



Sub-Group Agrochemical Analysis (AA) (1972)

CORESTA AP2017

Santa Cruz do Sul, Brazil

23rd October 2017



AA SG – Objectives

- ❖ To perform **regular proficiency testing** of **Multi-Residue Methods** for the analysis of agrochemical residues on tobacco.
- ❖ To undertake **joint experiments** to resolve unanswered questions arising from proficiency tests; to expand knowledge base on agrochemical residues and their analysis.
- ❖ To produce and maintain a series of **Technical Notes** (on different agrochemical residue classes and selected individual compounds) to supplement the **Technical Guideline** and aid method development and improvement.



AA SG – Governance

Coordinator

- Masahiro Miyoshi – JT Leaf Tobacco Research Center, Oyama, Japan

Secretary

- Heather Westberg – Global Laboratory Services, Wilson – NC, USA

Liaison

- Keisuke Nakayama – JT Scientific & Regulatory Affairs Division, Tokyo, Japan

AA SG moved from Product Technology into Agronomy & Leaf Integrity Study Group



Proficiency test 2017 (FAPAS FT0113)

- CPAs defined in CORESTA Guide No.1 and its candidates
- Test materials (artificially spiked and agronomically incurred)
 - 17 CPAs spiked on blank tobacco
 - 12 CPAs in incurred tobacco
- 27 laboratories from 19 countries
- z-score evaluation
- FAPAS Report (May 2017)
- Analytical methods from the laboratories included in the FAPAS Report

Proficiency test 2017 (FAPAS FT0113) – spiked sample

Laboratory Number	24-D	Azoxystrobin	Bifentrin	Buprofen	Chlorantraniliprole	Chlorfenapyr	Dimethomorph (sum)	Flubendiamide	Indoxacarb (sum)	Iprodione (sum)	Iprodione	Iprodione metabolite	Iprovalicarb	Methoxy(+)-Thiodicarb (sum)	Methomyl	Thiodicarb	Permethrin (sum)	Profenofos	Propiconazole	Spirotetramat (sum)	Spirotetramat	BY069330-enoI	BY069330-ketohydroxy	Tebuconazole	Total n° of z-score	N° of z >2	% z >2	
1	-0.2	0.7	0.2	-2.1	0.8	0.8	0.7	-7.5	0.4	-0.3	-5.5	-4.5	0.0	-2.8	na	0.9	-0.2	0.4	-0.6	na	8.6	0.1	0.0	1.2	22	16	73	
2	-0.1	0.2	0.0	0.8	0.9	1.1	1.2	0.4	0.7	0.6	0.6	-4.5	0.3	0.8	na	0.9	0.2	0.5	3.0	na	-2.7	1.0	6.5	0.6	22	18	82	
3	-4.5	-0.5	0.5	0.0	0.6		0.8	1.7	2.1		-0.6		2.2	-2.9	na	0.4	-0.2	-1.0	0.9	na	-1.8	-4.9	5.3	-1.1	19	13	68	
4	-0.1	0.1	3.3	3.4	-0.4	1.9	0.5	0.3	-0.1		-0.1		-0.4	-0.3	na	-0.4	1.4	-0.5	-0.9		-2.6			0.5	18	15	83	
5	-4.5	0.1	-0.3	0.3	-1.0	1.0	0.8	0.4	0.6		0.5		0.6		na	-1.5	-0.8	-0.6	-2.0						15	14	93	
6	-0.4	0.2	4.2	0.8	3.2	4.4	2.5	-1.2	0.3	1.2	0.7	0.3	-0.2	0.8	na	1.3	1.1	0.5	-1.3	na	-1.3	17.3	-4.2	-6.1	22	15	68	
7	0.3	-0.2	-1.2	-2.3	-1.0	-1.9	-0.5	0.5	-1.9	-1.3	-1.3		-0.9	-0.2	na	-1.1	-1.6	-0.9	0.2	na	-1.3	2.2	-0.8	0.4	21	19	90	
8	6.1			0.4	1.4				3.8		5.0			1.0	na	0.6	-5.3	0.4	1.0						10	6	60	
9		-4.2	1.1				-2.8		-2.8						na		-0.9								5	2	40	
10		1.3	1.4	-0.7	0.6	1.4	2.1	0.8	1.3	0.7	0.2	0.0	-1.4	1.3	na	1.5	0.0	0.5	3.2	na	11.7	-0.1	-0.8	0.6	21	18	86	
11	-4.5	-0.8	-0.8	-1.3	6.8	-0.5	-0.9	-1.0	-1.5	0.1			0.1		na	-1.2	0.1	0.9	-6.7		6.7			0.3	17	13	76	
12	-4.5	-3.0	-2.2	-5.4	-3.6	-6.7	-1.7	0.9	-1.8		-5.5	-4.5	-6.6	-6.3	na	-0.1	-8.3	-2.3	-4.5	na	9.7	-1.1	-0.3	-5.5	22	6	27	
13	0.7	2.0	-0.7	1.0	-7.8		0.0				8.0					0.7	-1.1								9	7	78	
14	1.8	0.5	1.5	0.2	0.7	0.4	-1.9	0.0	0.2		0.7				na	-0.4	0.5	0.0	0.1		0.6			0.6	16	16	100	
15	-0.3	-0.7	-0.2	7.6	0.5	0.6	0.1	0.1			-0.3		0.0	2.4		-1.0	0.6	0.0	-6.7		0.2			-0.8	17	14	82	
16	-4.5	-1.8	-2.7	-3.5	-1.6	-6.7	-1.3	-1.1	-2.0		-1.6	-1.7		-0.8	na	-1.8	-4.3	1.8	-6.7	na	-0.2			-0.7	18	12	67	
17	-0.1	0.9	0.7	-0.3	-1.4	-1.2	-1.1	0.0			-3.2		-0.7	-3.8	na	-3.9	0.5		-3.2		211.8			3.7	16	10	63	
18																												
19	-1.8	1.0	2.2	1.1		0.9	0.5		0.1	0.4		0.1	8.3	na	9.4	0.9	0.5	-0.9						-0.3	15	12	80	
20	0.0	1.0	1.6	-1.8	0.0	-0.7	0.7	-0.3	-0.7	0.3	-0.1	0.0	0.0	0.0	na	0.0	0.6	2.8	-2.7	na	0.8	-1.6	0.6	-0.4	22	20	91	
21			-2.5	-2.8			-1.2			-1.3	-1.3						-3.6									7	3	43
22		1.6	-0.7	2.2	-2.6	-0.4	-3.1		-1.7		-0.6				na		-1.7	-0.1			-3.7					11	7	64
23	-1.2	0.0	-1.3	-0.8	-2.5	-0.5	0.7	-0.9	0.2	-0.1	-1.3	0.1	0.8			1.3	1.4	-1.8	0.8	na	-1.5	3.8	0.0	-0.3	21	19	90	
24	-4.5	-3.1	-1.6	-5.2	-3.4	-2.2	-1.6	-4.2	-3.1	-5.5	-5.5		-2.3	29.8	na	25.8	-1.3	-2.3	0.1	na	1.4	-2.4	0.3	-3.3	21	6	29	
25	0.7	-0.9	-0.5	-1.8	0.0	0.2	na	-0.8	na	-1.4			-0.7	-3.9	na	-4.0	-1.2	-0.5	-0.6	na	7.9	-6.4	na	-4.7	17	12	71	
26		-4.0	-4.1	-2.5			-2.6		-2.0				-2.8	-5.2	na	0.7	-1.9	-1.3	2.8					-2.3	12	4	33	
27		-5.5	3.6	4.0	-7.7			-5.6								-2.6	4.5									8	0	0
Total number of z-scores	17	24	25	25	22	19	22	20	22	11	23	7	18	18		22	25	22	24		18	11	10	19	424			
Number of z >2	10	19	17	15	14	14	17	17	18	9	17	4	14	9		17	20	19	13		9	5	7	13	297			
% z >2	59	79	68	60	64	74	77	85	82	82	74	57	78	50		77	80	86	54		50	45	70	68	69			

= |z|≤2 = not found
 = |z|>2 = not tested for
 = <LoQ = for information only
na = non available x,x = z-score

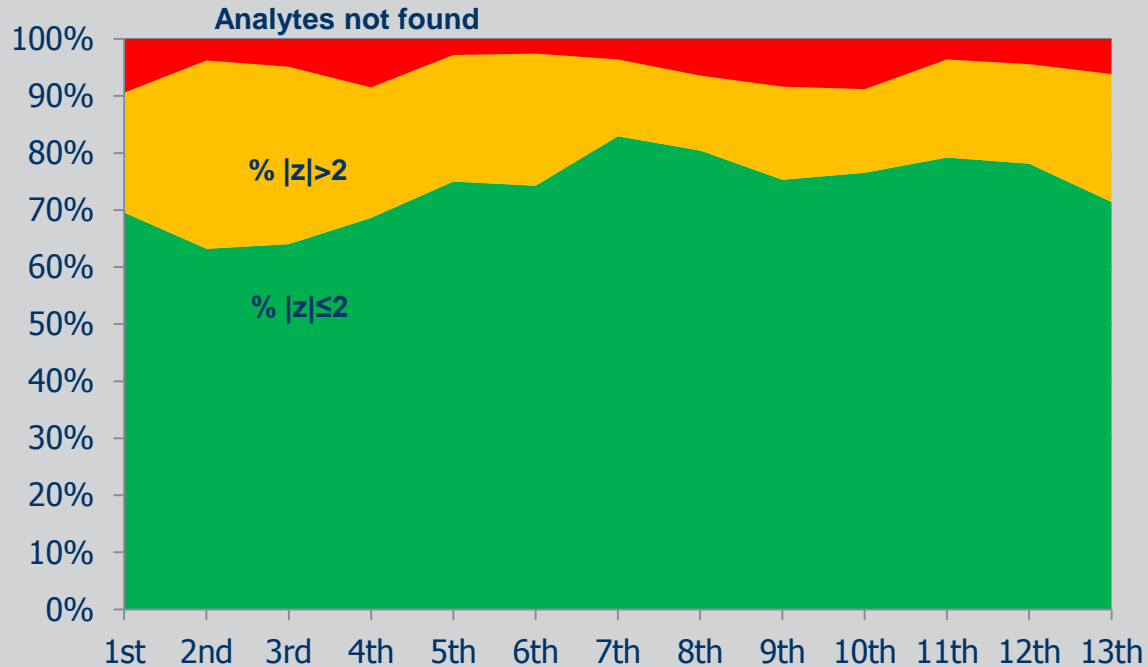
Proficiency test 2017 (FAPAS FT0113) – incurred sample

Laboratory Number	Axoxystrobin	Bifenbutin	Chlorantraniliprole	Chlorpyrifos (.stbu)	Clothianidin	Dimethomorph (sum)	Dithiocarbamates	Flubendamide	Flumezalin	Indoxacarb	Propamocarb	Teflufenuron	Thiamethoxam	Total n° of z-score	N° of z ≤2	% z ≤2
1	0.7	-0.6	0.7	-4.5	-0.7	0.0	-5.3	1.6	-3.4	-0.1	-0.4	0.0	na	12	9	75
2	-0.3	-0.6	0.3	0.2	-1.3	-3.1	1.1	0.3	0.7	1.3	0.2	na	11	10	91	
3	-0.7	-0.3	0.5	-0.6	-0.6	-0.2	1.8	2.5	2.3	1.5	0.2	na	11	9	82	
4	0.2	2.0	-0.3	-1.0	0.0	0.4	-3.2	0.2	0.7	0.2	-2.4	0.9	na	12	10	83
5	-0.2	-1.5	-1.0	-4.5	-0.5	1.4	-1.7	0.5	0.4	0.3	-1.8	na	11	10	91	
6	-0.3	4.1	1.2	-2.5	0.2	0.3	-0.3	0.8	0.8	1.0	-6.3	na	11	8	73	
7	0.6	-0.1	-0.1	0.6	0.9	0.3	1.4	-1.0	-0.7	0.1	1.6	na	11	11	100	
8			2.0			0.7		4.6	7.6	0.1		na	5	3	60	
9	-5.3	-1.1				-2.7			-5.5			na	5	1	20	
10	0.6	0.9	-1.0	-0.6	1.0	1.2	0.0	-1.3	0.5	1.1	-0.1	na	11	11	100	
11	-0.9	-1.0	7.7	4.0	-4.5	-0.2	0.9	-0.6	-1.4	-0.5	-7.0	-0.2	na	12	8	67
12	-2.4	-1.9	-3.7	-4.5	-2.8	-0.3	-3.8	-1.0	-6.3	-1.6	-4.7	-3.6	na	12	4	33
13	2.1	0.5	-7.9	2.2	1.6			-0.8	0.3				na	7	4	57
14	-1.2	-1.0	0.7	0.6	1.1	0.0		-0.5	-1.1	0.3	-2.0	0.0	na	11	11	100
15	-1.6	-1.1	5.7	0.8	-4.5	-0.5	0.8	0.5	-1.0	0.8	-7.0	-1.0	na	12	9	75
16	0.9	0.2	-2.0		-4.5	-1.2	-1.6	1.2	-0.3	-0.3	-7.0	0.2	na	11	9	82
17	1.6	1.0	-0.5			-1.5	-7.4	-1.3		0.0	485.4	4.3	na	9	6	67
18													-	-	-	-
19	0.6	1.2		1.2		0.5	2.1		0.3	0.2	0.1	-0.7	na	9	8	89
20	4.0	0.1	2.0	1.9	0.2	2.8	-0.9	-1.9	-3.5	-1.1	1.5	0.4	na	12	9	75
21		-2.3		-4.5		-1.4	-3.7		-1.3		-2.7		na	6	2	33
22	2.8	-4.1	-2.0		0.0	-2.0		-6.3	-0.2	0.9			na	8	5	63
23	-1.5	-0.9	-0.4	-1.0	-0.5	0.6	0.7	0.5	-2.1	-1.0	0.3	-0.8	na	12	11	92
24	3.8	-0.9	0.4	1.7	-4.5	-0.1	-0.2	4.1	-0.2	-2.0	-1.2	-2.9	na	12	8	67
25	0.7	-0.1	0.9	-0.3	-1.3	-0.5		1.4	-2.4	-2.4	0.6	-4.5	na	11	8	73
26	-4.9	-6.3		-0.6		-4.0	0.0		-2.0	-4.3			na	8	4	50
27	-3.1	4.3	-7.3					-6.0	1.6		1.1		na	6	2	33
Total number of z-score	24	25	22	17	18	23	20	20	24	23	23	19		258		
Number of z ≤2	16	20	17	11	12	20	12	18	16	18	16	14		190		
% z ≤2	67	80	77	65	67	87	60	90	67	78	70	74		73.4		

 = z ≤2	 = not found
 = z >2	 = not tested for
 = <LoQ	 = for information only
na = non available	x,x = z-score



z-score trend (FAPAS FT0101-FT0113)



Communication at external event

- Participated in LAPRW 2017 (6th Latin American Pesticide Residue Workshop) in San Jose, Costa Rica
- A poster presentation entitled “Proficiency Testing for Pesticide Residues Analysis in Tobacco”, reviewing all previous rounds of proficiency test
- Some of the participants showed great interests in the proficiency test.

Proficiency Testing for Pesticide Residues Analysis in Tobacco

Masahiko MIYOSHI¹, Marco PRAET², Dominik ANDERSON³ and Mark SYKES⁴
¹ Japan Tobacco Inc., Leaf Tobacco Research Center, 1900, Idei, Oyama, Tochigi 323-0808, Japan; E-mail: masahiko.miyoshi@jti.com
² Japan Tobacco International, Germany GmbH, Diendenhofener Str 20, 54294, Trier, Germany
³ Fera, Nere Science Ltd, Sand Hutton, York, YO41 1LZ, United Kingdom

INTRODUCTION

There is an increasing demand for laboratories to demonstrate their performance and reliability in pesticide residue analysis. Proficiency Testing (PT) schemes provide an independent and unbiased assessment of performance. The Cooperation Centre for Scientific Research Relative to Tobacco (CORESTA) Agrochemical Analysis Sub-Group (AA-SG) has been implementing a PT on pesticide residue analysis in tobacco test materials every year since 2005 in collaboration with Fera from Nere Science Ltd (UK, Fera), in order to evaluate the quality of an analytical laboratory's results.

FLOW OF CORESTA-Fapas PT

- Fapas prepares test materials.
- CORESTA lab carries out homogeneity testing of materials
- After homogeneity test pass, Fapas sends test materials to each participant.
- Participants analyse test materials and return their own results.
- Fapas analyses the submitted results statistically and makes a report.
- CORESTA AA-SG holds a meeting to discuss the outcome and makes recommendations for the next round of testing.

Flow chart of CORESTA-Fapas PT

55 laboratories from 27 countries participated in CORESTA-Fapas PT since 2015. Around 23 laboratories have been taking part in every round.

Table 1. Tested analytes with rate of satisfactory z-scores in CORESTA-Fapas PTs since 2005

Tested analyte	2005		2006		2007		2008		2009		2010		2011		2012		2013		2014		2015	
	n	%	n	%	n	%	n	%	n	%	n	%	n	%	n	%	n	%	n	%	n	%
AA-SG	10	100	10	100	10	100	10	100	10	100	10	100	10	100	10	100	10	100	10	100	10	100
AFRICA	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100
ASIA	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100
EUROPE	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100
NA	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100
SA	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100	1	100

TEST MATERIALS

- Artificially spiked and/or agrochemically incurred test materials were provided for participants to determine the identity of and the levels of pesticide residues present in each test material.
- A total 80 pesticides which were chosen from those listed in CORESTA Guide No. 1 and its candidates have been tested in 12 rounds of this PT since 2005 (Table 1).

EVALUATION

- z-scores are calculated as:

$$z = \frac{x - X_0}{\sigma}$$
 where:
 - x: the participant's reported result,
 - X_0 : the assigned value
 - σ : the standard deviation for PT
- Obtained z-scores can be interpreted as:
 - |z| ≤ 2 satisfactory
 - 2 < |z| ≤ 3 questionable
 - |z| > 3 unsatisfactory

RESULTS

- The rate of satisfactory z-scores for all participants has been increasing from a minimum of 45% to a maximum of 83% and is stable at around 80% in the last 5 rounds.
- To resolve questions arising from each round of PT, CORESTA AA-SG hold an annual discussion which expands knowledge based on these pesticide residues.

CONCLUSIONS

- PT for pesticide residues analysis in tobacco has contributed to improve overall laboratory performance over 12 years.
- Future PT could be more effective with an increase in the number of participating laboratories (e.g. from Africa or Latin American regions).

ACKNOWLEDGMENT

The authors wish to thank the members of CORESTA AA-SG and all laboratories participating in the CORESTA-Fapas PT.

Reference: Cooperation Centre for Scientific Research Relative to Tobacco (CORESTA), Guide No. 1: The Concept and Implementation of Agrochemical Guidance Residue Levels, July 2016. https://www.coresta.org/sites/default/files/technical_documents/main/Guide-No1-CR1601-tissue-July-2016.pdf

Joint Experiment Technical Study (JETS) 17/1 on Maleic Hydrazide

- **Coordinator: Alvino Rodrigues (Souza Cruz)**
- **Background:**
 - The ISO 4876:1980 (Tobacco and tobacco products -Determination of maleic hydrazide residues) was systematically reviewed in 2011. Two revision proposals were submitted to the ISO/TC 126 from that time.
 - The JETS 16/2 was formulated to evaluate the capacity of different methods; the ISO+ISO modified; Renaud modified, YC/T modified and other methods.
 - Results from the YC/T modified method were comparable to ISO+ISO modified, although the limited number of labs applying the same method weakens the statistical analysis in achieving conclusive findings.
- **Objective:**
 - To evaluate the YC/T modified and ISO methods performance to quantitate maleic hydrazide on tobacco, using both artificially spiked and naturally incurred tobacco samples



Joint Experiment Technical Study (JETS) 17/1 on Maleic Hydrazide (cont'd)

- Six test samples (one artificially spiked and five naturally incurred Flue-cured)
- 17 laboratories from 11 countries
- Report issued in August 2017
- **Outcome:**
 - The report concluded the YC/T modified method was not able to provide equivalent results to the reference method (the ISO 4876:1980) in the six evaluated samples.
 - However, another statistical evaluation indicated the differences between YC/T modified method and ISO method seemed not-significant for most of the samples.
- **Next step:**
 - Consult with CORESTA experts on the statistical approach for similar studies conducted by other SG and TF
 - Compare the methods to collect information related with sample throughput, cost, environmental impact, etc.



Technical Guideline (CORESTA Guide No. 5)

- **Technical Guideline for Pesticide Residues Analysis on Tobacco and Tobacco Products → to be reviewed by 2018**

Technical Note

- **Technical Note #006 (Dithiocarbamates) to be completed**
- **New Technical notes under consideration**

Joint Experiment Test Study on matrix effects from DAC tobaccos

- **Study design to be considered**



2017 AA SG meeting

- ❖ Jujuy (Argentina) on September 5-6, 2017
- ❖ Hosted by Alliance One Tobacco Argentina, Cooperativa de Productores Tabacaleros de Salta and Cooperativa de Tabacaleros de Jujuy with the contribution of LANaRT
- ❖ 25 participants from 9 countries



Thank you for attention!