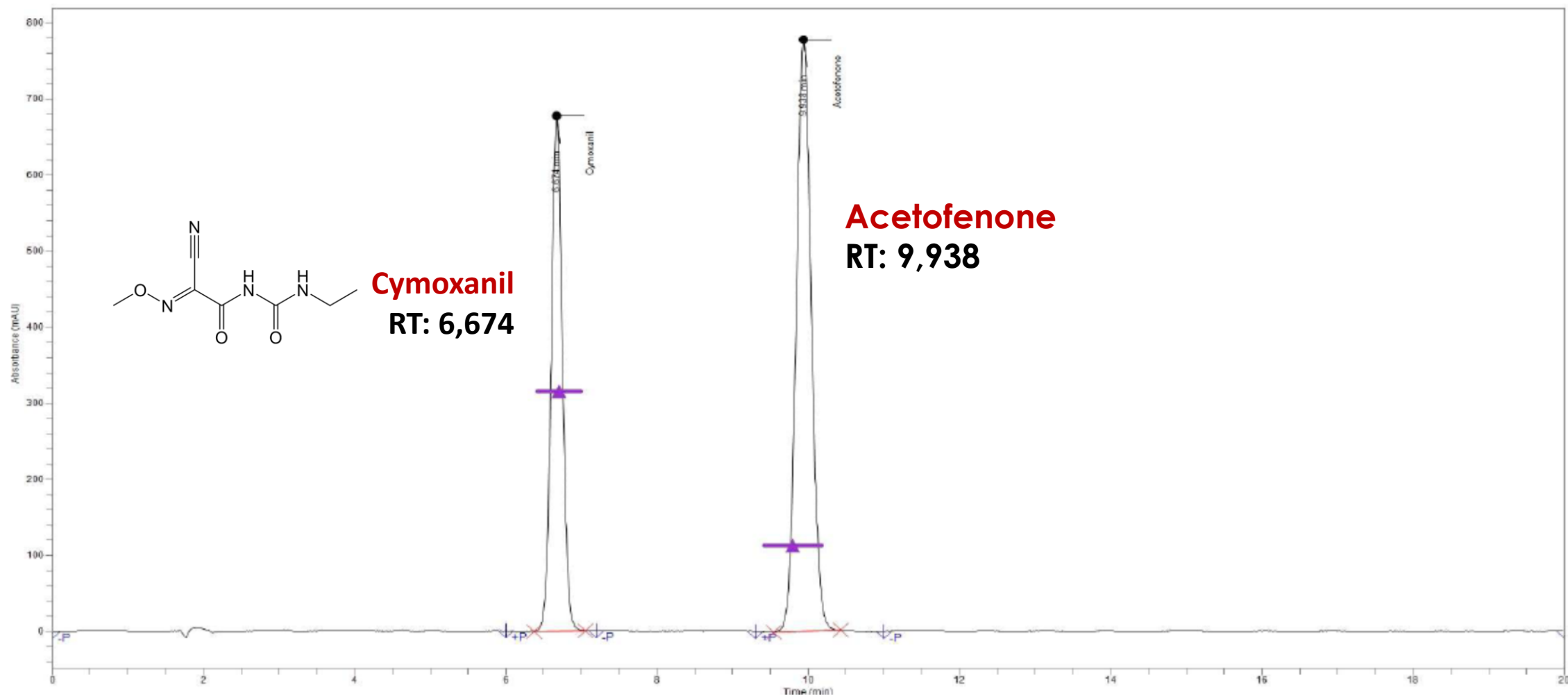
Z values falling outside the range of $-3,5 \leq Z_i \leq 3,5$ were marked as outliers.

RESULTS



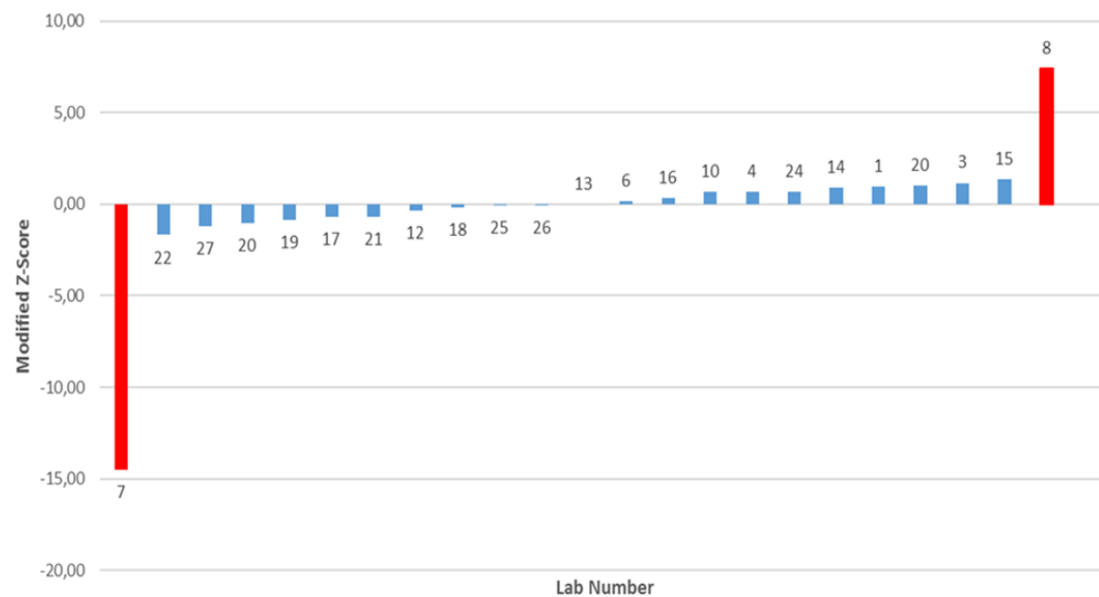


Campione : Injection 1

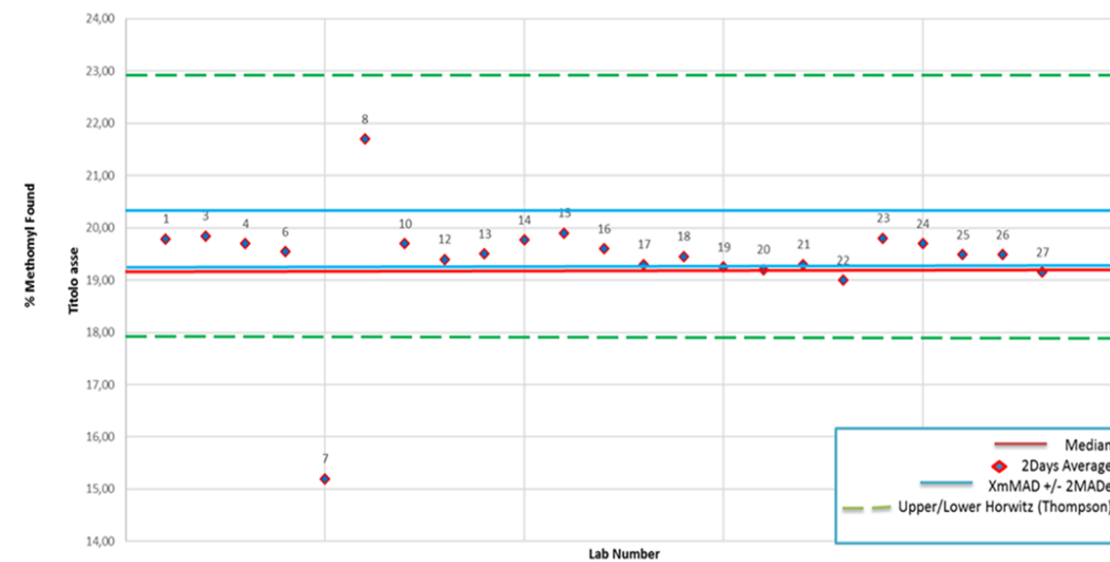


RESULTS

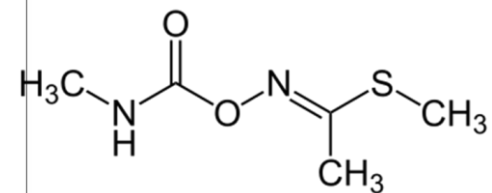
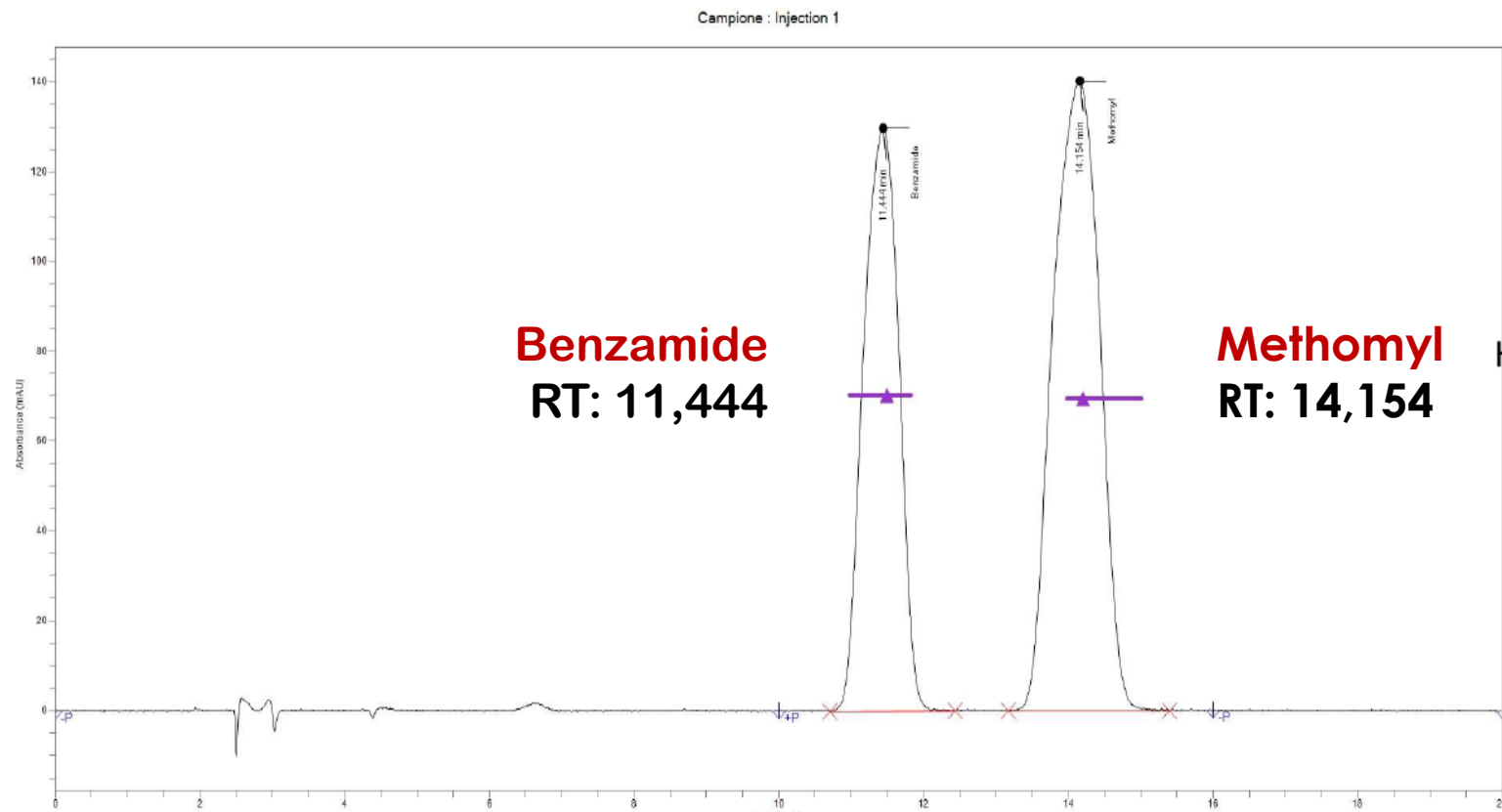
ITPT-01 Z-Score: Methomyl



ITPT 2018 PPP02 Lab Data Summary: METHOMYL

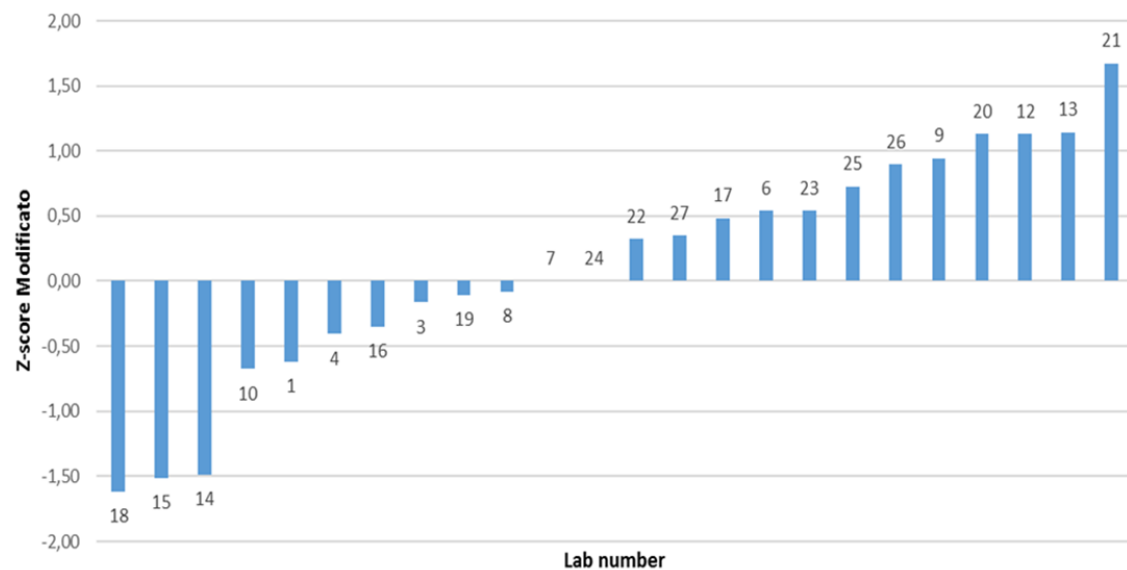


RESULTS

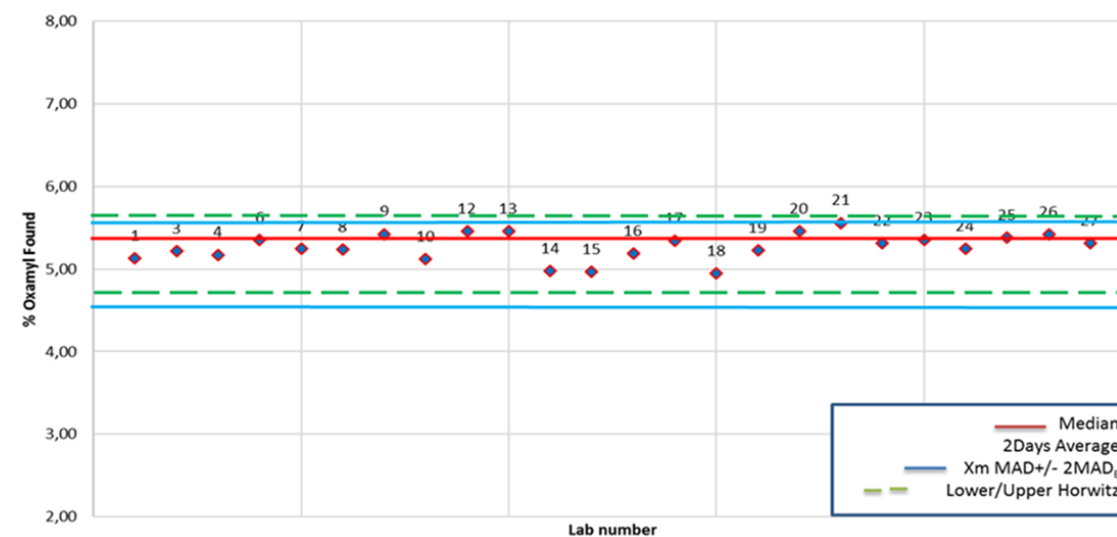


RESULTS

ITPT-01 Z-Score: Oxamyl



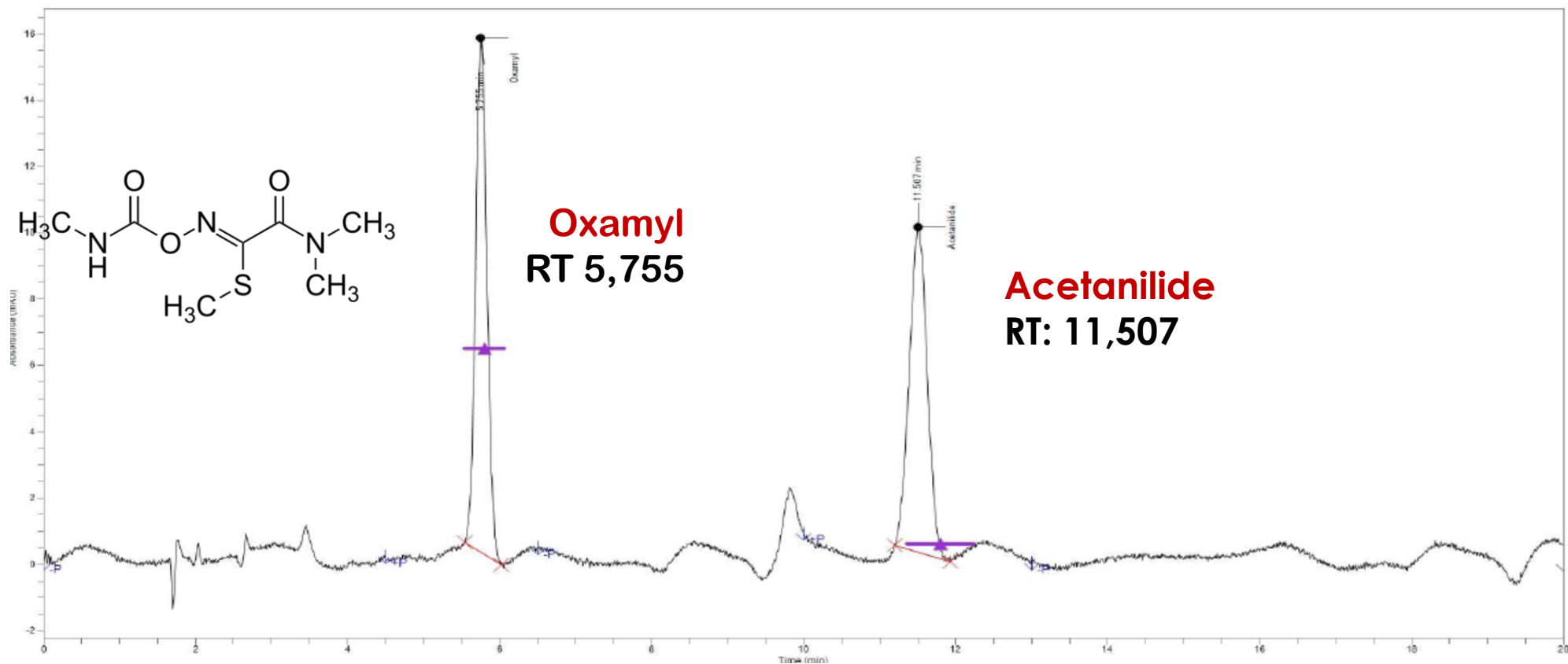
ITPT 2018 PPP03 Lab Data Summary: Oxamyl





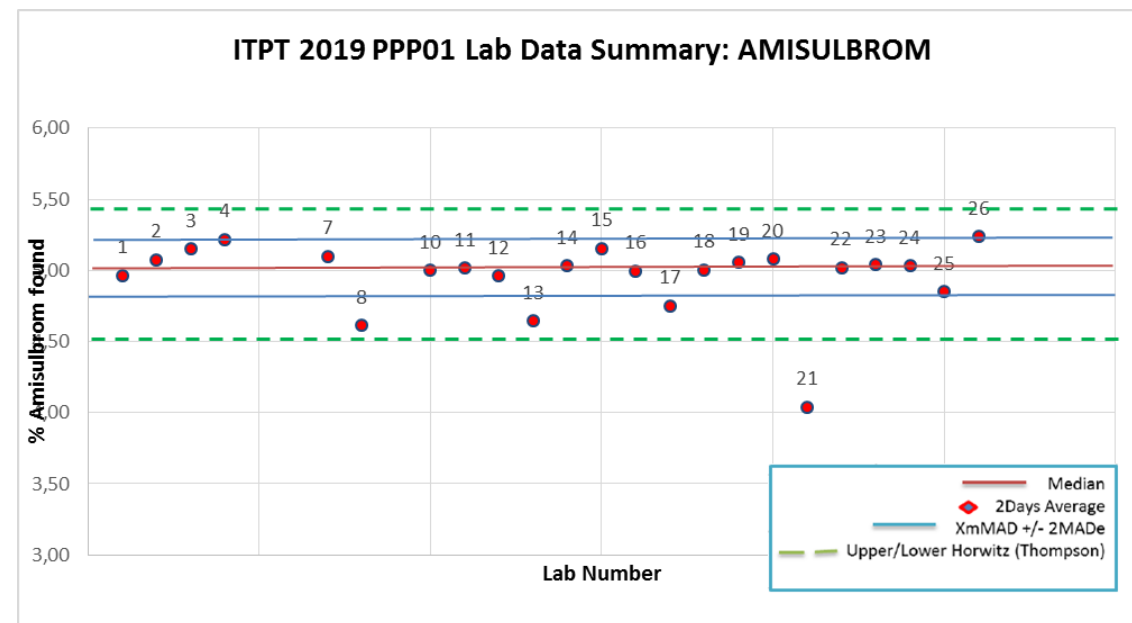
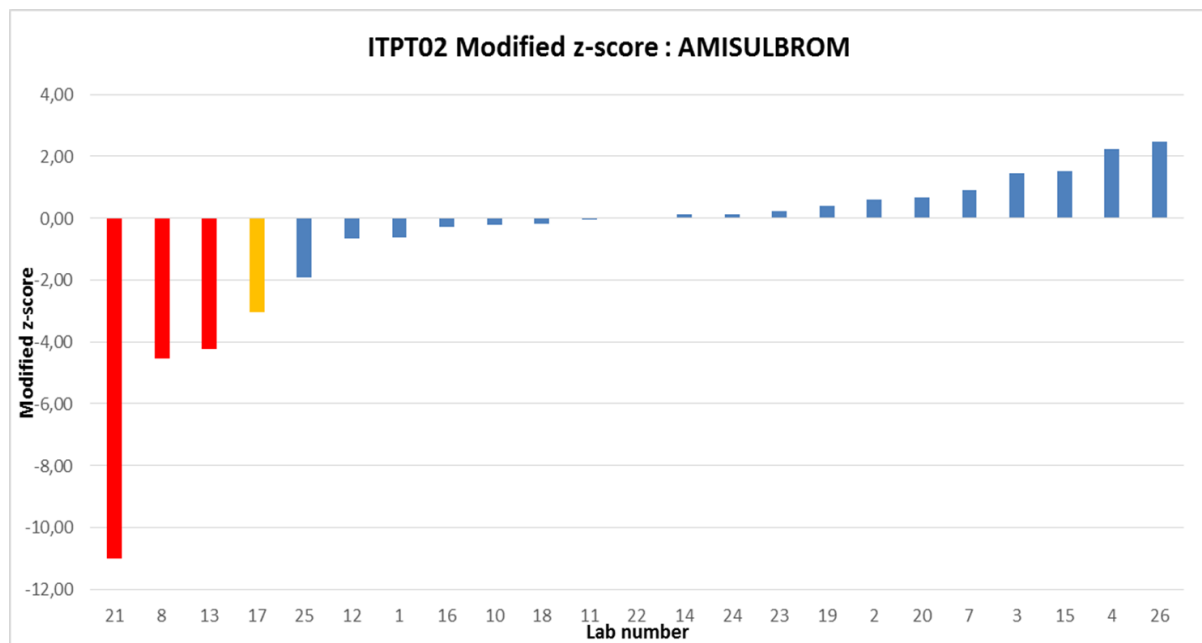
RESULTS

Campione : Injection 1

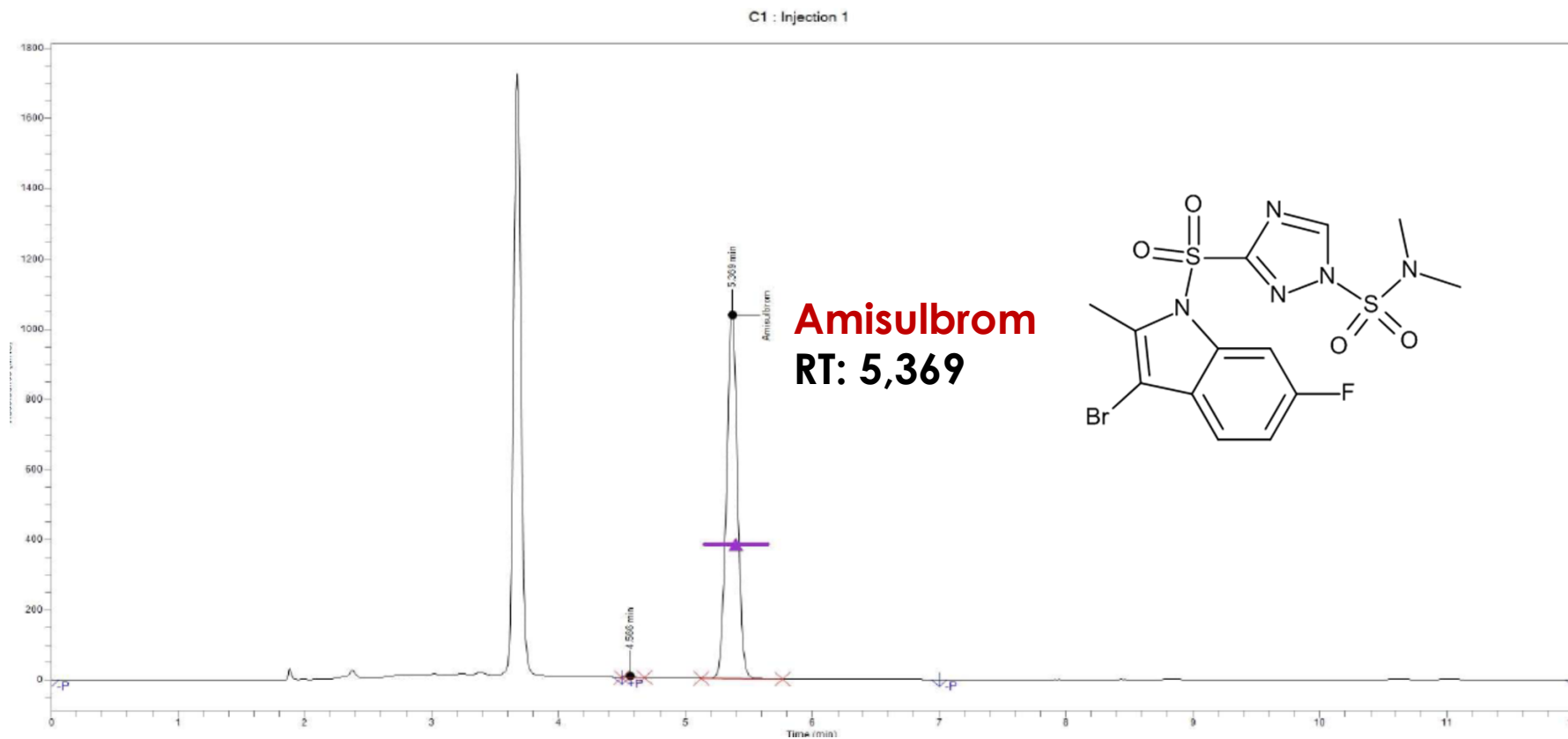




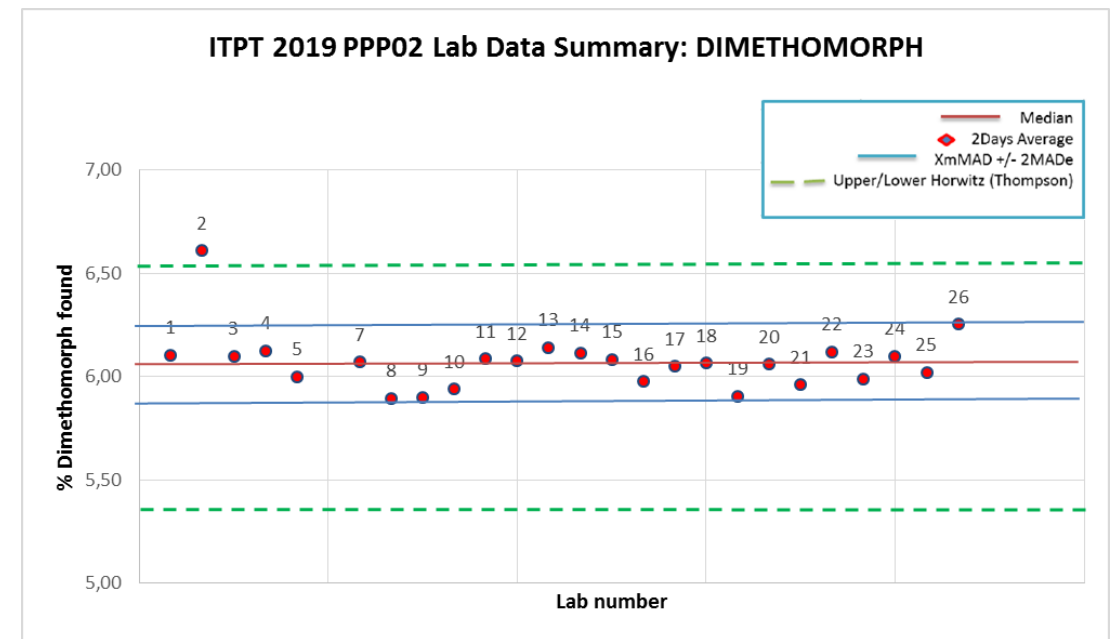
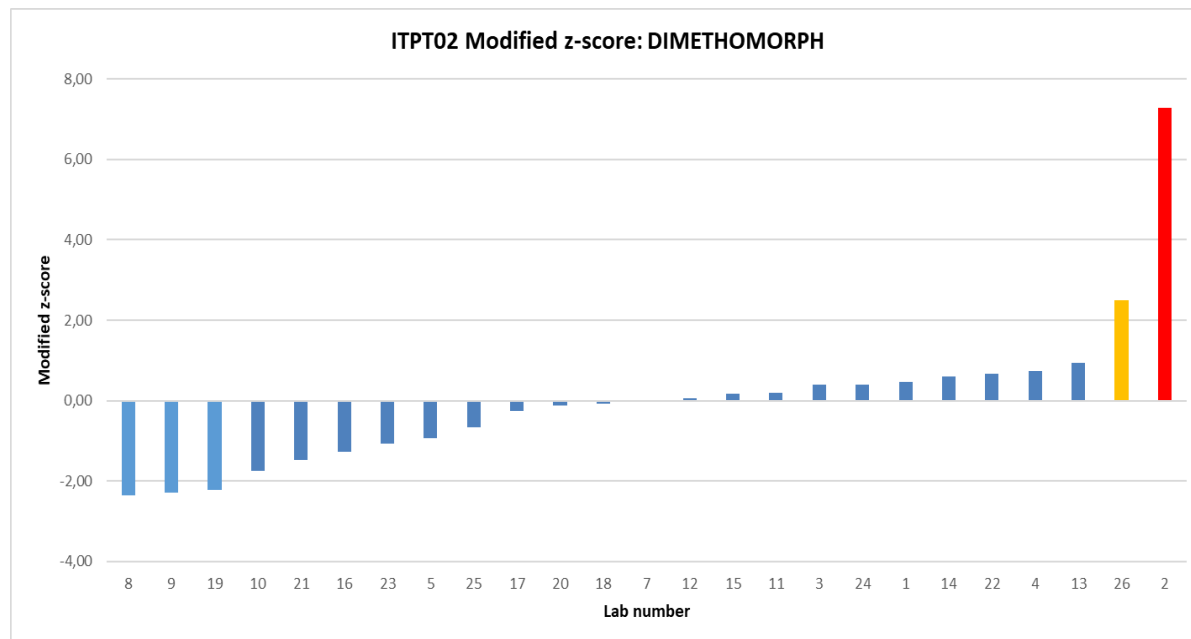
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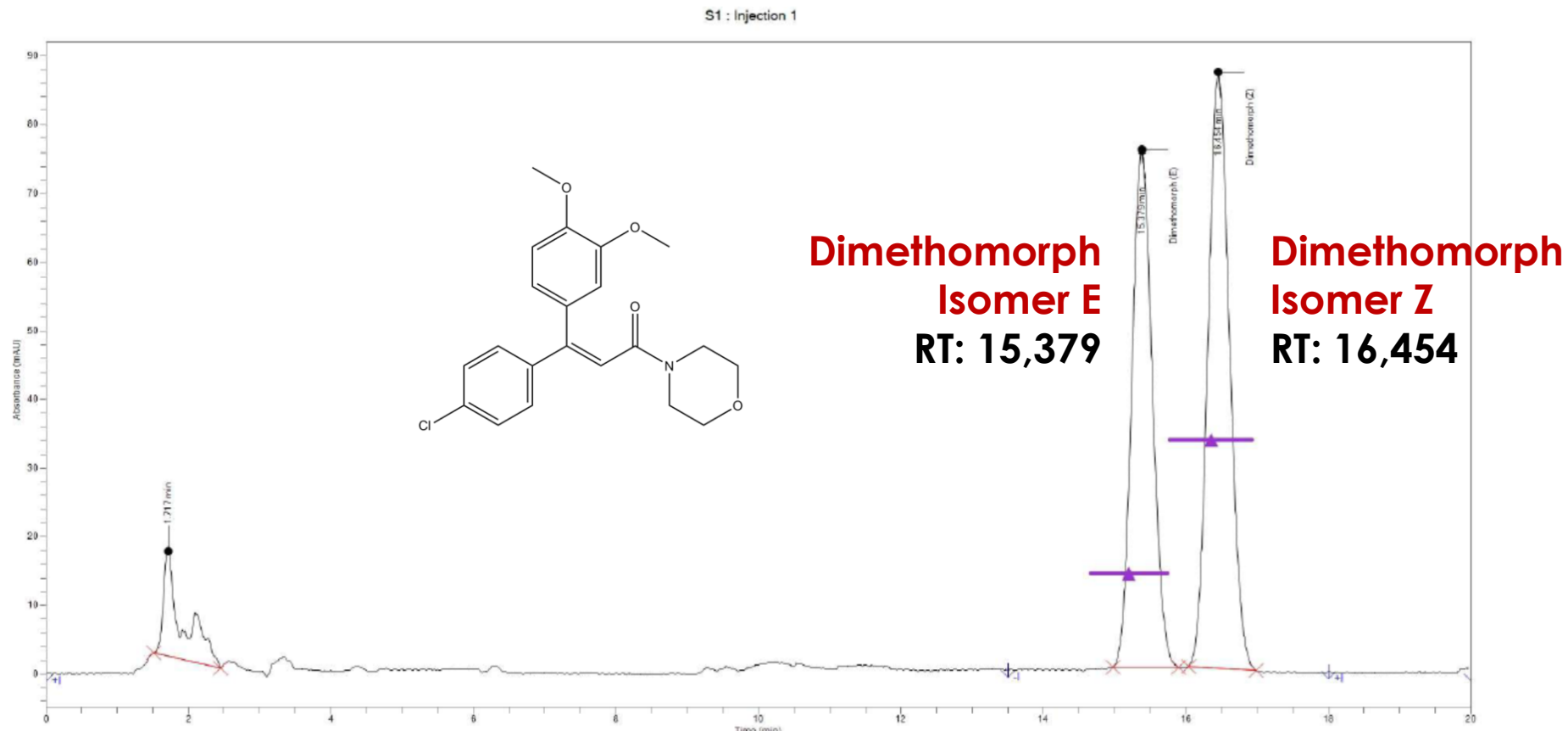
RESULTS



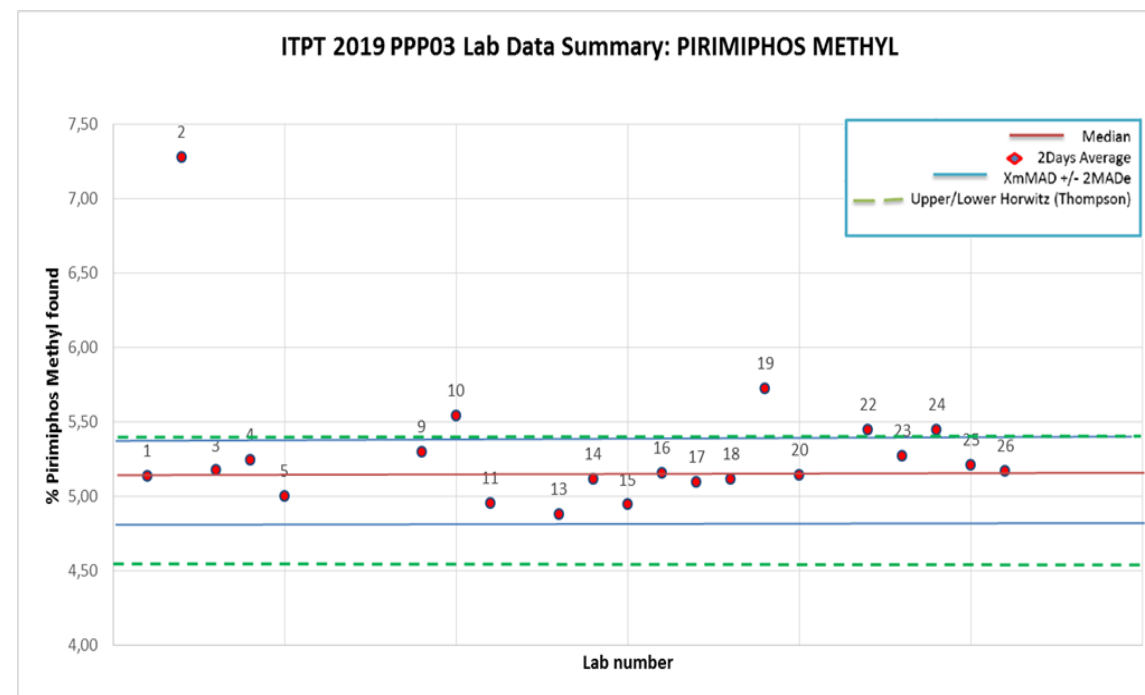
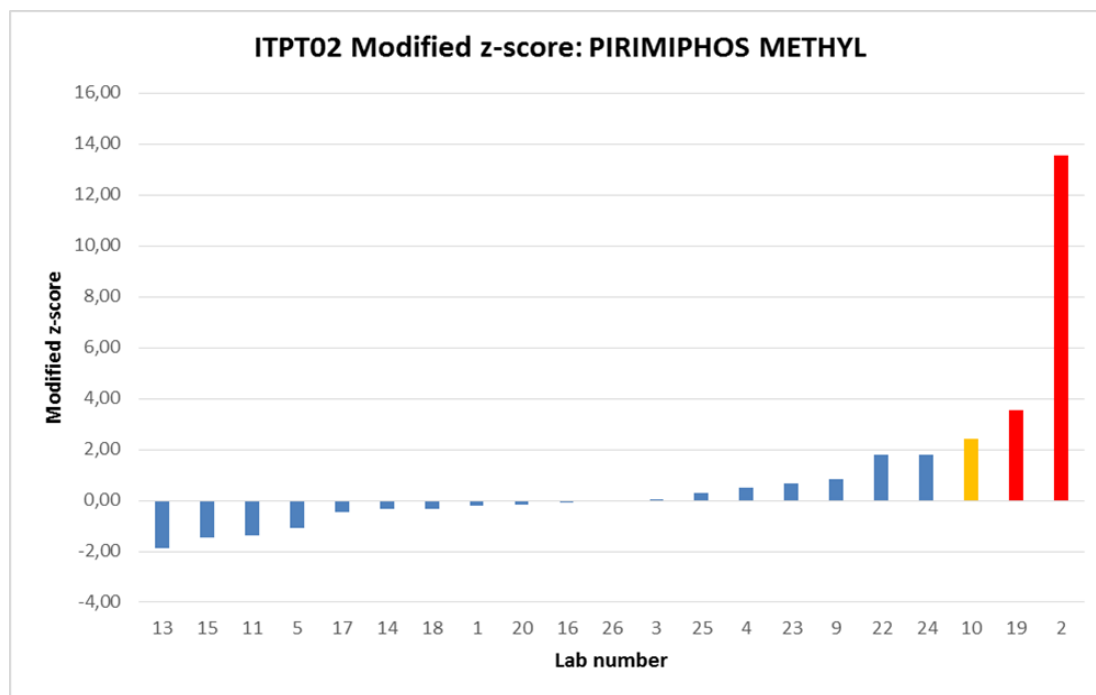
RESULTS



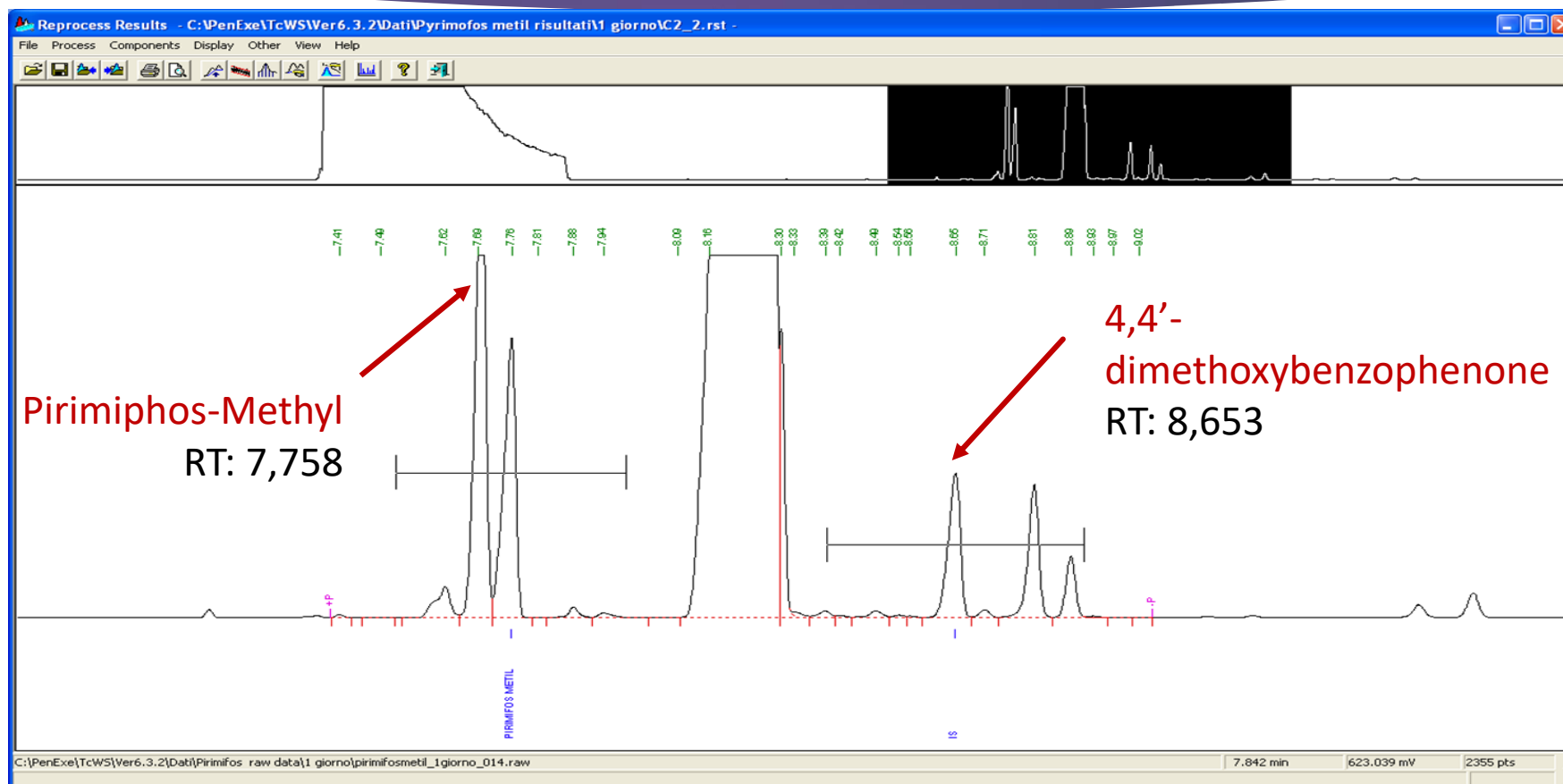
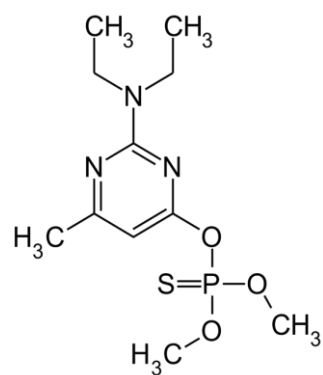
RESULTS



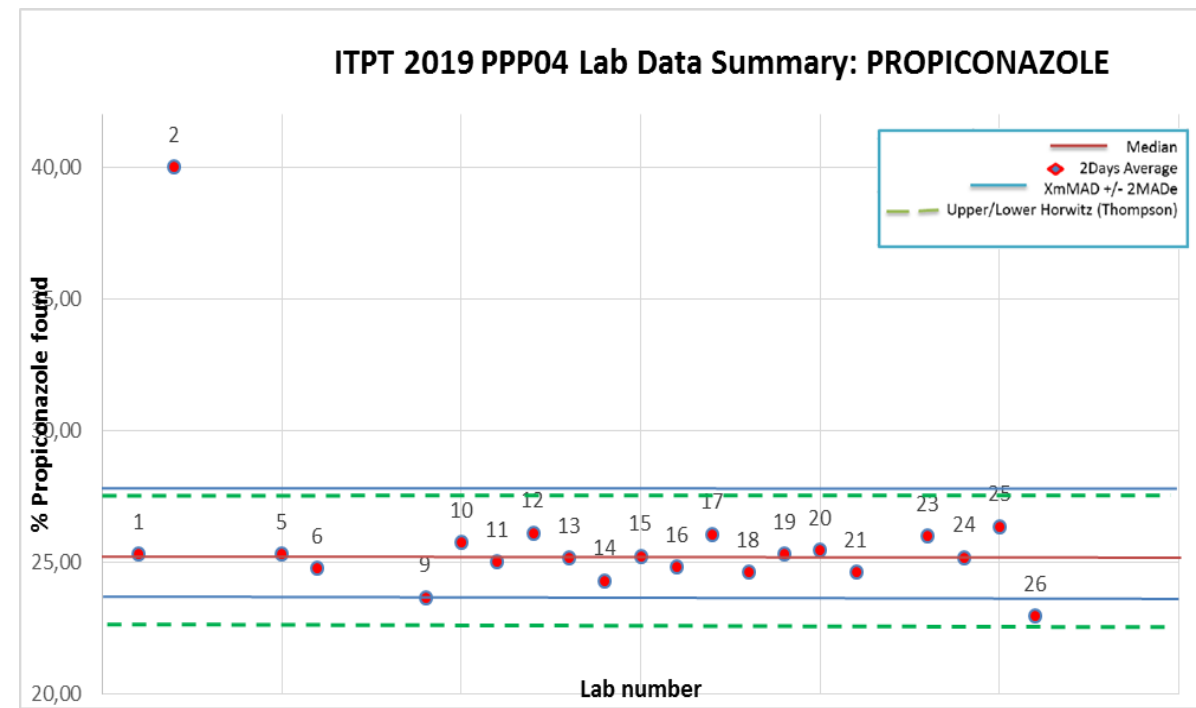
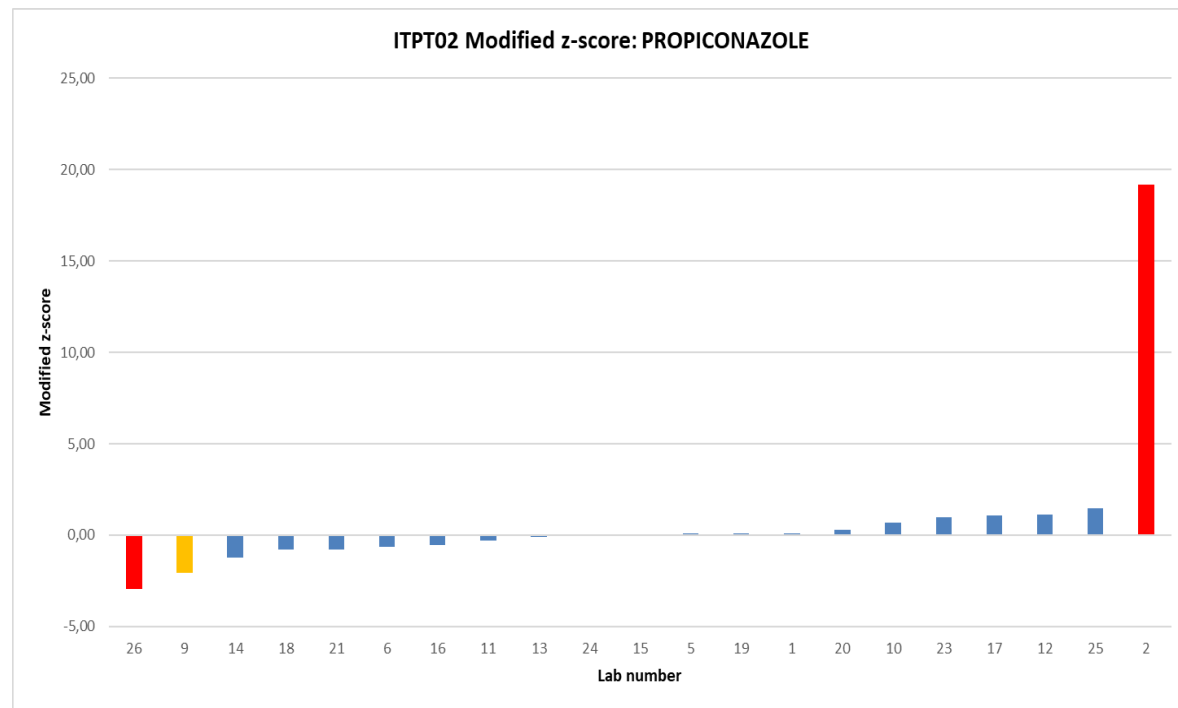
RESULTS



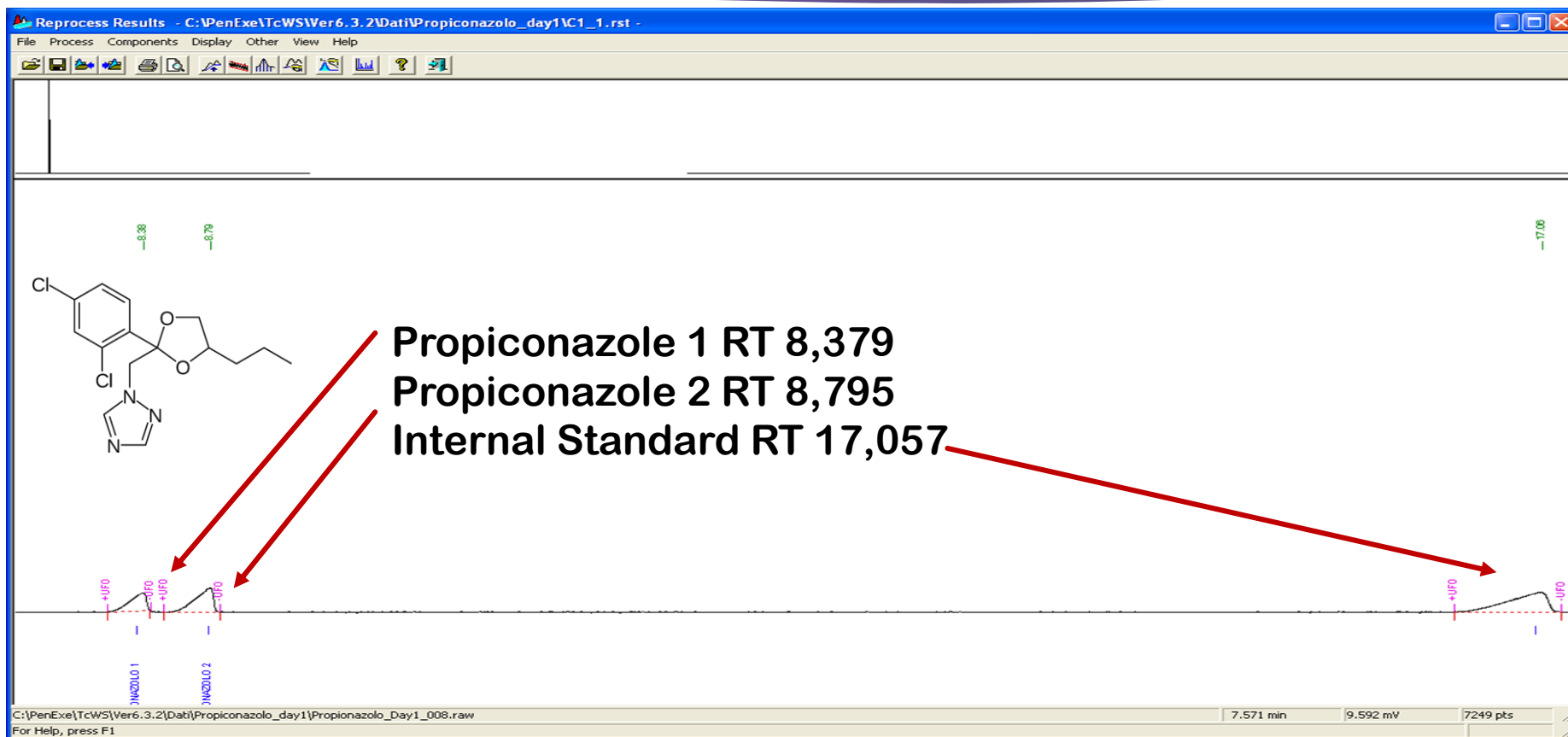
RESULTS



RESULTS



RESULTS





RESULTS

Method	Z-score values						
	Amisulbron	Cymoxanil	Dimethomorph	Methomyl	Oxamyl	Pirimiphos methyl	Propiconazole
In-house	(-4.22) – 1.46	(-2.62) - +1.79	(-2.23) -7.28	(-14.6) - 7.34	(-1.62) – 1.13	13.55 - (-1.86)	19.92 - (-1.26)
CIPAC	(-11.02) – 2.47	-0.86 – 1.43	(-2.36) – 2.50	(-0.11) - 7.34	(-1.48) – 1.14	0.84 – (-1.38)	1.51 – (- 3.08)
Manufacturer	(-0.06) – 0.00	- 1.65	---	(-1.76) – 0.89	(-0.67) – 1.67	0.67	1.01



CONCLUSION



CIPAC Method

→ Different column (packaged vs capillary)

→ No IS used

House Method

→ Different instruments (QQQ vs FID/DAD)

CONCLUSION

- ▶ The outcome of the ITPT PPP2018 and PPP2019 is satisfactory.
- ▶ The performance of the laboratories expressed in terms of modified z-score were satisfactory by almost all participants for all substances.
- ▶ Outlier were obtained for Methomyl (2 laboratories); Amisulbron (3 laboratories); Dimethomorph (1 laboratory); Pirimiphos methyl (1 laboratory); Propiconazole (2 laboratories). These laboratories should analyzed the reason of their results.

CONCLUSION



THANK YOU FOR ATTENTION

