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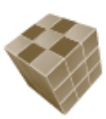

AMBIENTE
E SALUTE

ISTITUTO SUPERIORE DI SANITÀ

Results of the proficiency test on plant protection products in 2020

Angela Santilio, Chiara Pompili,
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Dipartimento Ambiente e Salute

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2020, v, 46 p. Rapporti ISTISAN 20/15

In 2019, the third Proficiency Test (PT) on plant protection products available on the Italian market was organized. The aim of the trial was to find out the quantity of active ingredient on the different formulations of the plant protection products. Eight Italian laboratories and seventeen to worldwide laboratories, which routinely deal with pesticides, were invited to participate. Laboratories are not obligated to take part in the PT; by the way, all the participants sent their results. All laboratories obtained data with acceptable values of z-score within the limits, except for three of them which got higher than -3.5 z-score values for the active substances Azoxystrobin, two laboratories obtained values > +3,5 in the analysis of Epiconazole, two laboratories obtained values > +3,5 and value < 3,5 for Fludioxonil, for Metalaxyl-M and for Thiabendazole.

Key words: Proficiency test; Plant protection products; Azoxystrobin; Epoxiconazole; Fludioxonil; Metalaxyl-M; Pyraclostrobin; Thiabendazole

Istituto Superiore di Sanità
Risultati dell'esercizio interlaboratorio sui prodotti fitosanitari nel 2020.
Angela Santilio, Chiara Pompili, Roberto Cammarata, Arianna Giambenedetti
2020, v, 46 p. Rapporti ISTISAN 20/15 (in inglese)

Nel 2019 è stato organizzato il terzo esercizio interlaboratorio su prodotti fitosanitari disponibili sul mercato nazionale. L'esercizio riguardava la determinazione del contenuto di principio attivo presente in prodotti fitosanitari di diversa formulazione. Sono stati invitati a partecipare 8 laboratori italiani preposti al controllo dei prodotti fitosanitari e 17 laboratori mondiali interessati ai controlli sui prodotti fitosanitari. La partecipazione è su base volontaria e hanno aderito tutti i partecipanti. Tutti i laboratori hanno ottenuto risultati con valori di z-score entro i limiti definiti ad eccezione di 3 laboratori che hanno ottenuto valori di z-score > -3,5 per la sostanza Azoxystrobin, 2 laboratori hanno ottenuto un valore > +3,5 nell'analisi dell'Epoxiconazole, 2 laboratori hanno ottenuto un valore > +3,5 e uno < di 3,5 per il Fludioxonil, per il Metalaxyl-M e per il Thiabendazole.

Parole chiave: Esercizio interlaboratorio; Prodotti fitosanitari; Azoxystrobin; Epoxiconazole; Fludioxonil; Metalaxyl-M; Pyraclostrobin; Thiabendazole

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ABBREVIATIONS

AFSCA	Agence Fédérale pour la Sécurité de la Chaîne Alimentaire (Federal Agency for the Safety of the Food Chain)
AAPCO	Association of American Pesticide Control Officials
CAS	Chemical Abstract Service
CIPAC	Collaborative International Pesticide Analytical Council
CV	Coefficient of Variation
GC	Gas Chromatography
GR	Granules
ISO	International Organization for Standardization
ITPT	Italian Proficiency Test
LC	Liquid Chromatography
MAD	Median absolute deviation
MS	Mass Spectrometry
N/A	Not Available
PDA	PhotoDiode Array
PPP	Plant Protection Product
PPP01	Plant Protection Product number 1
PPP02	Plant Protection Product number 2
PPP03	Plant Protection Product number 3
PPP04	Plant Protection Product number 4
PT	Proficiency Test
SD	Standard Deviation
SE	Suspo-Emulsion
SL	Soluble Concentrate
UV	UltraViolet
VWD	Variable Wavelength Detector
z-score	Standard Score

Symbols

σ_P	standard deviation for proficiency test
T-test	statistic test of Student's t distribution

PREFACE

The European legislation – Regulation (EC) 1107/2009 – on Plant Protection Products (PPPs) regulates the authorisation, placing on the market, use and control of PPPs and of any active substance, safener, synergist, co-formulant and adjuvant, which they might contain or of which they might consist of. The objective of those rules is to ensure a high level of protection of both human and animal health and of the environment through evaluation of the risks posed by PPPs, while improving the functioning of the Union market through harmonisation of the rules for their placing on the market and improving agricultural production.

In addition, the Regulation (EU) 2017/625 establishes a harmonised European Union framework for the organisation of official controls and official activities taking into account the rules on official controls laid down in Regulation (EC) 882/2004 and in relevant sectoral legislation, and the experience gained from the application of those rules.

The laboratories designated by the competent authorities to perform analyses on PPP samples taken in the context of official controls should possess the expertise, equipment, infrastructure and staff to carry out such tasks to the highest standards. To ensure sound and reliable results, those laboratories should be accredited for the use of these methods according to standard EN ISO/IEC 17025.

One of the instruments to reach a high-quality standard and performance is the participation in the interlaboratory test (Proficiency Test, PT) to demonstrate that the analytical data obtained from laboratories are reliable.

In the area of PPPs there are two organizations that plan PTs:

- Association of American Pesticide Control Officials (AAPCO)
  International organization that schedules PT on the active ingredient content on PPP on the basis of the American monitoring programmes.
- Agence Fédérale pour la Sécurité de la Chaîne Alimentaire (AFSCA)
  European organization that plans PT on physical chemical properties for PPPs.

For this reason, it is important to organize PTs for the active ingredient content for the national official laboratories. This activity was planned in the framework of the collaboration with Ministry of Health and the Istituto Superiore di Sanità (ISS, the National Institute of Health in Italy). As the national monitoring programs are in comply with the European monitoring programs, it is useful to enlarge the invitation to European Member State laboratories that work on these issues. In addition, two laboratories from Argentina and Brazil joined.

INTRODUCTION

In January 2020, all relevant Italian laboratories, 15 European Member State laboratories and 2 laboratories from Argentina and Brazil were invited to participate in the 3rd Italian PT on PPPs (later indicated as ITPT2020).

The announcement letter (Appendix A) sent to the laboratories on 15th January, according to the calendar the laboratories was asked to forward the invitation. The invitation was sent to 8 Italian laboratories, 15 European Member State laboratories and 2 laboratories from Argentina and Brazil.

For the PT four different commercial products containing six active ingredients (Azoxystrobin 1.33%, Epoxiconazole 6.02%, Fludioxonil 3.32%, Metalaxyl-M 2.57%, Pyraclostrobin 8.17%, and Thiabendazole 26.55%) were shipped to the laboratories.

1. PROFICIENCY TEST ON PLANT PROTECTION PRODUCTS

1.1. Test materials

The test materials of the ITPT2020 consisted of four PPPs obtained from manufacturer and available from Italian market.

The product types are: Soluble Concentrate (SL) and Suspo-Emulsion (SE) at a declared concentration reported in Table 1.

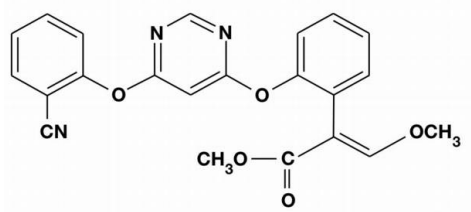
Table 1. Test materials of ITPT2020

Check Sample N.	Product description	Active ingredient	Declared level %
PPP01	Soluble Concentrate	Azoxystrobin	1.33
PPP02	Suspo-Emulsion	Epoxiconazole	6.02
PPP03	Soluble Concentrate	Fludioxonil	3.32
PPP04	Soluble Concentrate	Metalaxyl-M	2.57
PPP05	Suspo-Emulsion	Pyraclostrobin	8.17
PPP06	Soluble Concentrate	Thiabendazole	26.55

For the preparation of the subsamples to send each laboratory, the PPPs were mixed mechanically and shared in 25 samples for a total of 50 plastic containers sealed and stored at ambient temperature before the shipment to the participants. Each laboratory received two samples. Nothing was added to our samples.

1.2. Description of the active substances in the PPPs

1.2.1. Azoxystrobin



Common name

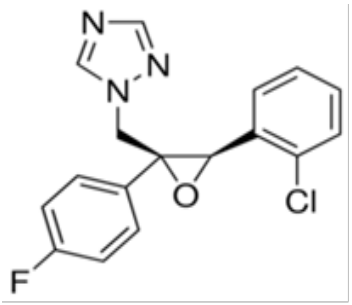
Methyl (2E)-2-{2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate

Structure formula $C_{22}H_{17}N_3O_5$

CAS number 131860-33-8

Azoxystrobin has a molecular weight of 403.388 g/mol. It has moderate solubility in water, formulations aid its use in water sprays by creating an emulsion when diluted; is compatible with many others pesticides and adjuvants when mixed. It belongs to the class of QoI (Quinone outside Inhibitors) Fungicides. It is often used on more than 50 crops and in the year 2000 it was announced that it had been granted UK Millennium product status.

1.2.2. Epoxiconazole



Common name

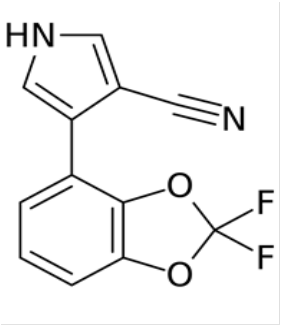
(2RS,3SR)-1-[3-(2-chlorophenyl)-2,3-epoxy-2-(4-fluorophenyl)propyl]-1H-1,2,4-triazole

Structure formula $C_{17}H_{13}ClFN_3O$

CAS number 135319-73-2

Epoxiconazole is a fungicide from the class of the azoles developed to protect corps with the inhibition of the metabolism of fungi cells preventing the growth of the mycelia (fungal cells) and limiting the production of conidia (mitospores). It has a molecular weight of 329.76 g/mol. Epoxiconazole is used on many crops like cereals, soybeans, banana, rice, coffee.

1.2.3. Fludioxonil



Common name

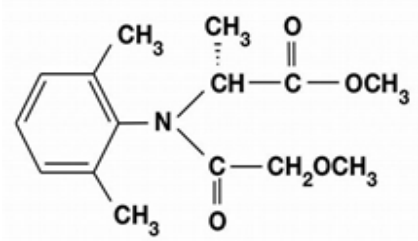
4-(2,2-Difluoro-1,3-benzodioxol-4-yl)-1H-pyrrole-3-Carbonitrile

Structure formula $C_{12}H_6F_2O_2N_2$

CAS number 131341-86-1

Fludioxonil is a non-systemic fungicide, used for the treatment of crops like cereals, fruit and vegetables in combination with another fungicide. Its mode of action is to inhibit transport-associated phosphorylation of glucose which reduces mycelia growth rate. It is toxic to fish and other aquatic organisms. It has a molecular weight of 248.189 g/mol.

1.2.4. Metalaxyl-M



Common name

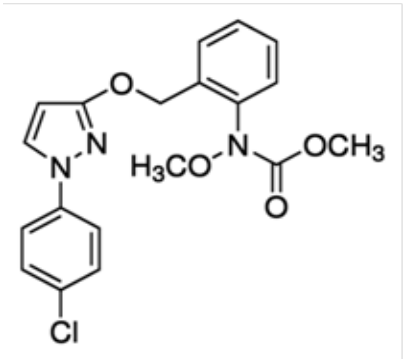
Methyl 2-[(2,6-dimethylphenyl) (methoxyacetyl)amino]propanoate

Structure formula $C_{15}H_{21}NO_4$

CAS number **57837-19-1**

Metalaxyl-M is an acylalanine fungicide with a systemic function. Metalaxyl-M is the name for the optically pure (-)/ D/ R active stereoisomer which is also known as Mefenoxam. It has a molecular weight of 279.33 g/mol. Metalaxyl-M is used agriculturally as a systemic fungicide on fruits like oranges or apples and potatoes.

1.2.5. Pyraclostrobin



Common name

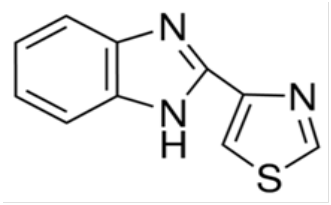
Methyl {2-[1-(4-chlorophenyl)-1H-pyrazol-3-yloxymethyl]phenyl}methoxycarbamate

Structure formula $C_{19}H_{18}ClN_3O_4$

CAS number 175013-18-0

Pyraclostrobin is a fungicide belonging to the group which is collectively known as strobilurins, which inhibit mitochondrial respiration. It has a molecular weight of 387.82 g/mol and it is largely used on grapes and potatoes.

1.2.6. Thiabendazole



Common name

2-(4-thiazolyl)-1H-benzimidazole

Structure formula $C_{10}H_7N_3S$

CAS number 148-79-8

Thiabendazole is a preservative, an anti-fungal agent and an anti-parasitic agent. It is used primarily to control mold, blight, and other fungal diseases in fruits and vegetables. It is also used as a food additive, a preservative with E number E233 (INS number 233). For example, it is applied to bananas to ensure freshness, and is a common ingredient in the waxes applied to the skins of citrus fruits. It has a molecular weight of 201.25 g/mol.

1.3. Homogeneity and stability test

Homogeneity and stability tests were performed according to the ISO 13528:2015(E) - Annex B and the International Harmonized Protocol.

1.3.1. Homogeneity

Regarding the homogeneity test, ten bottles were randomly chosen and analysed in duplicate, in two different days.

Considering that the σ_{PT} is unknown, the statistically significant differences between PT items used was evaluated with the analysis of variance T-test at α=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 homogeneous.

The results are shows in the Table 2 for all compounds.

Table 2. Homogeneity results of the PT samples

Sample ID	Azoxystrobin		Epoxiconazole		Fludioxonil		Metalaxyl-M		Pyrachlostrobin		Thiabendazole	
	a	b	a	b	a	b	a	b	a	b	a	b
#1	1.32	1.34	6.04	6.07	3.34	3.08	2.32	2.41	8.42	8.35	27.60	27.40
#2	1.31	1.27	5.97	5.96	3.30	3.35	2.44	2.41	8.39	8.34	27.48	27.35
#3	1.25	1.30	6.05	6.11	3.28	3.23	2.36	2.57	8.33	8.33	27.51	26.57
#4	1.23	1.25	5.98	6.04	3.34	3.45	2.51	2.49	8.34	8.38	27.33	27.46
#5	1.29	1.25	6.08	5.93	3.47	3.22	2.57	2.41	8.43	8.45	27.42	25.95
#6	1.25	1.22	6.09	6.03	3.39	3.03	2.48	2.41	8.35	8.36	26.26	26.00
#7	1.26	1.27	6.01	5.96	3.33	3.44	2.69	2.51	8.32	8.39	25.68	25.67
#8	1.32	1.27	5.88	5.91	3.40	3.28	2.38	2.60	8.41	8.45	25.71	25.66
#9	1.28	1.20	6.01	5.96	3.37	3.27	2.55	2.57	8.39	8.46	26.03	25.79
#10	1.27	1.25	5.96	5.98	3.44	3.39	2.52	2.54	8.34	8.42	25.87	26.12
Mean	1.27		6.00		3.32		2.49		8.38		26.54	
SD	0.04		0.06		0.12		0.09		0.05		0.79	
t**	1.09		0.43		1.92		0.21		1.01		0.83	
P***	0.29		0.64		0.07		0.83		0.33		0.42	
Homogeneity	YES		YES		YES		YES		YES		YES	

a, b: replicates of the same sample
t**: T of Student Test
P***: significativity level;
SD: Standard Deviation

1.3.2. Stability

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

- *Day 1*: before the shipment of the samples in January 2020;
- *Day 2*: at the deadline for reporting results in May 2020.

Stability test was judged acceptable as the percentage difference of concentration, for each active substance was found less than 10%. As presented in Table 3, there was a slight decrease in the pesticide concentration of Metalaxyl-M showed during the PT, but still acceptable.

Table 3. Summary of stability data (ITPT2020)

Active Ingredient	Analysis January	Analysis May	Declared Level %
Azoxystrobin	1.26	1.32	1.33
Epoxiconazole	6.15	5.98	6.02
Fludioxonil	3.48	3.21	3.32
Metalaxyl-M	2.74	2.63	2.57
Pyraclostrobin	8.22	8.48	8.17
Thiabendazole	26.08	26.61	26.55

Tables 4, 5, 6, 7, 8 and 9 show the individual results for each substance. The deviation calculated with reference to the 1st analysis and to the declared label shows a deviation less than 10% for all substances. The products are stable.

Table 4. AZOXYSTROBIN: results of stability test (ITPT2020)

Parameter	January				May			
	Replicate 1		Replicate 2		Replicate 1		Replicate 2	
	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2
Sample 1	1.27	1.27	1.24	1.2	1.26	1.50	1.35	1.27
Sample 2	1.37	1.36	1.25	1.21	1.18	1.25	1.29	1.34
Mean	1.31		1.21		1.29		1.34	
SD	0.06		0.02		0.14		0.04	
Mean of 2 days	1.26				1.32			
Standard Deviation of 2 days	0.02				0.07			
Deviation (ref 1st Analysis %)/ [(M2-M1)/M1]*100	4.35							
Deviation (ref to declared label %)/ [(SM-1.33)/1.33]*100	-2.91							
Stability Mean	1.29		Declared Label		1.33			
Stability Standard Deviation	0.03		CV %		2.70			

Table 5. EPOXICONAZOLE: results of stability test (ITPT2020)

Parameter	January				May			
	Replicate 1		Replicate 2		Replicate 1		Replicate 2	
	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2
Sample 1	6.03	6.04	6.07	5.99	5.99	6.03	6	5.82
Sample 2	6.02	6.18	6.18	6.24	6.08	6.02	6.02	5.92
Mean	6.07		6.24		6.03		5.92	
SD	0.08		0.11		0.04		0.09	
Mean of 2 days	6.15				5.98			
Standard Deviation of 2 days	0.03				0.04			
Deviation (ref 1st Analysis %)/ [(M2-M1)/M1]*100	-2.90							
Deviation (ref to declared label %)/ [(SM-6.02)/6.02]*100	0.74							
Stability Mean	6.06		Declared Label		6.02			
Stability Standard Deviation	0.01		CV %		0.14			

Table 6. FLUDIOXONIL: results of stability test (ITPT2020)

Parameter	January				May			
	Replicate 1		Replicate 2		Replicate 1		Replicate 2	
	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2
Sample 1	3.28	3.4	3.36	3.31	2.99	3.62	3.24	3.18
Sample 2	3.63	3.61	3.39	3.47	3.29	3.5	3.02	3.06
Mean	3.48		3.47		3.35		3.06	
SD	0.17		0.07		0.28		0.10	
Mean of 2 days	3.48				3.21			
Standard Deviation of 2 days	0.07				0.12			
Deviation (ref 1st Analysis %)/ [(M2-M1)/M1]*100	-7.77							
Deviation (ref to declared label %)/ [(SM-3.32)/3.32]*100	0.60							
Stability Mean	3.34		Declared Label		3.32			
Stability Standard Deviation	0.04		CV %		1.07			

Table 7. METALAXYL-M: results of stability test (ITPT2020)

Parameter	January				May			
	Replicate 1		Replicate 2		Replicate 1		Replicate 2	
	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2
Sample 1	2.77	2.73	2.63	2.67	2.74	2.64	2.84	2.82
Sample 2	2.58	2.68	2.71	2.79	2.59	--	2.63	2.61
Mean	2.69		2.79		2.66		2.61	
SD	0.08		0.07		0.08		0.12	
Mean of 2 days	2.74				2.63			
Standard Deviation of 2 days	0.01				0.03			
Deviation (ref 1st Analysis %)/ [(M2-M1)/M1]*100	-3.89							
Deviation (ref to declared label %)/ [(SM-2.57)/2.57]*100	4.54							
Stability Mean	2.69		Declared Label		2.57			
Stability Standard Deviation	0.02		CV %		0.59			

Table 8. PYRACLOSTROBIN: results of stability test (ITPT2020)

Parameter	January				May			
	Replicate 1		Replicate 2		Replicate 1		Replicate 2	
	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2
Sample 1	8.31	8.33	8.2	8.14	8.42	8.4	8.61	8.57
Sample 2	8.18	8.13	8.23	8.20	8.34	8.33	8.57	8.58
Mean	8.24		8.2		8.37		8.58	
SD	0.10		0.04		0.04		0.02	
Mean of 2 days	8.22				8.48			
Standard Deviation of 2 days	0.04				0.02			
Deviation (ref 1st Analysis %)/ [(M2-M1)/M1]*100	3.13							
Deviation (ref to declared label %)/ [(SM-8.17)/8.17]*100	2.17							
Stability Mean	8.35		Declared Label		8.17			
Stability Standard Deviation	0.02		CV %		0.21			

Table 9. THIABENDAZOLE: results of stability test (ITPT2020)

Parameter	January				May			
	Replicate 1		Replicate 2		Replicate 1		Replicate 2	
	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2	inj 1	inj 2
Sample 1	26.25	26.09	26.15	26.12	26.25	26.11	26.93	26.5
Sample 2	25.91	25.96	26.06	26.11	26.21	25.32	27.22	27.24
Mean	26.05		26.11		25.97		27.24	
SD	0.15		0.04		0.44		0.35	
Mean of 2 days	26.08				26.61			
Standard Deviation of 2 days	0.08				0.07			
Deviation (ref 1st Analysis %)/ [(M2-M1)/M1]*100	2.01							
Deviation (ref to declared label %)/ [(SM-26.55)/26.55]*100	-0.78							
Stability Mean	26.34			Declared Label		26.55		
Stability Standard Deviation	0.01			CV %		0.04		

1.4. Distribution of the samples and instructions for the participants

Two plastic transparent containers with red cup were filled (one with SL and SE products). Each sample was shipped to the participating laboratories at ambient temperature. An information message was sent out by e-mail during shipment so that laboratories make their own arrangements for the reception of the package, and a protocol was sent by e-mail.

The participants (Appendix B) were asked:

- to inform on the safe recipient of the samples in their laboratories;
- to report results in the appropriate form and send them to the organizer by e-mail along with the details of methodology used.

The samples were sent to the participant on 15th January 2020.

The deadline for results was 30th of June 2020.

The final report was dispatched to all participant at the end of July 2020.

1.5. Statistical evaluation of results

This PT has been evaluated using the modified z-score parameter to rate the laboratory performance for each active substance according to AAPCO protocol.

The outliers were calculated using the modified z-score.

1.5.1. Robust mean

The purpose of using a robust estimator for the mean was to cope with the possibility of outlying data points without having to remove them from the sample.

The robust mean estimator used was the median.

1.5.2. Robust estimate of standard deviation

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:

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

Calculate MAD_E:

$$MAD_E = K \times MAD$$

For normally distributed data, K= 1.483:

$$MAD_E = 1.483 \times MAD$$

1.5.3. Calculation of modified z-scores

Modified z-scores (Zi) for each laboratory were calculated as:

$$Zi = 0.6745 \times {}^{(Xi - median)} / MAD$$

Z values falling outside the range of $-3.5 \leq Zi \leq 3.5$ were marked as outliers.

1.5.4. Presentation of data

Data is presented graphically in two ways:

– a scatter plot showing each participating laboratory's two-day mean value for each analyte along with the associated standard deviation. These plots also show the upper and lower Horwitz (Thompson) limits for the sample, as well as median ±2 MAD_E.
– a plot of modified z-scores.

2. ANALYSIS OF THE SUBSTANCES

Description and statistical evaluation of the results are presented for each compound separately. This year we decide to not apply Horwitz theorem, because the active substances concentrations are high enough to make it unnecessary.

2.1. Azoxystrobin

Regarding the active substance Azoxystrobin, 25 boxes were sent all over the world, in particular 8 to Italian laboratories and 17 to worldwide laboratories outside Italy. We received 21 participation results; the four laboratories missing are all from Italy. Eleven of the laboratories used for the analysis an LC instrument and the other ten the GC: 10 of them with a UV Detector, 9 with an FID Detector and 2 with a MS Detector. It is interesting to note that almost all of the laboratories choose to use an in-house method and just a few of them a CIPAC (Collaborative International Pesticide Analytical Council) method and just two applied a manufacturer's method, as shown in Table 10. At the same time, all the methods gave appreciable data.

Table 10. AZOXYSTROBIN: methods applied for analysis (ITPT2020)

Laboratories	In-house	CIPAC	Manufacturer's
Number	16	3	2

On the collected data it was applied a statistical evaluation based on a robust estimator (median) instead the mean. The purpose of this choice was to cope the possibility of outlying data points without having to remove them, so it was used the median and the standard deviation.

Figure 1 shows the lab's values of modified z-score.

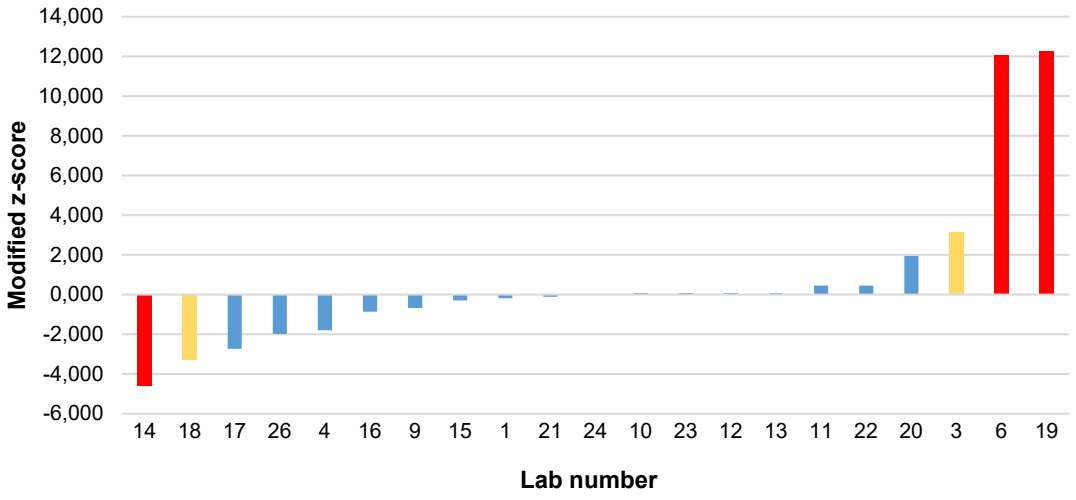


Figure 1. AZOXYSTROBIN: modified z-scores (ITPT2020)

The results obtained are laudable data, in fact most of them are inside the modified z-score range of $-3.5 \leq Z \leq +3.5$, three of them are outliers so outside the range of the modified z-score and two are in a "border line zone" so questionable but still an acceptable value.

One laboratory obtained an excellent value of modified z-score of 0.

2.2. Epoxiconazole

For the active substance Epoxiconazole, 25 boxes were sent all over the world, in particular 8 to Italian Laboratories and 17 to worldwide laboratories outside Italy. We received 19 participation results. Fourteen laboratories used for the analysis an LC instrument and the other 5 the GC: 13 of them with a UV Detector, 5 with an FID Detector and 1 with a MS Detector. To carry out this analysis 15 laboratories applied an in-house method, 3 the CIPAC method and just one used the manufacturer's method, as shown in Table 11. At the same time, both the methods gave appreciable data, except for two laboratories who gave unacceptable values, as Figure 2 shows.

Table 11. EPOXICONAZOLE: methods applied for analysis (ITPT2019)

Laboratories	In-house	CIPAC	Manufacturer's
Number	15	3	1

As for the Azoxystrobin, on the collected data it was applied a statistical evaluation based on a robust estimator instead the mean. The purpose of this choose was to cope the possibility of outlying data points without having to remove them, so it was used the median and the standard deviation. Figure 2 shows the lab's values of modified z-score.

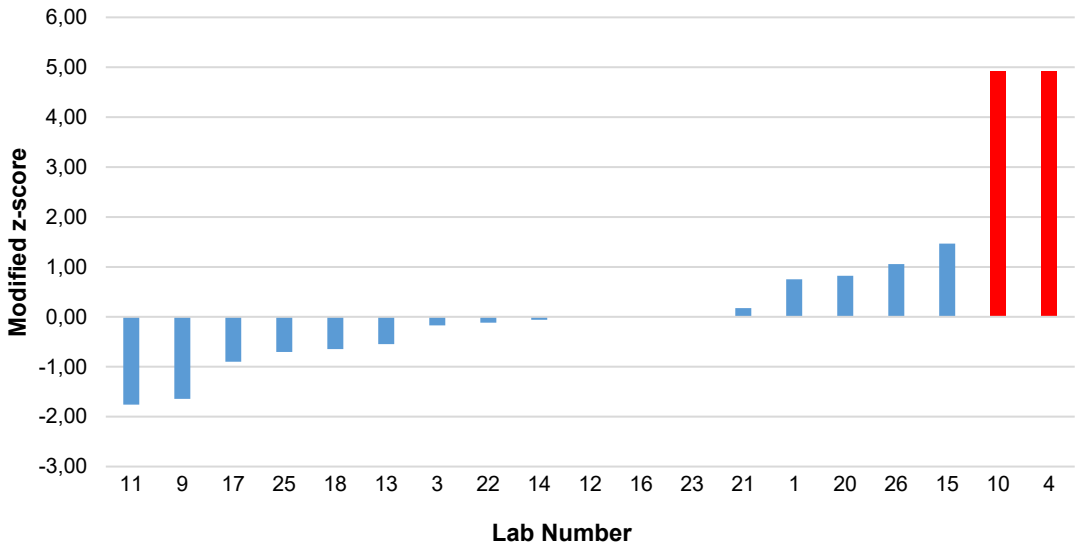


Figure 2. EPOXICONAZOLE: modified z-scores (ITPT2020)

The results obtained are valuable data, in fact most of them are inside the z-score range of $-3.5 \leq Z \leq +3.5$ and two of them are completely unacceptable in in the positive zone and one is questionable.

Three laboratories obtained the excellent value of modified z-score of 0.

2.3. Fludioxonil

Fludioxonil was the third active substance and, as the other two, 25 boxes were sent all over the world, in particular 8 to Italian laboratories and 17 to worldwide laboratories outside Italy. We received 20 participation results; 4 laboratories missing are from Italy and 1 is from outside Italy. The analysis was performed using LC instrument for 15 laboratories and the other 5 decide to use the GC: 14 of them with a UV Detector, 4 with FID Detector and 2 with a MS Detector. Some of the laboratories choose to use an in-house method, others a CIPAC method and few others applied a manufacturer's method, as shown in Table 12. At the same time, all the methods gave appreciable data.

Table 12. FLUDIOXONIL: methods applied for analysis (ITPT2020)

Laboratories	In-house	CIPAC	Manufacturer's
Number	18	0	2

As for the other two active substances mentioned before, on the collected data it was applied a statistical evaluation based on a robust estimator (median) instead the mean. The purpose of this choose was to cope the possibility of outlying data points without having to remove them, so it was used the median and the standard deviation.

Figure 3 shows the lab's values of modified z-score.

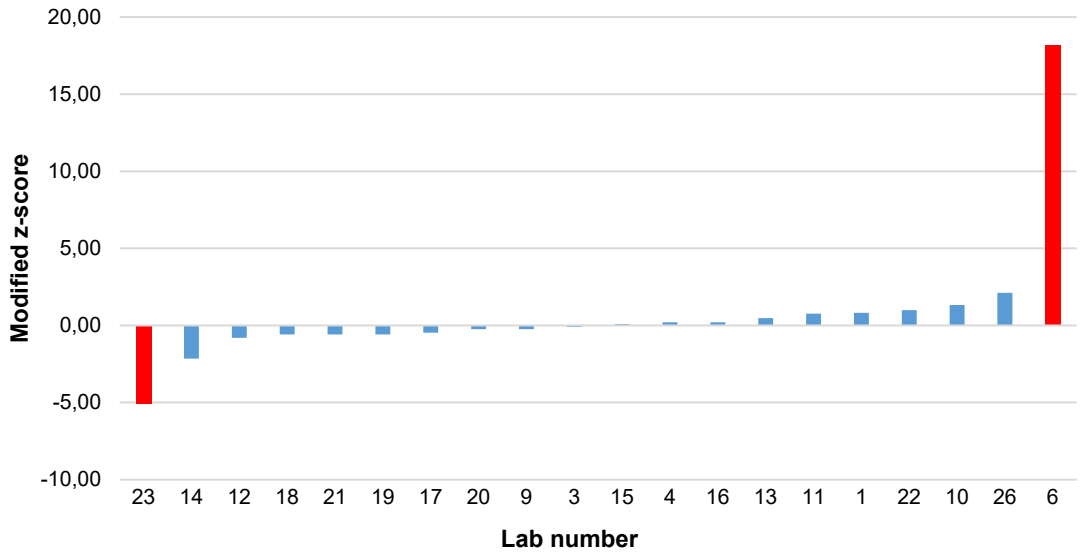


Figure 3. FLUDIOXONIL: modified z-scores (ITPT2020)

The results obtained are valuable data, in fact most of them are inside the z-score Range of -3.5 ≤ Z ≤ +3.5, two of them is completely unacceptable one in the positive zone and the other one on the negative zone.

Any of the laboratories obtained the excellent value of modified z-score of 0.

2.4. Metalaxyl-M

Metalaxyl-M was the fourth active substance and, as the other three mentioned before, 25 boxes were sent all over the world, in particular 8 to Italian laboratories and 17 to worldwide laboratories outside Italy. We received 20 participation results; 4 laboratories missing are from Italy and 1 is from outside Italy. The analysis was performed using LC instrument for 12 laboratories, 11 of them with a UV Detector and 1 with a MS Detector, 8 laboratories preferred to use GC-FID and 1 GC-MS.

Some of the laboratories choose to use an in-house method, others a CIPAC method and few others applied a manufacturer's method, as shown in Table 13. At the same time, all the methods gave appreciable data.

Table 13. METALAXYL-M: methods applied for analysis (ITPT2020)

Laboratories	In-house	CIPAC	Manufacturer's
Number	17	1	2

On the collected data it was applied a statistical evaluation based on a robust estimator (median) instead the mean. The purpose of this choose was to cope the possibility of outlying data points without having to remove them, so it was used the median and the standard deviation.

Figure 4 shows the lab's values of modified z-score.

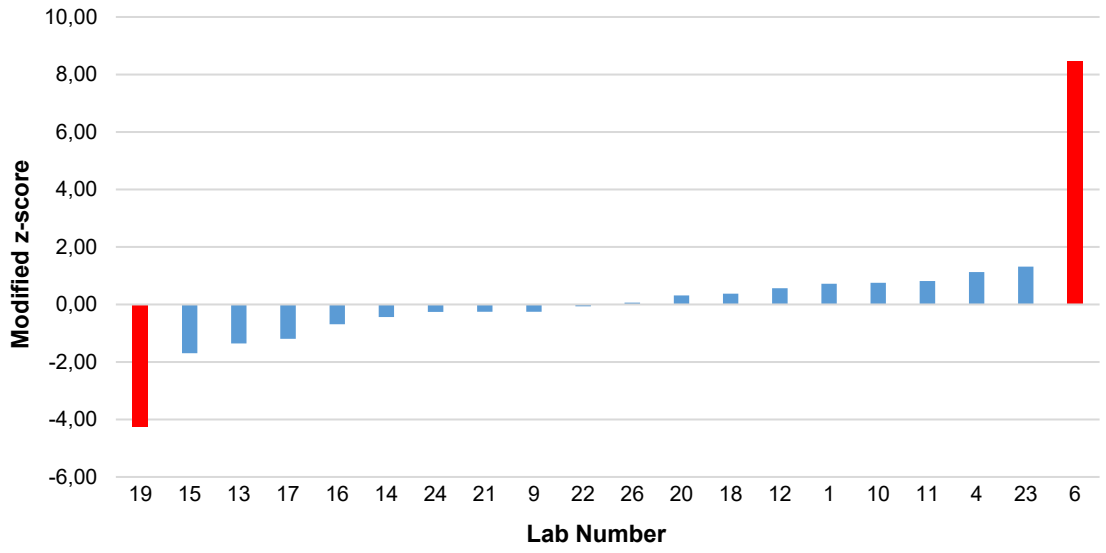


Figure 4. METALAXYL-M: modified z-scores (ITPT2020)

The results obtained are valuable data, in fact most of them are inside the z-score range of $-3.5 \leq Z \leq +3.5$, two of them are completely unacceptable one in the positive zone and the other one in the negative zone.

No laboratory obtained the excellent value of modified z-score of 0.

2.5. Pyraclostrobin

Pyraclostrobin was the fifth active substance and, as the other four mentioned before, 25 boxes were sent all over the world, in particular 8 to Italian laboratories and 17 to worldwide laboratories outside Italy. We received 21 participation results; 4 laboratories missing are all from Italy. All the analysis was performed using LC instrument: 20 of them with a UV Detector and 1 with a MS Detector. Some of the laboratories choose to use an In-house method, others a CIPAC method and few others applied a manufacturer's method, as shown in Table 14. At the same time, all the methods gave appreciable data.

Table 14. PYRACLOSTROBIN: methods applied for analysis (ITPT2020)

Laboratories	In-house	CIPAC	Manufacturer's
Number	16	4	1

On the collected data it was applied a statistical evaluation based on a robust estimator (median) instead the mean. The purpose of this choose was to cope the possibility of outlying data points without having to remove them, so it was used the median and the standard deviation.

Figure 5 shows the lab's values of modified z-score. The results obtained are valuable data, in fact most all of them are inside the z-score range of $-3.5 \leq Z \leq +3.5$, just two of them are in the questionable zone.

No laboratory obtained the excellent value of modified z-score of 0.

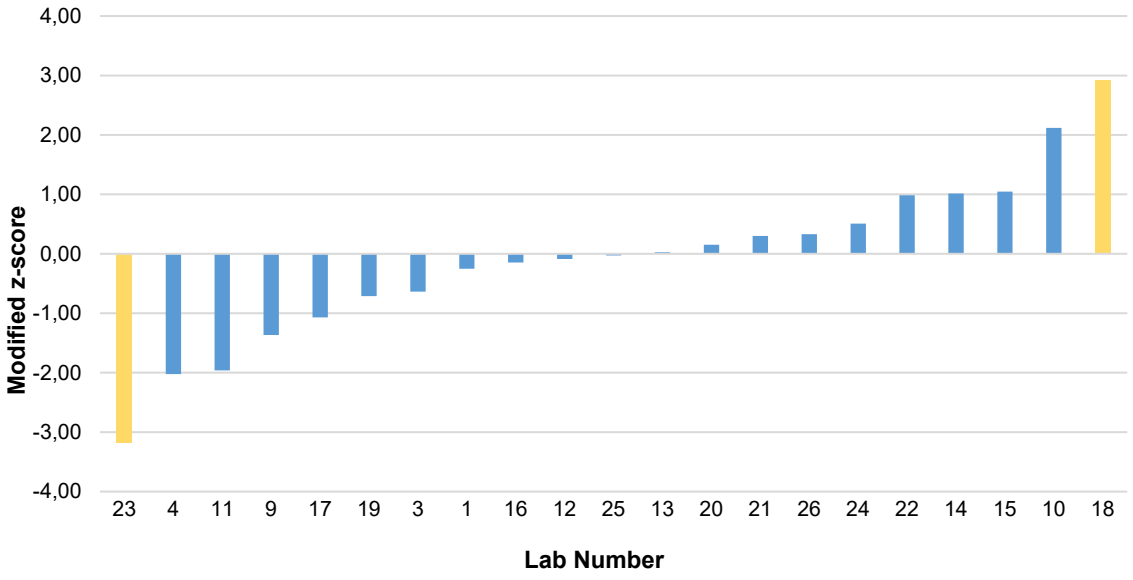


Figure 5. PYRACLOSTROBIN: modified z-scores (ITPT2020)

2.6. Thiabendazole

Thiabendazole was the sixth active substance, 25 boxes were sent all over the world, in particular 8 to Italian laboratories and 17 to worldwide laboratories outside Italy. We received 17 participation results; 4 laboratories missing are all from Italy and 4 Laboratories missing all from Worldwide. Sixteen laboratories used for the analysis an LC instrument: 15 of them with a UV Detector and 1 with a MS Detector. Just one lab used the GC-FID.

To carry out this analysis 9 laboratories applied an in-house method, 7 the CIPAC method and just one used the manufacture's method, as shown in Table 15. At the same time, both the methods gave appreciable data, except for two laboratories, which gave unacceptable values, as Figure 6 shows.

Table 15. Thiabendazole: methods applied for analysis (ITPT2020)

Laboratories	In-house	CIPAC	Manufacturer's
Number	9	7	1

On the collected data it was applied a statistical evaluation based on a robust estimator (median) instead the mean. The purpose of this choose was to cope the possibility of outlying data points without having to remove them, so it was used the median and the standard deviation.

Figure 6 shows the lab's values of modified z-score. The results obtained are valuable data, in fact most all of them are inside the z-score range of $-3.5 \leq Z \leq +3.5$, and two of them are completely unacceptable one in the positive zone and one in the negative zone. One laboratory obtained the excellent value of modified z-score of 0.

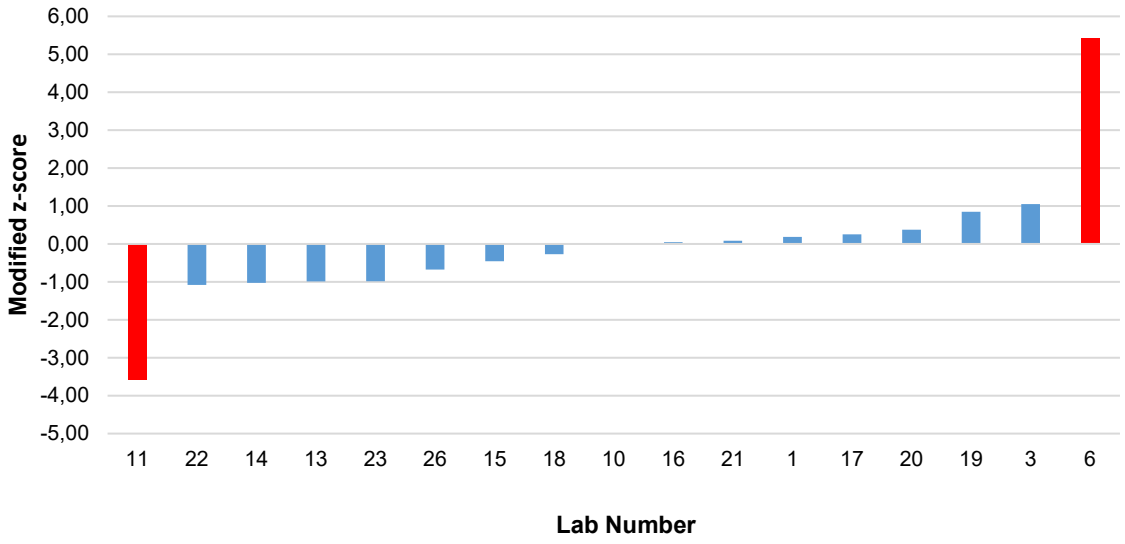


Figure 6. THIABENDAZOLE: modified z-scores (ITPT2020)

3. RESULTS

The outcome of the ITPT2020 can be considered satisfactory due to the third PT organized by Italy.

The participation of the Italian and worldwide laboratories was good. For Italy, 8 laboratories participated distributed as 5 from the North, 1 from Centre and 2 from South of the Country. Due to the virus situation, 4 laboratories could not take part to our activity. The European laboratories were 15, excluding Italy, distributed as one of the South, 10 of the Centre and 4 of the North of Europe.

The performance of the laboratories expressed in terms of modified z-score was satisfactory by almost all participants for all substances. For each active substance there are outlier values, and the analysis of Azoxystrobin was the most critical while Pyraclostrobin was the most successful.

Almost all of the laboratories preferred to use an in-house method, inspired from the CIPAC and adapted to their lab conditions so with some modification, for example, without using the internal standard.

Based on the results it can be concluded that the PT was successfully organized and we are very glad to say a satisfactory number of people took part with all the inconvenient of this year and we run out our third edition!

Tables 16, 17 and 18 summarize the participation per active ingredient and the results per active ingredient including and excluding the outliers.

For each active substance there were a percentage of failing results obtained with the modified z-score, as Table 16 shows.

Table 16. Summary of participation per active ingredient (ITPT2020)

Check sample n.	Product description	Active ingredient	Participants (n.)	Labs using GC (n.)	Labs using LC (n.)	Failing results[1](%)
PPP01	Soluble Concentrate	Azoxystrobin	21	10	11	0
PPP02	Suspo-Emulsion	Epoxiconazole	19	5	14	10.52
PPP03	Soluble Concentrate	Fludioxonil	20	5	15	10
PPP04	Soluble Concentrate	Metalaxyl-M	20	8	12	10
PPP05	Suspo-Emulsion	Pyraclostrobin	21	0	21	0
PPP06	Soluble Concentrate	Thiabendazole	17	1	16	11.76

[1] Where failing indicates a mean assay result outside the modified z-score defined acceptable limits.

Table 17. Summary of lab results per active ingredient, including outliers (ITPT2020)

Check sample n.	Analyte (Label claim)	Minimum result	Maximum result	Grand Average	Grand %CV
PPP01	Azoxystrobin 1.33%	1.19	1.67	1.35	8.47
PPP02	Epoxiconazole 6.02%	5.79	6.63	6.04	2.73
PPP03	Fludioxonil 3.32%	3.1	4.32	3.37	6.14
PPP04	Metalaxyl-M 2.57%	2.3	3.39	2.71	0.15
PPP05	Pyraclostrobin 8.17%	7.41	8.7	8.14	3.21
PPP06	Thiabendazole 26.55%	24.2	30.2	26.63	4.16

Table 18. Summary of lab results per active ingredient, excluding outliers

Check sample n.	Analyte (Label claim)	N. of outliers[1]	Average excluding outliers	%CV excluding outliers
PPP01	Azoxystrobin 1.33%	0	1.35	8.47
PPP02	Epoxiconazole 6.02%	2	5.99	1.24
PPP03	Fludioxonil 3.32%	2	3.34	2.45
PPP04	Metalaxyl-M 2.57%	2	2.69	2.91
PPP05	Pyraclostrobin 8.17%	0	8.15	2.87
PPP06	Thiabendazole 26.55%	2	26.47	1.83

[1] An outlier is flagged when the modified z-score falls outside the range of -3.5 ≤ Zi ≤ 3.5; see Appendix for calculations.

The performance of the laboratories expressed in terms of modified z-score was satisfactory by almost all participants for all substances. For each active substance there are outlier values, and the analysis of Azoxystrobin was the most critical while Pyraclostrobin was the most successful. Almost all of the laboratories used in-house methods, inspired from the CIPAC and adapted to their laboratories' conditions so with some modification, for example, without using the internal standard. Based on the results it can be concluded that the PT was successfully organized. Despite the coronavirus pandemic that occurred during the PT ì, the number of participants was satisfactory in order to conclude the third edition of the PT.

Details of the z-score values for each laboratory are given in Tables 19, 20, 21, 22, 23 and 24 with the analytical technique used for each substance.

Table 19. AZOXYSTROBIN Sample PPP01: summary results (ITPT2020)

ID Lab	Analytical technique	Two day average[1]	RPD[1]	Modified z- score[2]	Outlier[2]
1	GC-MS	1.32	3.93	-0.19	no
3	HPLC-PDA	1.41	3.97	3.15	no
4	HPLC-MS/MS QQQ	1.28	1.56	-1.80	no
6	HPLC-DAD	1.65	1.21	12.07	no
9	HPLC-UV	1.31	-1.53	-0.68	no
10	GC-FID	1.33	0	0.08	no
11	HPLC-DAD	1.34	-5.97	0.45	no
12	HPLC-DAD	1.33	-1.5	0.08	no
13	HPLC-DAD	1.33	-1.5	0.08	no
14	HPLC-UVD	1.21	-2.49	-4.61	no
15	GC-FID	1.32	-7.58	-3.30	no
16	GC-FID	1.31	2.30	-0.86	no
17	HPLC-UV	1.26	2.39	-2.74	no
18	GC-FID	1.24	1.61	-3.30	no
19	HPLC-UV	1.66	1.81	12.25	no
20	GC-FID	1.38	-2.90	1.95	no
21	HPLC-VWD	1.33	-2.26	-0.11	no
22	GC-FID	1.34	5.97	0.45	no
23	GC-FID	1.33	1.50	0.08	no
24	GC-FID	1.33	3.61	0.00	no
26	GC-FID	1.28	-7.06	-1.99	no
Grand Average[3]	1.35				
Total SD	0.11				
Total Median[4]	1.33				
MAD	2.64				
MAD_E	3.91				

[1] Average yield and Relative Percent Difference between the two-day determinations per laboratory.
[2] An outlier is flagged when the modified z-score falls outside the range of -3.5 ≤ Zi ≤ 3.5; see Glossary.
[3] Grand average, standard deviation and median.
[4] Median Absolute Deviation Robust estimate of standard deviation; see Glossary for calculations.

Table 20. EPOXICONAZOLE Sample PPP02: summary results (ITPT2020)

ID Lab	Analytical technique	Two day average[1]	RPD[1]	Modified z-score[2]	Outlier[2]
1	HPLC-DAD	6.07	2.21	0.75	no
3	HPLC-PDA	5.99	-0.48	-0.17	no
4	HPLC-MS/MS	6.43	-1.40	4.93	yes
9	HPLC-UV	5.87	-1.88	-1.64	no
10	HPLC-DAD	6.43	-6.38	4.93	yes
11	HPLC-DAD	5.86	2.22	-1.76	no
12	HPLC-DAD	6.01	-2.16	0	no
13	GC-FID	5.96	-1.59	-0.55	no
14	HPLC-UV	6.00	-0.67	-0.06	no
15	GC-FID	6.13	0	1.47	no
16	HPLC-DAD	6.01	0.17	0	no
17	HPLC-DAD	5.93	-0.51	-0.90	no
18	GC-FID	5.95	-1.01	-0.65	no
20	HPLC-PDA	6.08	3.79	0.82	no
21	HPLC-VWD	6.02	0.66	0.18	no
22	UHPLC-DAD	6.00	-0.17	-0.12	no
23	GC-FID	6.01	-1.17	0	no
25	HPLC-DAD	5.95	-1.51	-0.70	no
26	GC-FID	6.1	0.82	1.06	no

Grand Average[3]	6.04
Total SD	0.16
Total Median[4]	6.01
MAD	0.01
MAD_E	0.09

[1] Average yield and Relative Percent Difference between the two-day determinations per laboratory.
[2] An outlier is flagged when the modified z-score falls outside the range of $-3.5 \leq Zi \leq 3.5$; see Glossary.
[3] Grand average, standard deviation and median.
[4] Median Absolute Deviation Robust estimate of standard deviation; see Glossary for calculations.

Table 21. FLUDIOXONIL sample PPP03: summary results (ITPT2020)

ID Lab	Analytical technique	Two day average[1]	RPD[1]	Modified z-score[2]	Outlier[2]
1	GC-MS	3.38	-8.00	0.82	no
3	HPLC-PDA	3.34	0.75	-0.10	no
4	HPLC-MS/MS	3.35	-11.34	0.21	no
6	HPLC-DAD	4.15	8.19	18.19	yes
9	HPLC-UV	3.33	1.20	-0.24	no
10	HPLC-DAD	3.4	-1.76	1.33	no
11	HPLC-DAD	3.38	-6.22	0.77	no
12	HPLC-DAD	3.31	-0.30	-0.80	no
13	HPLC-DAD	3.36	-0.48	0.48	no
14	HPLC-UV	3.25	-0.31	-2.15	no
15	GC-FID	3.35	8.67	0.10	no
16	HPLC-DAD	3.35	-0.60	0.21	no
17	HPLC-DAD	3.32	-0.60	-0.47	no
18	GC-FID	3.32	-0.90	-0.58	no
19	HPLC-UV	3.32	1.51	-0.58	no
20	GC-FID	3.33	1.20	-0.24	no
21	HPLC-VWD	3.32	0.30	-0.58	no
22	HPLC-DAD	3.39	0.30	0.99	no
23	HPLC-DAD	3.12	-0.96	-5.08	yes
26	GC-FID	3.44	-2.62	2.12	no

Grand Average[3]	3.37
Total SD	0.21
Total Median[4]	3.34
MAD	0.03
MAD_E	0

[1] Average yield and Relative Percent Difference between the two-day determinations per laboratory.
[2] An outlier is flagged when the modified z-score falls outside the range of $-3.5 \leq Zi \leq 3.5$; see Glossary.
[3] Grand average, standard deviation and median.
[4] Median Absolute Deviation Robust estimate of standard deviation; see Glossary for calculations.

Table 22. METALAXYL-M sample PPP04: summary results (ITPT2020)

ID Lab	Analytical technique	Two day average[1]	RPD[1]	Modified z-score[2]	Outlier[2]
1	GC-MS	2.75	3.53	0.72	no
4	HPLC-MS/MS	2.78	-2.88	1.13	no
6	HPLC-DAD	3.37	1.49	8.47	yes
9	HPLC-UV	2.67	0	-0.25	no
10	HPLC-DAD	2.75	-1.45	0.75	no
11	HPLC-DAD	2.76	-7.62	0.82	no
12	HPLC-DAD	2.74	0.37	0.56	no
13	HPLC-DAD	2.58	-2.25	-1.36	no
14	HPLC-UV	2.66	0.38	-0.44	no
15	GC-FID	2.56	1.96	-1.69	no
16	GC-FID	2.64	0.38	-0.69	no
17	HPLC-DAD	2.6	-1.93	-1.19	no
18	GC-FID	2.72	0	0.38	no
19	HPLC-UV	2.35	4.26	-4.27	yes
20	GC-FID	2.72	2.58	0.31	no
21	HPLC-VWD	2.67	0.75	-0.25	no
22	GC-FID	2.69	6.33	-0.06	no
23	GC-FID	2.8	-1.79	1.32	no
24	GC-FID	2.67	-0.41	-0.26	no
26	HPLC-DAD	2.7	0.37	0.06	no

Grand Average[3]	2.71
Total SD	0
Total Median[4]	2.69
MAD	0.05
MAD_E	0.08

[1] Average yield and Relative Percent Difference between the two-day determinations per laboratory.
[2] An outlier is flagged when the modified z-score falls outside the range of $-3.5 \leq Zi \leq 3.5$; see Glossary.
[3] Grand average, standard deviation and median.
[4] Median Absolute Deviation Robust estimate of standard deviation; see Glossary for calculations.

Table 23. PYRACLOSTROBIN sample PPP05: summary results (ITPT2020)

ID Lab	Analytical technique	Two day average[1]	RPD[1]	Modified z-score[2]	Outlier[2]
1	HPLC-DAD	8.12	2.79	-0.25	no
3	HPLC-PDA	8.06	1.95	-0.64	no
4	HPLC-MS/MS	7.83	-10.61	-2.02	no
9	HPLC-UV	7.94	-1.13	-1.37	no
10	HPLC-DAD	8.52	-0.47	2.12	no
11	HPLC-DAD	7.84	1.66	-1.96	no
12	HPLC-DAD	8.15	0	-0.09	no
13	HPLC-DAD	8.17	1.2	0.03	no
14	HPLC-UV	8.34	-2.76	1.02	no
15	HPLC-PDA	8.34	1.2	1.05	no
16	HPLC-DAD	8.14	-0.49	-0.15	no
17	HPLC-DAD	7.97	-0.50	-1.07	no
18	HPLC-DAD	8.66	-1.04	2.92	no
19	HPLC-UV	8.05	2.36	-0.71	no
20	HPLC-DAD	8.19	1.47	0.15	no
21	HPLC-VWD	8.22	1.10	0.30	no
22	HPLC-DAD	8.33	-1.92	0.99	no
23	HPLC-DAD	7.63	-3.93	-3.18	no
24	HPLC-UV	8.25	-100	0.51	no
25	HPLC-DAD	8.16	-0.98	-0.03	no
26	HPLC-DAD	8.22	-0.49	0.33	no

Grand Average[3]	8.14
Total SD	0.26
Total Median[4]	8.16
MAD	0.12
MAD_E	0.18

[1] Average yield and Relative Percent Difference between the two-day determinations per laboratory.
[2] An outlier is flagged when the modified z-score falls outside the range of $-3.5 \leq Zi \leq 3.5$; see Glossary.
[3] Grand average, standard deviation and median.
[4] Median Absolute Deviation Robust estimate of standard deviation; see Glossary for calculations.

Table 24. THIABENDAZOLE sample PPP06: summary results (ITPT2020)

ID Lab	Analytical technique	Two day average[1]	RPD[1]	Modified z-score[2]	Outlier[2]
1	HPLC-DAD	26.71	0.15	0.19	no
3	HPLC-MS/MS	27.29	0.11	1.05	no
6	HPLC-DAD	30.20	0	5.42	yes
10	HPLC-DAD	26.59	0.56	0	no
11	HPLC-DAD	24.20	-100	-3.57	yes
13	HPLC-DAD	25.93	-0.87	-0.99	no
14	HPLC-UV	25.90	-0.46	-1.03	no
15	HPLC-PDA	26.28	2.13	-0.46	no
16	HPLC-DAD	26.62	-0.19	0.04	no
17	HPLC-DAD	26.76	0.86	0.25	no
18	HPLC-DAD	26.41	-0.04	-0.27	no
19	HPLC-UV	27.15	-3.31	0.85	no
20	GC-FID	26.84	2.05	0.37	no
21	HPLC-VWD	26.64	-0.45	0.08	no
22	HPLC-DAD	25.87	1.82	-1.08	no
23	HPLC-DAD	25.93	0.31	-0.98	no
26	HPLC-DAD	26.14	0.65	-0.67	no

Grand Average[3]	26.63
Total SD	1.11
Total Median[4]	26.59
MAD	0.45
MAD_E	0.67

[1] Average yield and Relative Percent Difference between the two-day determinations per laboratory.
[2] An outlier is flagged when the modified z-score falls outside the range of $-3.5 \leq Zi \leq 3.5$; see Glossary.
[3] Grand average, standard deviation and median.
[4] Median Absolute Deviation Robust estimate of standard deviation; see Glossary for calculations.

Table 25, 26, 27, 28, 29 and 30 report the information on analytical methods used for each substance and each laboratory.

Table 25. AZOXYSTROBIN representative method for the determination (ITPT2020)

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
1	In-house method	N/A	Acetone	In contact for 24 hours	2 µL	Gradient	MS	Equity5, 30 m*0.25 mm*0.25 µm
3	In-house method	N/A	MetOH/Water 90:10	Dissolve sample in 5 mL of water, fill to mark with MetOH, diluted with MetOH and filtered with0.45	10µL	25°C	PDA	Synergy 4 µm Hydro-RP 80 A, 4 µm, 150 mm* 2mm
4	In-house method	Triphenyl-phosphate	Acetone	Sonicate for 10 min	10 µL	40°C	MS/MS QQQ	Ascentis Express RP-AMIDE 2.7 µm, 150 mm* 2.1 mm
6	In-house method	N/A	ACN	Sonicate for 15 min dilute and filter through 0.45 µm nylon	10 µL	35°C	DAD	Agilent Zorbax Eclipse XDB C8 5 µm, 150 mm*4.6 mm
9	In-house method	N/A	ACN	Sonicate for 5 min	2 µL	30°C	UV	Xterra RP18 150 mm* 2.1mm* 3.5 µm
10	CIPAC 571	3-(2-pyridyl)-5,6 diphenyl-1,2,4-traizine	Acetone	Ultrasonication 15 min, dilute and filter with 0.45 µm PTFE	1 µL	280°C	FID	CP Sil 8 CB-MS 30 m* 0.25 mm* 0.5 µm
11	In-house method	N/A	Water/THF (50:50 v/v)	Sonicate for 15 min, shake for homogenization	10 µL	35°C	DAD	Nucleodur C18 Gravity 5 µm* 250mm* 3 mm
12	In-house method	N/A	ACN	Dissolution in 50 mL ACN, 15 min sonication, filtration through 0.45 µm regenerated cellulose disk	2 µL	30°C	DAD	LiChrospher 100 RP18 5 µm* 250 mm* 4.0 mm
13	In-house method	N/A	ACN	Dilute the mg in 50 mL volumetric flasks with ACN	10 µL	35°C	DAD	Nucleodur C18 Gravity 5 µm* 150 mm* 4.6 mm
14	In-house method	N/A	ACN	Sonicate for 15 min	5 µL	Ambient	Dionex UVD 170S	Zorbax SB-C18 5 µm 4.6 mm* 250 mm
15	In-house method	N/A	Ethyl acetate	Weigh, sonicate approx. 10 min allow to cool to room temp, make up to volume, filter	0.2 µL	Gradient	FID	HP 5 MS 30 m* 0.25 mm* 0.25 µm

to be followed

continues

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
16	In-house method	N/A	Acetone	Sonicate for 5 min	1 µL	Gradient	FID	HP 5MS 30 m* 250 mm* 0.25 µm
17	In-house method	N/A	Water: MetOH 5/95	For sample dispersing with water, sonicated for 1 min, then fill with MetOH, filter on 0.2 µm nylon disk	1µL	40°C	DAD	Phenomenex Kinetex C18 2.6 µm* 100 mm* 4.6 mm
18	CIPAC 571	3-(2-pyridyl)- 5, 6 diphenyl-1,2,4-traizine	Acetone	Sonicate for 30 min	1µL	Gradient	FID	CP-Sil 13 CB 25 m* 0.32mm* 0.20 µm
19	In-house method	N/A	MetOH	N/A	1 µL	Ambient	UV	Spherisorb S5 ODS2 C18 5 µm* 250 mm* 4.6 mm
20	Manufacturer's method	Diphenyl phthalate	Acetone	Test sample/SI to solution, sonicate for 20 min, filter through 0.2 µm nylon disk	1µL	Gradient	FID	Agilent DB 5MS 30 m* 0.25 mm* 0.25 µm
21	In-house method	N/A	Acetonitrile	Sonication for 10 min, filtration through nylon 0.45 µm disk	5 µL	30°C	VWD	Zorbax Eclipse XDB C18 5 µm* 4.6 mm* 150 mm
22	In-house method	Dicyclohexyl phthalate	Acetone	Sonicate for 8 min, filter through 0.45 µm PTFE syringe filter	1 µL	Gradient	FID	TG-5MS 30 m* 0.25 mm* 0.26 µm
23	CIPAC 571	3-(2-pyridyl)- 5, 6 diphenyl-1,2,4-traizine	N/A	N/A	1 µL	Gradient	FID	Thermo 30 m* 0.25 mm* 250 µm
24	In-house method	Diocthyl phthalate	Tetrahydrofuran	Sonicate for 20 min, centrifuge to separate insoluble material	1 µL	Gradient	FID	CP Sil 13 CB 30 m* 0.25 mm* 250 µm
26	Manufacturer's method	Dipentyl phthalate	Acetone	Sonicate for 10 min, filtered with 0.45 µm PTFE disk	1 µL	Gradient	FID	DB-10.25 µm, 30 m* 0.25 mm

Table 26. EPOXICONAZOLE: representative method for the determination (ITPT2020)

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
1	In-house method	N/A	ACN	Sonicate for 20 min, filtered 0.45 µm PTFE disk	5 µL	40°C	DAD	Zorbax ODS C18 5 µm*, 150 mm* 4.6 mm
3	In-house method	N/A	MetOH: Water 90:10	Dissolve sample in 5 mL of water. Fill to mark with MetOH, diluted with MetOH and filter with 0.45 µm	10 µL	25°C	PDA	Synergy 4 µm Hydro-RP 80 A, 4 µm, 150 mm* 2 mm
4	In-house method	Triphenyl phosphate	Acetone	Sonicate for 10 min	10 µL	40°C	MS/MS QQQ	Ascentis Express RP-AMIDE 2.7 µm, 150 mm* 2.1 mm
9	In-house method	N/A	ACN	Sonicate for 5 min	2 µL	30°C	UV	Xterra RP18 150 mm* 2.1 mm* 3.5 µm
10	In-house method	N/A	Water: ACN 10:90	Ultrasonication 15 min, diluite and filter with 0.45 µm PTFE	10 µL	30°C	DAD	Kintex C18 5 µm, 150 mm* 4.6 mm
11	In-house method	N/A	Acid Water: THF (50:50)	Sonicate for 15 min, shake for homogeneization, filter through 0.2 µm PP disk	10 µL	35°C	DAD	Nucleodur C18 5 µm, 250 mm* 3 mm
12	In-house method	N/A	MetOH	Dissolution in 50 mL MetOH, 15 min sonication, filtration through 0.45 µm regenerated cellulose disk	2 µL	30°C	DAD	LiChrospher 100 RP18, 5 µm* 250 mm*4.0 mm
13	CIPAC 609	N/A	THF	Follow the method	1 µL	250°C	FID	DB-1 30 m 0.53 mm* 1.5 µm
14	In-house method	N/A	ACN	Sonicate for 15 min	5 µL	Ambient	Dionex UVD	Zorbax SB-C18, 5 µm* 4.6 mm* 250 mm
15	In-house method	N/A	Ethyl Acetate	Weigh, sonicate approx 10 min, allow to cool to room temp, make up to volume, filter	0.2 µL	Gradient	FID	HP 5 MS, 30 m* 0.25 mm* 0.25 µm
16	In-house method	N/A	ACN: Water 6:4	Sonicate for 1 min	3 µL	25°C	DAD	Altima C18, 5 µm, 250 mm* 4.6 mm

to be followed

continues

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
17	In-house method	N/A	ACN: Water 95:5	Sonicate for 1 min filtered on 0.2 µm nylon disk	1µL	30°C	DAD	Phenomenex Kinetex C18 5 µm 100 mm* 4.6 mm
18	CIPAC 609	Tetraphenyl ethene	THF	Sonicate for 15 min	1 µL	230°C	FID	DB-1 30 m 0.32 mm* 0.25 µm
20	Manufacturer's method	N/A	Water: ACN 40:60	Solvent extraction, sonicate 20 min, filtered through 0.2 µm nylon disk	1 µL	40°C	PDA	Phenomenex Luna C18 5 µm, 4.6 mm* 150 mm
21	In-house method	N/A	ACN	Sonicate for 10 min, filter through 0.45 µm nylon disk	5 µL	30°C	VWD	Zorbax Eclipse XDB-C18 5 µm* 150 mm* 4.6 mm
22	In-house method	N/A	ACN	Sonicate for 8 min filter through 0.22 µm PTFE syringe filter	0.5 µL	25°C	DAD	Phenomenex Kinetex 2.6 µm, 2.1 mm* 100 mm
23	In-house method	N/A	N/A	N/A	1 µL	230°C	FID	Thermo 30 m* 0.25 mm* 0.25 µm
25	In-house method	N/A	MetOH: Acetic Acid 73:27	Shake the sample for 3 min, dilute and filter 0.45 µm PTFE filter	5 µL	30°C	DAD	Poroshell 120 EC-C18 2.7 µm 4.6 mm* 50 mm
26	CIPAC 609	Di N Butyl phthalate	THF	Follow the method	1 µL	Gradient	FID	DB-1 0.25 µm 30 m* 0.25 mm

Table 27. FLUDIOXONIL: representative method for the determination (ITPT2020)

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
1	In-house method	N/A	Acetone	In contact for 24 Hours	2 µL	Gradient	MS	Equity 5, 30 m* 0.25 mm* 0.25 µm
3	In-house method	N/A	MetOH: Water 90:10	Dissolve sample in 5 mL of water, fill to mark with MetOH, diluted with MetOH and filter with 0.45 µm	10 µL	25°C	PDA	Synergy 4 µm Hydro-RP 80 A 4 µm* 150 mm* 2 mm
4	In-house method	Triphenyl phosphate	Acetone	Sonicate for 10 µm	10 µL	40°C	MS/MS QQQ	Ascentis Express RP-AMIDE 2.7 µm 150 mm* 2.1 mm
6	In-house method	N/A	ACN	Sonicate for 15 min dilute and filter through 0.45 µm nylon disk	10 µL	35°C	DAD	Agilent Zorbax Eclipse XDB C8 5 µm 150 mm* 4.6 mm
9	In-house method	N/A	ACN	Sonicate for 5 min	2 µL	30°C	UV	Xterra RP18 150 mm* 2.1 mm* 3.5 µm
10	In-house method	N/A	Water: ACN 10:90	Ultrasonication 15 min dilute and filter with 0.45 µm PTFE	10 µL	30°C	DAD	Kintex C18 µm 150 mm* 4.6 mm
11	In-house method	N/A	Acid Water: THF (50:50)	Sonicate for 15 min shake for homogenization filter through 0.2 µm PP disk	10 µL	35°C	DAD	Nucleodur C18 5 µm 250 mm* 3 mm
12	In-house method	N/A	ACN	Dissolution in 50 mL ACN 15 min sonication filtration through 0.45 µm regenerated cellulose disk	3 µL	30°C	DAD	LiChrospher 100 RP18, 5 µm* 250 mm* 3mm
13	In-house method	N/A	ACN	Diluted and fill to mark	10 µL	35°C	DAD	Nucleodur C18 5 µm, 250 mm* 3 mm
14	In-house method	N/A	ACN	Sonicate for 15 min	5 µL	Ambient	Dionex UVD	Zorbax SB-C18 5 µm* 4.6 mm* 250 mm
15	In-house method	N/A	Ethyl Acetate	Weigh sonicate approx 10 min allow to cool to room temp make up to volume filter	0.2 µL	Gradient	FID	HP 5 MS 30 m* 0.25 mm* 0.25 µm
16	In-house method	N/A	ACN: Water 6:4	Sonicate for 1 min	6 µL	25°C	DAD	Altima C18 5 µm 250 mm* 4.6 mm

to be followed

continues

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
17	In-house method	N/A	Water: MetOH 5:95	Sonicate for 1 min fill to mark with MetOH filtered with 0.2 µm nylon disk	1 µL	40°C	DAD	Phenomenex Kinetex C18 2.6 µm 100 mm* 4.6 mm
18	In-house method	Dibutyl phthalate	MetOH: Toluene (50:50)	Sonicate for 15 min	1 µL	205°C	FID	DB-17 30 m 0.25 mm* 0.5 µm
19	In-house method	N/A	MetOH	N/A	20 µL	Ambient	UV	Spherisorb S5 ODS2 C18 5 µm* 250 mm* 4.6 mm
20	Manufacturer's method	Diphenil-phthalate	Acetone	Solvent extraction sonicate 20 min filtered through 0.2 µm nylon disk	1 µL	Gradient	FID	Agilent DB 5 MS 30 m* 0.25 mm* 0.25 µm
21	In-house method	N/A	ACN	Sonicate for 10 min Filter through 0.45 µm nylon disk	5 µL	30°C	VWD	Zorbax Eclipse XDB-C18 5 µm* 150 mm 4.6 mm
22	In-house method	N/A	ACN	Sonicate for 8 min filter through 0.22 µm PTFE syringe filter	2 µL	30°C	DAD	Zorbax SB-C18 5 µm 4.6 mm* 250 mm
23	In-house method	N/A	N/A	N/A	10 µL	N/A	DAD	Zorbax Eclipse C18 5 µm* 250 mm* 4.6 mm
26	Manufacturer's method	Dipentyl phthalate	Acetone	Sonicate for 10 min Filter through 0.45 µm PTFE disk	1 µL	Gradient	FID	DB-1 0.25 µm 30 m* 0.25 mm

Table 28. METALAXYL-M: representative method for the determination (ITPT2020)

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
1	In-house method	N/A	Acetone	In contact for 24 hours	2 µL	250°C	MS	Equity 5 30 m* 0.25 mm* 0.25 µm
4	In-house method	Triphenyl phosphate	ACN	Sonicate for 10 min	10 µL	40°C	MS/MS QQQ	Ascentis Express RP-AMIDE 2.7 µm 150mm* 2.1 mm
6	In-house method	N/A	ACN	Sonicate for 15 min dilute and filter through 0.45 µm nylon disk	10 µL	35°C	DAD	Agilent Zorbax Eclipse XDB C8 5 µm 150 mm* 4.6 mm
9	In-house method	N/A	ACN	Sonicate for 5 min	2 µL	30°C	UV	Xterra RP18 150 mm* 2.1 mm* 3.5 µm
10	In-house method	N/A	Water: ACN 50:50	Ultrasonication 15 min dilute and filter with 0.45 µm PTFE	10 µL	30°C	DAD	Kintex C18 5 µm 150 mm* 4.6 mm
11	In-house method	N/A	Acid Water: THF (50:50)	Sonicate for 15 min shake for homogenization filter through 0.2 µm PP disk	10 µL	35°C	DAD	Nucleodur C18 5 µm 250 mm* 3 mm
12	In-house method	N/A	ACN	Dissolution in 50 mL ACN 15 min sonication filtration through 0.45 µm regenerated cellulose disk	2 µL	30°C	DAD	LiChrospher 100 RP18 5 µm* 250mm* 4.0 mm
13	In-house method	N/A	ACN	Dilution and fill to mark	10 µL	35°C	DAD	Nucleodur C18 5 µm 250 mm* 3 mm
14	In-house method	N/A	ACN	Sonicate for 15 min	5 µL	Ambient	Dionex UVD	Zorbax SB-C18, 5 µm* 4.6 mm* 250 mm
15	In-house method	N/A	Ethyl Acetate	Weigh sonicate approx. 10 min allow to cool to room temp make up to volume filter	0.2 µL	Gradient	FID	HP 5 MS 30 m* 0.25 mm* 0.25 µm
16	In-house method	N/A	ACN: Water 6:4	Sonicate for 5 min	1 µL	Gradient	FID	HP-5MS 30 m 250 mm 0.25 µm
17	In-house method	N/A	Water:MetOH 5:95	Sonicate for 1 min fill to mark with MetOH filtered with 0.2 µm nylon disk	1 µL	40°C	DAD	Phenomenex Kinetex C18 2.6 µm 100 mm* 4.6 mm

to be followed

continues

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
18	In-house method	Dibutyl phthalate	MetOH: Toluene (50:50)	Sonicate for 15 min	1 µL	205°C	FID	DB 17 30 m 0.25 mm* 0.5 µm
19	In-house method	N/A	MetOH	N/A	20 µL	Ambient	UV	Spherisorb S5 ODS2 C18 5 µm* 250 mm* 4.6 mm
20	Manufacturer's method	Diphenil-phthalate	Acetone	Solvent extraction sonicate 20 min filtered through 0.2 µm nylon disk	1 µL	Gradient	FID	Agilent DB 5 MS 30m* 0.25 mm* 0.25 µm
21	In-house method	N/A	ACN	Sonicate for 10 min filter through 0.45 µm nylon disk	5 µL	30°C	VWD	Zorbax Eclipse XDB-C18 5 µm* 150 mm* 4.6 mm
22	In-house method	Dicyclohexyl-phthalate	Acetone	Sonicate for 8 min filter through 0.22 µm PTFE syringe filter	1 µL	Gradient	FID	TG-5 MS 0.25 µm 0.25 mm* 30 m
23	CIPAC 365	Methyl Stearate	N/A	N/A	1 µL	225°C	FID	Thermo 30 m* 0.25 mm* 250 µm
24	In-house method	Diocthyl phthalate	THF	Sonicate for 20 min centrifuge to separate insoluble material	1 µL	Gradient	FID	CP Sil 13 CB 30 m* 0.25 mm* 250 µm
26	Manufacturer's method	N/A	ACN: Water 5:5	Sonicate for 15 min dilute and filter through 0.45 µm nylon disk	5 µL	25°C	DAD	Chiracel OD-RH 5 µm 150 mm* 2.1 mm

Table 29. PYRACLOSTROBIN: representative method for the determination (ITPT2020)

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
1	In-house method	N/A	ACN	Sonicate for 20 min filtered with 0.45 µm	5 µL	40 °C	DAD	Zorbax ODS C18 5 µm 150 mm* 4.6 mm
3	In-house method	N/A	MetOH: Water 90:10	Dissolve sample in 5 mL of water fill to mark with MetOH diluted with MetOH and filter with 0.45 µm	10 µL	25°C	PDA	Synergy 4 µm Hydro-RP 80 A 4 µm* 150 mm* 2 mm
4	In-house method	Triphenyl-phosphate	Acetone	Sonicate for 10 min	10 µL	40°C	MS/MS QQQ	Ascentis Express RP-AMIDE 2.7 µm 150 mm* 2.1 mm
9	In-house method	N/A	ACN	Sonicate for 5 min	2 µL	30°C	UV	Xterra RP18 150 mm* 2.1 mm* 3.5 µm
10	In-house method	N/A	Water: ACN 10:90	Ultrasonication 15 min dilute and filter with 0.45 µm PTFE	10 µL	30°C	DAD	Kintex C18 5 µm 150 mm* 4.6 mm
11	In-house method	N/A	Acid Water: THF (50:50)	Sonicate for 15 min shake for homogenization filter through 0.2 µm PP disk	10 µL	35°C	DAD	Nucleodur C18 5 µm 250 mm* 3 mm
12	In-house method	N/A	ACN/ 0.4% Acetic Acid 75:25	Dissolution in 50 mL ACN/ 0.4% Acetic Acid 75:25 15 min sonication	5 µL	30°C	DAD	LiChrospher 100 RP18 5 µm* 250mm* 4.0 mm
13	CIPAC 657	N/A	Water: ACN 25:75	Follow the method	5 µL	40°C	DAD	Phenomenex Luna C18 (2) 250 4.6 mm* 5 µm
14	In-house method	N/A	ACN	Sonicate for 15 min	5 µL	Ambient	Dionex UVD	Zorbax SB-C18, 5 µm* 4.6 mm* 250 mm
15	In-house method	N/A	ACN	Weigh sonicate approx. 10 min allow to cool to room temp make up to volume filter	5 µL	25 °C	PDA	Phenomenex Kinetex C18 2.6 µm 100 mm* 4.6 mm
16	In-house method	N/A	ACN: Water 6:4	Sonicate for 1 min	3 µL	25 °C	DAD	Altima C18 5 µm 250 mm* 4.6 mm
17	In-house method	N/A	ACN: Water 95:5	Sonicate for 1 min filtered with 0.2 µm nylon disk	1 µL	30°C	DAD	Phenomenex Kinetex 5 µm* 4.6 mm* 100 mm

to be followed

continues

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
18	CIPAC 657	N/A	ACN: Water 75:25	Sonicate for 15 min	5 µL	25°C	DAD	Zorbax Eclipse XDB-C18 5 µm* 250 mm* 4.6 mm
19	In-house method	N/A	MetOH	N/A	5 µL	Ambient	UV	Spherisorb S5 ODS2 C18 5 µm* 250 mm* 4.6 mm
20	Manufacturer's method	N/A	Water: CAN 40:60	Solvent extraction sonicate 20 min filtered through 0.2 µm nylon disk	1 µL	40 °C	PDA	Phenomenex Luna C18 5 µm 4.6 mm* 150 mm
21	In-house method	N/A	ACN	Sonicate for 10 min filter through 0.45 µm nylon disk	5 µL	30°C	VWD	Zorbax Eclipse XDB-C18 5 µm* 150 mm* 4.6 mm
22	In-house method	N/A	ACN	Sonicate for 8 min filter through 0.22 µm PTFE syringe filter	0.5 µL	45 °C	DAD	Phenomenex Kinetex 2.6 µm 2.1 mm* 100 mm
23	CIPAC 657	N/A	N/A	N/A	5 µL	N/A	DAD	Zorbax Eclipse C18 5 µm* 250 mm* 4.6 mm
24	In-house method	Cyproconazole	MetOH: CAN 10:2	Sonicate for 10 min centrifuge to separate insoluble material	1 µL	25 °C	UV	Eclipse XDB C18 150 m* 4.6 mm* 5 µm
25	In-house method	N/A	MetOH: Acetic Acid 73:27	Shake the sample for 3 min dilute and filter 0.45 µm PTFE filter	5 µL	30°C	DAD	Poroshell 120 EC-C18 2.7 µm 4.6 mm* 50 mm
26	CIPAC 657	N/A	ACN	Follow the method	5 µL	Ambient	DAD	Zorbax Eclipse C18 5 µm* 250 mm* 4.6 mm

Table 30. THIABENDAZOLE: representative method for the determination (ITPT2020)

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
1	In-house method	N/A	ACN: Water 80:20	Sonicate for 20 min filtered with 0.45 µm PTFE disk		40 °C	DAD	Luna 3U C18 3 µm 150 mm* 4.6 mm
3	In-house method	N/A	MetOH: Water 90:10	Dissolve sample in 5 mL of water fill to mark with MetOH diluted with MetOH and filter with 0.45 µm	10 µL	25°C	MS/MS	Synergy 4 µm Hydro-RP 80 A 4 µm 150 mm* 2 mm
6	In-house method	N/A	ACN	Sonicate for 15 min dilute and filter through 0.45 µm nylon disk	10 µL	35°C	DAD	Agilent Zorbax Eclipse XDB C8 5 µm 150 mm* 4.6 mm
10	CIPAC 323	N/A	Water: MetOH 5:95	Sonicate for 30 min dilute and filter with 0.45 µm PTFE	10 µL	35°C	DAD	Luna C18(2) 100A 5 µm 250 mm* 4.6 mm
11	In-house method	N/A	Acid Water: THF (50:50)	Sonicate for 15 min shake for homogenization filter through 0.2 µm PP disk	10 µL	35°C	DAD	Nucleodur C18 5 µm 250 mm* 3 mm
13	CIPAC 323	N/A	Met:OH Mobile Phase	Follow the method	10 µL	27°C	DAD	Phenomenex Luna C18 (2) 250 4.6 mm* 5 µm
14	In-house method	N/A	ACN	Sonicate for 15 min	5 µL	Ambient	Dionex UVD	Zorbax SB-C18 5 µm* 4.6 mm* 250 mm
15	CIPAC 323	N/A	ACN	Weigh sonicate approx. 10 min allow to cool to room temp make up to volume filter	5 µL	25°C	PDA	Phenomenex Kinetex C18 2.6 µm 100 mm* 4.6 mm
16	In-house method	N/A	ACN: Water 6:4	Sonicate for 1 min	6 µL	25 °C	DAD	Altima C18 5 µm 250 mm* 4.6 mm
17	In-house method	N/A	Water: MetOH 5:95	Sonicate for 1 min fill to mark with MetOH filtered with 0.2 µm nylon disk	1 µL	40 °C	DAD	Phenomenex Kinetex C18 2.6 µm 100 mm* 4.6 mm

to be followed

continues

ID Lab	Reference method	Internal standard	Extractants	Sample preparation	Injection volume	Column T°	Detector	Column
18	CIPAC 323	N/A	MetOH: Water 95:5	Sonicate for 15 min	10 µL	25 °C	DAD	Nucleosil 100-5 C18 5 µm* 250 mm* 4.0 mm
19	In-house method	N/A	MetOH	N/A	1 µL	Ambient	UV	Spherisorb S5 ODS2 C18 5 µm* 250 mm* 4.6 mm
20	Manufacturer's method	Diphenil phthalate	Acetone	Solvent extraction sonicate for 20 min filtered through 0.2 µm nylon disk	1 µL	Gradient	FID	Agilent DB 5 MS 30 m* 0.25 mm* 0.25 µm
21	In-house method	N/A	ACN	Sonicate for 10 min filter through 0.45 µm nylon disk	5 µL	30°C	VWD	Zorbax Eclipse XDB-C18 5 µm* 150 mm* 4.6 mm
22	CIPAC 323	N/A	MetOH	Sonicate for 8 min filter through 0.22 µm PTFE syringe filter	10 µL	30°C	DAD	Zorbax SB-C18 5 µm 4.6 mm* 250 mm
23	CIPAC 323	N/A	MetOH	N/A	10 µL	25°C	DAD	Agilent C18 250 mm* 4.6 mm* 5 µm
26	CIPAC 323	N/A	MetOH	Follow the method	10 µL	Ambient	DAD	Zorbax Eclipse C18 5 µm* 250 mm* 4.6 mm

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APPENDIX A
The announcement letter

ANNOUNCEMENT/INVITATION
ITPT2020

Dear Colleagues,

We herewith cordially invite you to participate in the Italian Proficiency Test on the analysis of PPPs in SL and SE. This exercise is organized by the Italian Laboratory of Istituto Superiore di Sanità (National Institute of Health) – Department of Environment and Health. The ITPT2020 is scheduled to run from 15th January until 30th May 2020.

AIMS
Participation in proficiency tests is part of the QA/QC system of laboratories and provides them with an assessment of their analytical performance as well as a comparison with the performance of other laboratories. The general aim is to help laboratories demonstrate adequate analytical performance and, in case of underperformance, to help them identify sources of errors so that the necessary measures for quality improvement can be taken.

TEST ITEM
Ca. 10 g of PPP test Item will be delivered to each participating lab.

TARGET ANALYTES
The analytes are: Azoxystrobin SL, Epoxiconazole SE, Fludioxonil SL, Metalaxyl-M SL, Pyraclostrobin SE, Thiabendazole SL.

SHIPMENT AND RECEIPT OF THE TEST ITEM
The shipment of the Test Item is planned to start on 15th January 2020. If any laboratory will be on holiday in the week of the shipment, please inform the organizer to rearrange shipment.
Participants must check the integrity and condition of the materials upon receipt and to report within 48 h if they accept the materials or not.

IMPORTANT DATES
- The shipment of the Test Items is planned to start on 15th January 2020.
- Submission of results and method information should be done by 30th May 2020.

PARTICIPATION FEE
The participation is free of charge.

RELEVANT DOCUMENTS
Participants are encouraged to employ the method typically run in their lab for these analytes.

SUPPORT AND CONTACT INFORMATION
For any questions about the ITPT2019, please mail to
angela.santilio@iss.it or chiara.pompili@iss.it

Best regards,

The ITPT2020 Organizing Team

APPENDIX B
Calendar and list of participants

CALENDAR for the ITPT2020

Activity	Dates
Opening of the ITPT2020	7th November 2019
Confirm the participation	30th November 2019
Shipment of the ITPT2020 Test Item	15th January 2020
Confirmation of Sample Receipt and Acceptance	Within 48 h of receipt
Result Submission	30th January – 30th April 2020
Preliminary Report	June 2020
Final Report	July 2020

LIST OF PARTICIPANTS

Italian participants

Cecilia Capannesi	*Laboratorio Sanità Pubblica Firenze*
Luca D'Ambrosio	*Agenzia Provinciale per l'Ambiente – Bolzano*
Francesca Ferrieri	*Polo Alimenti ARPA Puglia*
Luigi Bazzani	*ARPA Emilia Romagna, Sede secondaria laboratorio Multisito, sezione di Ferrara*
Leonardo Sabatino	*Ministero delle Politiche Agricole Alimentari e Forestali, Ispettorato centrale della tutela della qualità e repressione frodi dei prodotti agroalimentari - Laboratorio di Catania*
Antonella Salzarulo	*ARPA Piemonte – Laboratorio Specialistico Nord Ovest*
Chiara Pompili	*Istituto Superiore di Sanità, Roma*
Pierangela Rovellini	*INNOVHUB – SSOG, Milano*
Andrea Vantini	*ARPA Veneto, Verona*

Worldwide participants

Lajos Sándor Benke	*National Food Chain Safety Office- Hungary*
Florentina Ciotea	*National Phytosanitary Authority - Romania*
Amelie Coste	*Service Commun des Laboratories – Lyon, France*
Frantisek Csicsay	*ÚKSÚP - Bratislava, Slovakia*
Christoph Czerwenka	*AGES GmbH - Wien, Austria*
Kristina Dürkop	*Federal Office of Consumer Protection and Food Safety*
Jim Garvey	*The Pesticide Laboratory Control - Backweston, Ireland*
Kati Hakala	*Finnish Food Safety Authority EVIRA- Helsinki, Finland*
Eva Jacobsen	*Danish Technological Institute - Aarhus, Denmark*
Helen Karasali	*Benaki Phytopathological Institute – Athens, Greece*
Marek Miszczyk	*Institute of Plant Protection, National Research Institute - Sośnicowice, Poland*
Isabelle Monisse	*Laboratory of safety Food Agency – Wandre,Belgium*
Olga Nováková Vasilav Penev	*UKZUZ National Reference Laboratory – Brno, Czech Republic* *Bulgaria*
Estela Bonilha	*Ministero da Agricultura, Pecuaria e Abastecimento LFDA/SP – CGAL, Campinas - Brasil*
Andrew Plumb	*Fera Science Ltd – York, UK*
Ignacio Tristano	*Agrofina – Laboratorio de Desarrollo Analitico, Buenos Aires - Argentina*

GLOSSARY

Active Ingredient. An Active Ingredient (AI) is the ingredient in a pharmaceutical drug or plant-health drug that is biologically active. Some products may contain more than one active ingredient.

Analyte. An analyte, component, or chemical species is a substance or chemical constituent that is of interest in an analytical procedure.

CAS number. A CAS Registry Number, also referred to as CASRN or CAS Number, is a unique numerical identifier assigned by the Chemical Abstracts Service (CAS) to every chemical substance described in the open scientific literature (currently including all substances described from 1957 through the present, plus some substances from the early or mid-1900s) including organic and inorganic compounds, minerals, isotopes, alloys and no structural materials (UVCBs, of unknown, variable composition, or biological origin). The registry maintained by CAS is an authoritative collection of disclosed chemical substance information. It currently identifies more than 141 million unique organic and inorganic substances and 67 million protein and DNA sequences, plus additional information about each substance. It is updated with around 15,000 additional new substances daily.

Chemical formula. A chemical formula is a way that chemists describe a molecule. The formula says what atoms, and how many of each type, are in the molecule. Sometimes the formula shows how the atoms are linked, and sometimes the formula shows how the atoms are arranged in space. The letter shows what chemical element each atom is.[1] The subscript shows the number of each type of atom.

% CV. The coefficient of variation (CV) is defined as the ratio of the standard deviation σ to the mean μ multiplied 100: $CV = (\sigma / \mu) \times 100$.

E isomer. It is the IUPAC convention of a molecular configuration, if the two groups of higher priority are on opposite sides of the double bond, the bond is assigned the configuration E (from the German word for "opposite" *entgegen*).

Grand Average. The grand mean or average is the mean of the means of several subsamples, as long as the subsamples have the same number of data points. For example, consider several lots, each containing several items. The items from each lot are sampled for a measure of some variable and the means of the measurements from each lot are computed. The mean of the measures from each lot constitutes the subsample mean. The mean of these subsample means is then the grand mean.

Homogeneity. Homogeneity and heterogeneity are concepts often used in the sciences and statistics relating to the uniformity in a substance or organism. A material or image that is homogeneous is uniform in composition or character (i.e., colour, shape, size, weight, height, distribution, texture, language, income, disease, temperature, radioactivity, architectural design, etc.); one that is heterogeneous is distinctly non uniform in one of these qualities.

Internal Standard. An internal standard in analytical chemistry is a chemical substance that is added in a constant amount to samples, the blank and calibration standards in a chemical analysis. This substance can then be used for calibration by plotting the ratio of the analyte signal to the internal standard signal as a function of the analyte concentration of the standards. This is done to correct for the loss of analyte during sample preparation or sample inlet. The internal standard is a compound that is very similar, but not identical to the chemical species of interest in the samples, as the effects of sample preparation should, relative to the amount of each species, be the same for the signal from the internal standard as for the signal(s) from the species of interest in the ideal case.

MAD. In statistics, the Median Absolute Deviation (MAD) is a robust measure of the variability of a univariate sample of quantitative data. MAD = median of ($|X_i$ – median (Xi) $|_{i=1,2...n}$).

Median. The median is the value separating the higher half of a data sample, a population, or a probability distribution, from the lower half. For a data set, it may be thought of as the "middle" value. For a continuous probability distribution, the median is the value such that a number is equally likely to fall above or below it. The median is a commonly used measure of the properties of a data set in statistics and probability theory. The basic advantage of the median in describing data compared to the mean (often simply described as the "average") is that it is not skewed so much by extremely large or small values, and so it may give a better idea of a "typical" value. Because of this, the median is of central importance in robust statistics.

Modified z-score. The z-score of an observation is defined as $Zi = (X - \mu) / \sigma$, where X is a sample, μ the sample mean and σ the standard deviation. In other words, data is given in units of how many standard deviations it is from the mean. Although it is common practice to use z-scores to identify possible outliers, this can be misleading in particularly for small sample sizes, so is better to use the modified z-score:

$$Zi = 0.6745 \text{ x } {}^{(Xi - median)} / MAD$$

The modified z-scores with an absolute value of greater or lower than 3.5 be labelled as an outlier.

Outlier. An outlier is an observation that appears to deviate markedly from other observations in the sample. Identify potential outliers is important because it may indicate a bad data. For example, the data may have been coded incorrectly or an experiment may not have been run correctly. If it can be determined that an outlying point is in fact erroneous, then the outlying value should be deleted from the analysis (or corrected if possible). If it is not possible to simply delete the outlying observation, the use of robust statistical techniques may be considered.

Reference Method. A reference method is an analytic procedure sufficiently free of random or systemic errors to make it useful for validating proposed new analytic procedures for the same analyte. This method has to be accuracy of a definitive method already certified demonstrated through direct comparison and must use primary reference material (standards, glasses, instruments). An in-house method it means that the method is not certified and made with the laboratory's instruments and techniques. The CIPAC methods is an analytical method make following CIPAC's instructions as the Manufacturer's method is make with the Manufacturer's instructions.

SD. The standard deviation (SD, also represented by the Greek letter sigma σ or the Latin letter s) is a measure that is used to quantify the amount of variation or dispersion of a set of data values. A low standard deviation indicates that the data points tend to be close to the mean of the set, while a high standard deviation indicates that the data points are spread out over a wider range of values.

Stability. The stability is a molecular characteristic of a chemical or compound; is the tendency of a material to resist change or decomposition in its natural environment or when exposed to air, heat, light, pressure or other natural conditions or due to internal reaction.

Z isomer. It is the IUPAC convention of a molecular configuration, if the two groups of higher priority are on the same side of the double bond, the bond is assigned the configuration Z (from the German word for "together" *zusammen*).

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