

Progetto Trieste – Pesticide Residues

FINAL REPORT

Laboratory Proficiency Testing for Food Analysis

2017

Pesticide Residues

Round of October

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About this proficiency test, participant should contact:

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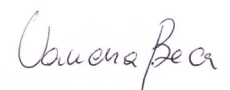
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Round coordinator

11/12/2017 rev.0

INTRODUCTION

The quality management system of *Test Veritas* S.r.l. has been assessed and certified by SGS Italia as meeting the requirements of ISO 9001 / UNI EN ISO 9001:2008 for development and production of materials for agri-food analyses and proficiency supply.

22 laboratories participated to “*Progetto Trieste 2017 pesticide residues*”

The test materials were dispatched on October 16th, 2017. The deadline for sending the results was November 17th, 2017.

17 laboratories returned some test results. All participants sent their results before the deadline.

This Proficiency Testing Scheme offered 1 spiked test material and 1 blank material (see Table a).

Table a: Test materials

Test material code	matrices	
VF1770	lyophilized lettuce	70g x 1
VF1770 blank	lyophilized lettuce	70g x 1

PREPARATION OF TEST MATERIALS, HOMOGENEITY, DISTRIBUTION

Preparation

Vegetables: spiked and blank (lettuce)

Blank matrices (from organic farming) were homogenized with a cutter mixer. One portion of them was used in order to obtain blank sample: the other portion was added with spiking solution.

The blank sample was checked for the absence of pesticides.

Both samples separately, were homogenized with a cutter mixer and lyophilized. After mixing thoroughly, samples were dispensed into foil-laminated pouches, checked for homogeneity and kept at controlled temperature until dispatch.

Subcontractor

In order to check the batch's homogeneity the analyses was performed by a competent subcontractor.

Homogeneity and stability

Appropriate homogeneity studies assessed that test materials are sufficiently homogeneous for the measurands under study.

Appropriate stability studies assessed that test materials are stable for the time that elapsed between the dispatch of the samples and the deadline for submission of results.

Information about homogeneity and stability studies are available under request.

Labels

To avoid labelling errors, spiked Test Material and blank material are labelled on different days.

Distribution

In accordance with the stability established, the test material were shipped in proper containers and conditions.

Dispatch was followed by the courier's parcel tracking system on the web site.

Shipments outside the EU follows different procedures.

The parcel contains:

- A number of units of test material (see Table a)
- A covering letter with the necessary instructions for use and storage of the materials and the answer form.
- A letter with recommendations on how to use lyophilized samples.

An e-mail informed participants that the materials were shipped. The e-mail contains an attached copy of the covering letter, answer form and MSDS.

PERFORMANCE EVALUATION CRITERIA

Laboratory code and confidentiality

Confidentiality is guaranteed. Participants are identified in the Final Report by a randomly assigned code.

The laboratory codes were communicated to participants by e-mail.

Result and concentration value

In confirmatory analysis, the compounds are separated by chromatographic techniques (GC, HPLC...); afterwards they are detected by MS, MS/MS etc...

Participants were asked to report results corrected for recovery and uncorrected for recovery.

- “ = ...” means that the analyte was detected and quantified.
- “ < of ...” means that the analyte was not detected.
- “ > of ...” means that the analyte was detected but not quantified.
- “NS” (Not Searched) means that the laboratory did not perform the analysis.

The participants could report two different results obtained by two technicians or two methods.

Limit of detection (LOD) and limit of quantification (LOQ)

Limit of detection, limit of quantification and uncertainty for the relative compounds were claimed by the laboratories.

“-” means “Not Reported”.

Elaboration of laboratory data

In the statistical data processing, all the data submitted by the participants are elaborated considering two decimal places. In case there are not declared decimal places, they are considered as corresponding to "zero" (E.g. 25=25,00 - 25,3=25,30 - 25,32=25,32).

CALCULATION OF THE ASSIGNED VALUE

The Assigned Value x_{pt}

The Assigned Value x_{pt} is the value attributed to a particular property of proficiency test items (definition from ISO13528:2015).

The procedure for determining the Assigned Value x_{pt} is described below.

After excluding results that are identified as invalid the data population was checked for normality and for the presence of outliers by applying appropriate statistics and visual presentations. x_{pt} represents the value of concentration obtained from Algorithm A (ISO 13528:2015) or from the median. The chosen value will be reported under the assigned value table.

The value is not assigned when $p < 8$, where “ p ” is the number of data after invalid results rejection.

In case of $8 \leq p < 15$ the uncertainty attributable to Assigned Value is not negligible.

z-score and σ_{pt} (standard deviation for proficiency assessment):

For quantitative data, the participant's result is converted into a z-score according to the equation:

$$z\text{-score} = (x_i - x_{pt}) / \sigma_{pt}$$

where:

- x_i is the analyte concentration value reported by the laboratory;
- x_{pt} is the assigned value (obtained with confirmatory methods);
- σ_{pt} is the standard deviation for proficiency assessment calculated from $b x_{pt}$.
- $b = \%RSD / 100$, (RSD = Relative Standard Deviation)

the %RSD value comes from the Horwitz equation (Horwitz, W., 1988, *Pure Appl. Chem.* 60, 855-864)

$$\%RSD = 2^{(1-0.5 \log X_{pt})}$$

where x_{pt} is expressed as a dimensionless concentration.

σ_{pt} is related to the concentration of the analyte: it comes from Horwitz equation (unless otherwise specified); in case of contamination less than 10 ppb the Thompson equation modified Horwitz equation (Thompson, M., 2000, *Analyst* 125, 385-386). In particular circumstance σ_{pt} is chosen from Proficiency Test provider's (PTp) experience, derived from previous rounds. The adopted criteria is reported in the specific test material table.

The laboratory performance evaluation was established taking into account the following criteria for z-score:

<i>acceptable (satisfactory)</i>	when	$ z \leq 2$
<i>warning signal (questionable)</i>	when	$2 < z \leq 3$
<i>action signal (unsatisfactory)</i>	when	$ z > 3$

The standard uncertainty of the assigned value $u(x_{pt})$

The standard uncertainty $u(x_{pt})$ is calculated as:

$$u(x_{pt}) = s^* / \sqrt{p}$$

where:

- s^* is the robust estimate of the participant standard deviation;
- p is the number of participants.

In case of median as estimator, the standard deviation is calculated as $s^* = MADe$ (where MADe is the Median Absolute Deviation).

When the standard uncertainty is too high, the assigned value could be inaccurate.

Therefore:

- In case $[u(x_{pt})]^2 / \sigma_{pt}^2 > 0.5$, the consensus value is not determined and individual laboratory performance scores are not reported. Summary statistics are provided only for information.
- In case $0.1 < [u(x_{pt})]^2 / \sigma_{pt}^2 \leq 0.5$, the assigned value and z-score will be given in *italic* (provided only for information).
In this case the uncertainty is not negligible, and evaluation could be affected.

It may happen that only few participants confirm the presence of some analytes in the test materials. In such cases, the presence of an analyte is considered:

- “unconfirmed”, when less than 25 % of participants detect the compound;
- “confirmed”, when 25% of participants, or more, detect the compound (the minimum number of positive results is anyway three).

Graphical presentation

When participants receive a z-score, it will be shown in the “bar-chart of z-score” (chart reported under the table “assigned value and standard deviations”).

PARTICIPANTS

BRAZIL:

- EUROFINS DO BRASIL ANÁLISES DE ALIMENTOS LTDA, Indaiatuba - San Paolo
- LANAGRO – MG, National Laboratory of the Ministry of Agriculture, Livestock and Food Supply of Brasil, Pedro Leopoldo

CHILE:

- Bureau Veritas - Andes Control, Colina, Santiago
- Comercial Analab Chile S.A., Macul, Santiago
- Gestión de Calidad y Laboratorio S.A., EUROFINS Vitacura, Santiago
- INIA-La Platina, Santiago
- Laboratorio Labser Ltda., Rancagua
- Servicio Agrícola y Ganadero - Laboratorio Química Ambiental y Alimentaria, Santiago

COSTA RICA:

- Ministerio de Agricultura y Ganadería (MAG), Servicio Nacional de Salud Animal (SENASA) - Laboratorio Nacional de Servicios Veterinarios (LANASEVE), Heredia

GERMANY:

- Gesellschaft für Lebensmittel – Forschung mbH, Berlin

ITALY:

- A.R.P.A. AGENZIA REGIONALE PER LA PROTEZIONE AMBIENTALE DEL LAZIO, Sezione Provinciale di ROMA, Roma
- Agenzia Provinciale per la protezione dell'ambiente, Trento
- Biocentro - I.r.b. S.r.l. , Mercato San Severino, Savona
- F.lli De Cecco di Filippo Fara San Martino S.p.A., Fara San Martino, Chieti
- Istituto Zooprofilattico Sperimentale del Mezzogiorno della Campania e della Calabria, Portici, Napoli
- Agenzia delle dogane e dei monopoli, Palermo

NIGER:

- Université CAMES / Université de Tillabéri/Université de Maradi, Niamey

SENEGAL:

- Régional Center for Research in Toxicology and Environmental Security (CERES - LOCUSTOX), Dakar

SPAIN:

- Conselleria de Samdade - Xefarura Territorial de Lugo, LABORATORIO DE SALUD PUBLICA DE LUGO, Lugo

THAILAND:

- ASIA MEDICAL AND AGRICULTURAL LABORATORY AND RESEARCH CENTER (AMARC)
- BETAGRO

ZAMBIA:

- National Institute for Scientific and Industrial Research, Lusaka

REFERENCES

“Progetto Trieste” is managed in agreement to:

- UNI CEI EN ISO/IEC 17043:2010 Conformity assessment – General requirements for proficiency testing
- EURACHEM Selection, Use and Interpretation of Proficiency Testing (PT) Schemes, 2nd edition, 2011
- ISO 13528:2015 Statistical method for use in proficiency testing by interlaboratory comparisons
- ISO GUIDE 35 Reference materials – General and statistical principles for certification, 2006
- IUPAC Technical Report The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, 2006
- EURACHEM/CITAC Guide CG4 Quantifying Uncertainty in Analytical Measurement, 3rd edition, 2012
- ILAC-P10:2013 ILAC Policy on Traceability of Measurement Results
- ILAC-G8:03/2009 Guidelines on the Reporting of Compliance with Specification

RESULTS

Proficiency Test VF1770, result contents

pesticides in lyophilized lettuce

- **Test material VF1770**

Test material VF1770, lyophilized lettuce

Table 1: results of analyses performed on test material VF1770 (spiked sample): pesticides detection.

VF1770						
assigned value atrazine: 178,20 µg/kg (corrected for recovery)						
satisfactory range: 104,27-252,13 µg/kg						
assigned value atrazine: 162,00 µg/kg (uncorrected for recovery)						
satisfactory range: 93,82-230,18µg/kg						
Lab. code	Result corrected for recovery (µg/kg)	Result uncorrected for recovery (µg/kg)	Recovery %	z-score (corrected)	z-score (uncorrected)	LOQ (µg/kg)
1	218,9	162,0	67,3	1,10	0,00	2
2	139	160	87	-1,06	-0,06	10
5						
7	-	199,06	85,82		1,09	10,00
8						
9	190,7	160,4	84,1	0,34	-0,05	20
10						
12	-	0,7	70		-4,73	0,05
13	NS					
14	141	141	99,4	-1,01	-0,62	10
15	147,64	149,62	98,68	-0,83	-0,36	10
16	155	154	99,2	-0,63	-0,23	10
17	156	168	108	-0,60	0,18	10
22						
23	-	271			3,20	10
27	238,0	228,8	104	1,62	1,96	1,7
30	-	133	90		-0,85	10
32						
39	-	212,53	60,05		1,48	10
41	-	202			1,17	10
45	191	147	77	0,35	-0,44	10
50	204,76	167,55	81,83	0,72	0,16	10

Test material VF1770, lyophilized lettuce

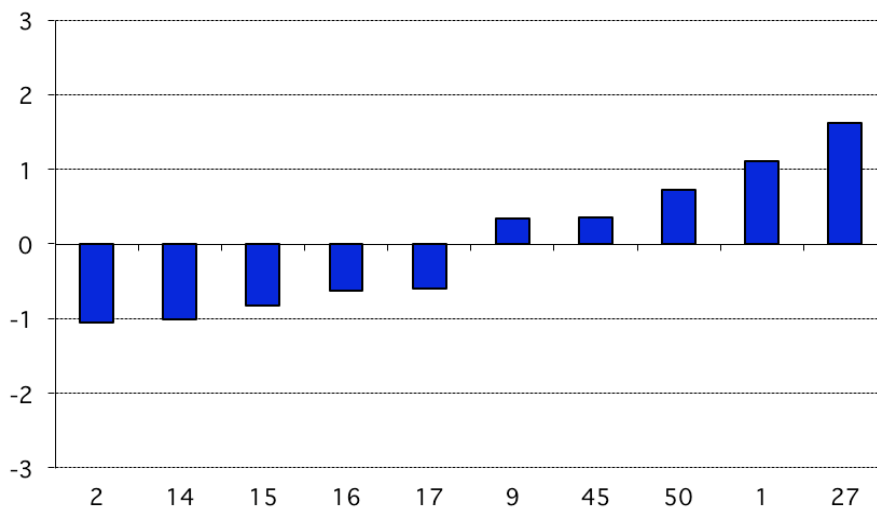
Corrected for recovery:
 Concentration, arithmetic mean (n=10) 178,20 µg/kg
 Standard deviation (n=10) 35,19 µg/kg
 Coefficient of variation (n=10) 19,75%

Table 2: assigned value and standard deviations (corrected for recovery data).

Analyte	Assigned value (µg/kg)				Standard deviation for proficiency assessment		
	Data points, n	Mean from Algorithm A	SD	CV	Standard uncertainty $u(x_{pt})$	b	$\sigma_{pt} = b \cdot x_{pt}$
Atrazine	10	178,20	39,88	22,38	12,61	0,21	36,96

$$[u(X_{pt})]^2 / \sigma_{pt}^2 \leq 0,1$$

Atrazine, assigned value: 178,20 µg/kg



$|z| \leq 2$ = satisfactory $2 < |z| \leq 3$ = questionable
 $|z| > 3$ = unsatisfactory * = outliers

Test material VF1770, lyophilized lettuce

Uncorrected for recovery:

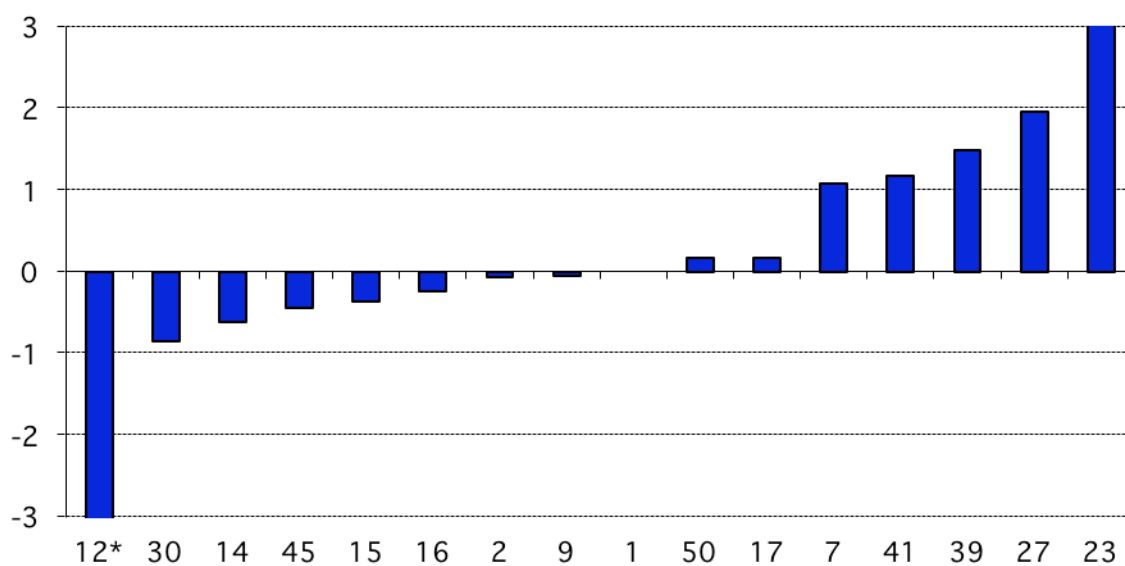
Concentration, arithmetic mean ($n=16$) 166,04 $\mu\text{g}/\text{kg}$
 Standard deviation ($n=16$) 57,40 $\mu\text{g}/\text{kg}$
 Coefficient of variation ($n=16$) 34,57%

Table 3: assigned value and standard deviations (uncorrected for recovery data).

Analyte	Assigned value ($\mu\text{g}/\text{kg}$)				Standard deviation for proficiency assessment		
	Data points, n	Median	MADe	CV	Standard uncertainty $u(x_{pt})$	b	$\sigma_{pt} = b \cdot x_{pt}$
Atrazine	15	162,00	22,24	13,73	5,74	0,21	34,09

$$[u(X_{pt})]^2 / \sigma_{pt}^2 \leq 0,1$$

Atrazine, assigned value: 162,00 $\mu\text{g}/\text{kg}$



$|z| \leq 2$ = satisfactory
 $|z| > 3$ = unsatisfactory

$2 < |z| \leq 3$ = questionable
 * = outliers

Test material VF1770, lyophilized lettuce

Table 4: results of analyses performed on test material VF1770 (spiked sample): pesticides detection.

VF1770						
assigned value difenoconazole: 106,00 µg/kg (corrected for recovery)						
satisfactory range : 58,95-153,55 µg/kg						
assigned value difenoconazole: 103,30 µg/kg (uncorrected for recovery)						
satisfactory range : 56,78-149,82 µg/kg						
Lab. code	Result corrected for recovery (µg/kg)	Result uncorrected for recovery (µg/kg)	Recovery %	z-score (corrected)	z-score (uncorrected)	LOQ (µg/kg)
1	622,5	547,8	88	21,72	19,11	3
2	105	135	78	-0,04	1,36	10
5						
7	-	170,16	108,26		2,87	10,00
8						
9	105,1	88,2	83,9	-0,04	-0,65	10
10						
12	NS					
13	112,05	98,60	88	0,25	-0,20	10
14	98	96	97,9	-0,34	-0,31	10
15	82,39	83,95	98,14	-0,99	-0,83	10
16	78,2	78	99,8	-1,17	-1,09	10
17	126	92	73	0,84	-0,49	10
22						
23	-	133			1,28	10
27	<1,0	<1,0				1,7
30	-	108	99		0,20	10
32						
39	-	147,02	110,47		1,88	10
41	-	111			0,33	10
45	109	63	58	0,13	-1,73	5
50	NS					

Test material VF1770, lyophilized lettuce

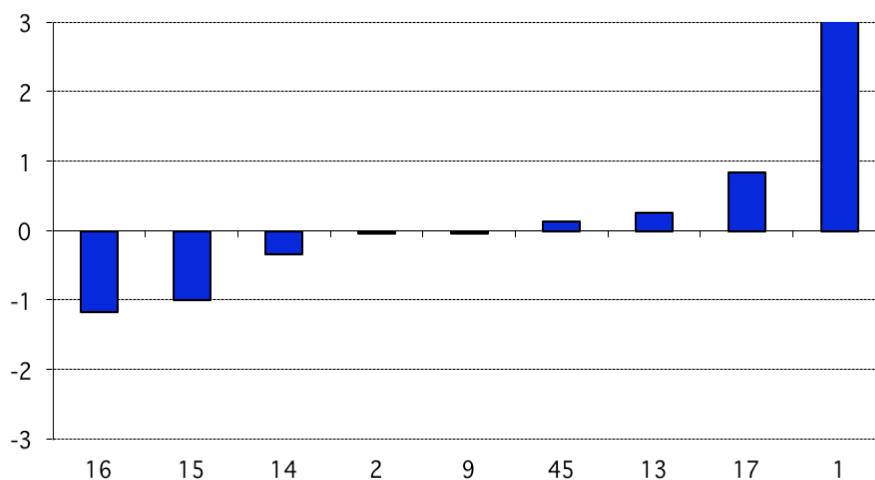
Corrected for recovery:
 Concentration, arithmetic mean ($n = 9$) 159,80 $\mu\text{g}/\text{kg}$
 Standard deviation ($n = 9$) 174,13 $\mu\text{g}/\text{kg}$
 Coefficient of variation ($n = 9$) 108,96%

Table 5: assigned value and standard deviations (corrected for recovery data).

Analyte	Assigned value ($\mu\text{g}/\text{kg}$)				Standard deviation for proficiency assessment		
	Data points, n	Mean from Algorithm A	SD	CV	Standard uncertainty $u(x_{pt})$	b	$\sigma_{pt} = b \cdot x_{pt}$
Difenoconazole	9	106,00	21,52	20,30	7,17	0,22	23,78

$$[u(X_{pt})]^2 / \sigma_{pt}^2 \leq 0,1$$

Difenoconazole, assigned value: 106,00 $\mu\text{g}/\text{kg}$



$|z| \leq 2$ = satisfactory $2 < |z| \leq 3$ = questionable
 $|z| > 3$ = unsatisfactory * = outliers

Test material VF1770, lyophilized lettuce

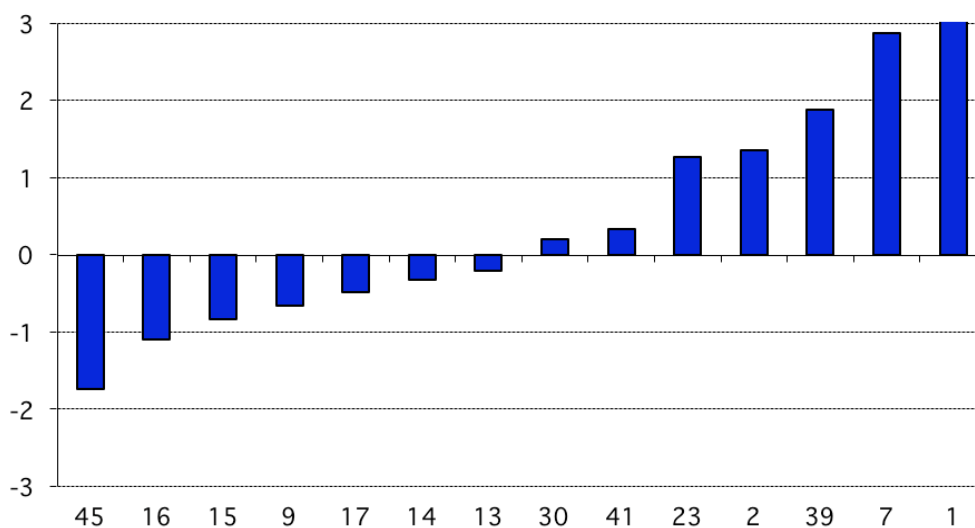
Uncorrected for recovery:
 Concentration, arithmetic mean ($n=14$) 139,41 $\mu\text{g}/\text{kg}$
 Standard deviation ($n=14$) 121,13 $\mu\text{g}/\text{kg}$
 Coefficient of variation ($n=14$) 86,89%

Table 6: assigned value and standard deviations (uncorrected for recovery data).

Analyte	Assigned value ($\mu\text{g}/\text{kg}$)				Standard deviation for proficiency assessment		
	Data points, n	Median	MADe	CV	Standard uncertainty $u(x_{pt})$	b	$\sigma_{pt} = b \cdot x_{pt}$
Difenoconazole	14	103,30	33,10	32,04	8,85	0,23	23,26

$$[u(X_{pt})]^2 / \sigma_{pt}^2 \leq 0,1$$

Difenoconazole, assigned value: 103,30 $\mu\text{g}/\text{kg}$



$|z| \leq 2$ = satisfactory $2 < |z| \leq 3$ = questionable
 $|z| > 3$ = unsatisfactory * = outliers

Test material VF1770, lyophilized lettuce

Table 7: results of analyses performed on test material VF1770 (spiked sample): pesticides detection.

VF1770						
assigned value dimethoate : 146,74 µg/kg (corrected for recovery)						
satisfactory range : 84,06-209,42 µg/kg						
assigned value dimethoate: 160,61 µg/kg (uncorrected for recovery)						
satisfactory range : 92,93-228,30 µg/kg						
Lab. code	Result corrected for recovery (µg/kg)	Result uncorrected for recovery (µg/kg)	Recovery %	z-score (corrected)	z-score (uncorrected)	LOQ (µg/kg)
1	342,8	301,7	88	6,26	4,17	3
2	131	162	81	-0,50	0,04	10
5						
7	-	201,52	113,09		1,21	5,00
8						
9	122,7	138,9	113,2	-0,77	-0,64	10
10						
12	NS					
13	<5	-				10
14	139	150	108,1	-0,25	-0,31	10
15	146,74	149,13	98,38	0,00	-0,34	10
16	116	116	100	-0,98	-1,32	10
17	189	147	77,5	1,35	-0,40	10
22						
23	-	176			0,45	10
27	<0,4	<0,4				1,7
30	-	170			0,28	10
32						
39	-	161,92	71,15		0,04	10
41	-	163			0,07	10
45	199	157	79	1,67	-0,11	10
50	172,68	162,89	94,33	0,83	0,07	10

Test material VF1770, lyophilized lettuce

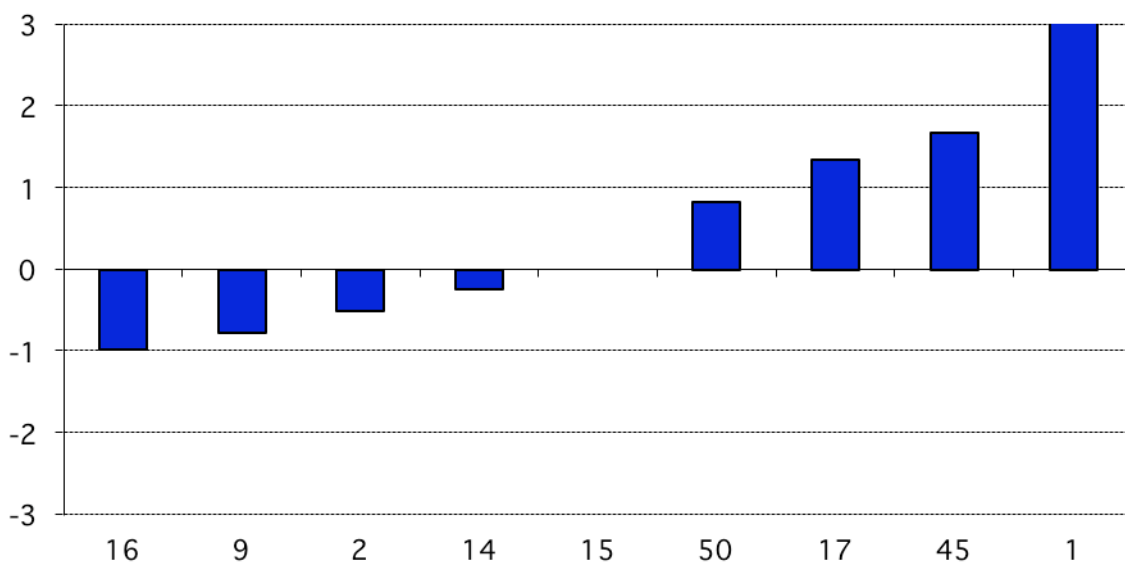
Corrected for recovery:
 Concentration, arithmetic mean ($n = 9$) 173,21 $\mu\text{g}/\text{kg}$
 Standard deviation ($n = 9$) 69,96 $\mu\text{g}/\text{kg}$
 Coefficient of variation ($n = 9$) 40,39%

Table 8: assigned value and standard deviations (corrected for recovery data).

Analyte	Assigned value ($\mu\text{g}/\text{kg}$)				Standard deviation for proficiency assessment		
	Data points, n	Median	MADe	CV	Standard uncertainty $u(x_{pt})$	b	$\sigma_{pt} = b \cdot x_{pt}$
Dimethoate	9	146,74	38,46	26,21	12,82	0,21	31,34

$$0,1 < [u(x_{pt})]^2 / \sigma_{pt}^2 \leq 0,5\%$$

Dimethoate, assigned value: 146,74 $\mu\text{g}/\text{kg}$



$|z| \leq 2$ = satisfactory $2 < |z| \leq 3$ = questionable
 $|z| > 3$ = unsatisfactory * = outliers

Test material VF1770, lyophilized lettuce

Uncorrected for recovery:

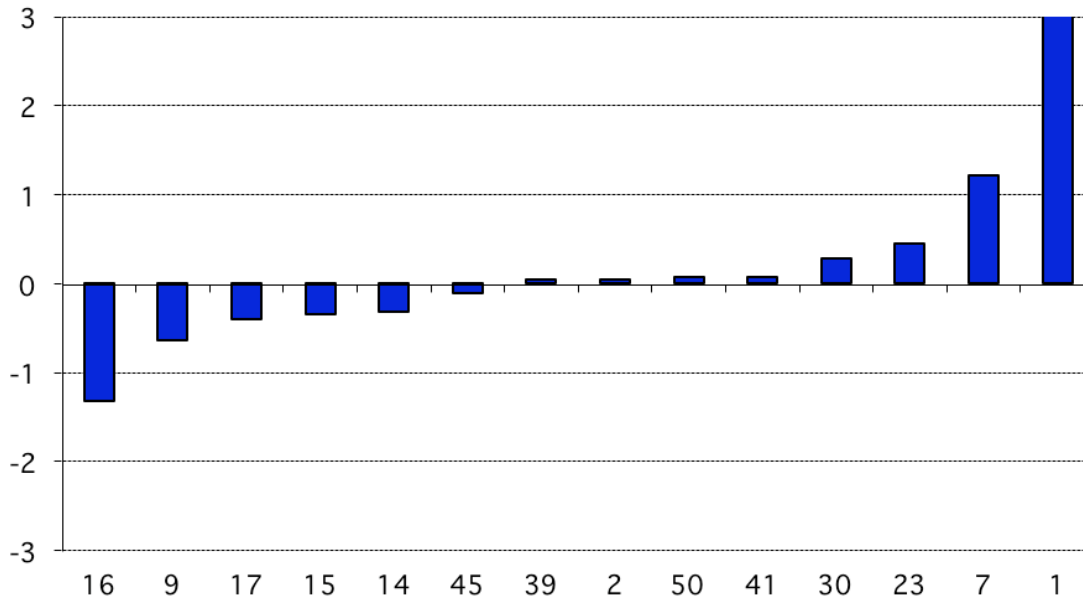
Concentration, arithmetic mean ($n=14$) 168,36 µg/kg
 Standard deviation ($n=14$) 42,95 µg/kg
 Coefficient of variation ($n=14$) 25,51%

Table 9: assigned value and standard deviations (uncorrected for recovery data).

Analyte	Assigned value (µg/kg)				Standard deviation for proficiency assessment		
	Data points, n	Mean from Algorithm A	SD	CV	Standard uncertainty $u(x_{pt})$	b	$\sigma_{pt} = b \cdot x_{pt}$
Dimethoate	14	160,61	19,28	12,01	5,15	0,21	33,84

$$[u(X_{pt})]^2 / \sigma_{pt}^2 \leq 0,1$$

Dimethoate, assigned value: 160,61 µg/kg



$|z| \leq 2$ = satisfactory $2 < |z| \leq 3$ = questionable
 $|z| > 3$ = unsatisfactory * = outliers

Test material VF1770, lyophilized lettuce

Table 10: results of analyses performed on test material VF1770 (spiked sample): pesticides detection.

VF1770 fenhexamid				
Lab. code	Result corrected for recovery (µg/kg)	Result uncorrected for recovery (µg/kg)	Recovery %	LOQ (µg/kg)
1	NS			
2	206	268	77	10
5				
7	NS	NS		
8				
9	138	154,4	119,9	20
10				
12	NS			
13	NS			
14	277	289	104,30	10
15	NS			
16	257,9	260	101	10
17	211	150	71	10
22				
23	-	152		10
27	266	266	100	1,8
30	-	135	70	10
32				
39	-	221,23	97,13	10
41	-	186		10
45	192	154	80	10
50	NS			

Test material VF1770, lyophilized lettuce

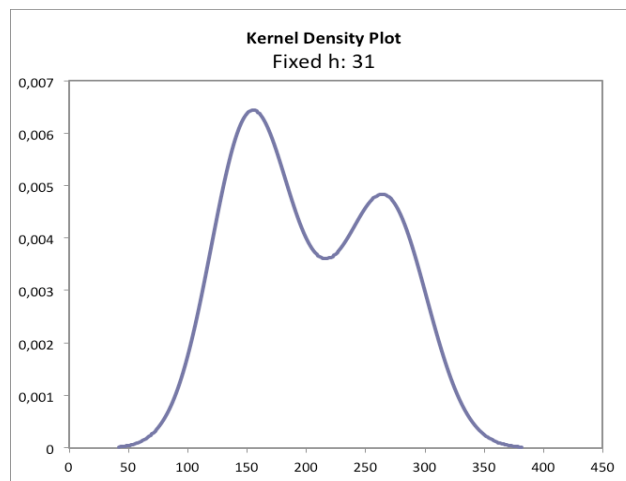
Corrected for recovery:

Concentration, arithmetic mean ($n=7$)	221,13 $\mu\text{g}/\text{kg}$
Standard deviation ($n=7$)	49,29 $\mu\text{g}/\text{kg}$
Coefficient of variation ($n=7$)	22,29%

Is not possible to provide assigned value for fenhexamid because the numbers of data are < 8 .

Uncorrected for recovery:

Concentration, arithmetic mean ($n=11$)	203,24 $\mu\text{g}/\text{kg}$
Standard deviation ($n=11$)	58,53 $\mu\text{g}/\text{kg}$
Coefficient of variation ($n=11$)	28,80%



It was not possible to assigned a value, because the data distribution is bimodal (see kernel diagram).
A group of participants have found a concentration about 150 $\mu\text{g}/\text{kg}$, another group about 250 $\mu\text{g}/\text{kg}$.

Test material VF1770, lyophilized lettuce

Table 11: results of analyses performed on test material VF1770 (spiked sample): pesticides detection.

Lab. code	VF1770 hexythiazox		Recovery %	LOQ (µg/kg)
	Result corrected for recovery (µg/kg)	Result uncorrected for recovery (µg/kg)		
1	NS			
2	157	199	79	10
5				
7	NS	NS		
8				
9	NS			
10				
12	NS			
13	NS			
14	129	151	117,0	10
15	NS			
16	138,6	140	101	10
17	211	148	70	10
22				
23	-	201		10
27	NS			
30	-	< 10		10
32				
39	-	>10		10
41	-	154		10
45	139	106	76	5
50	NS			

Test material VF1770, lyophilized lettuce

Corrected for recovery:

Concentration, arithmetic mean ($n=5$)	154,92 μ g/kg
Standard deviation ($n=5$)	32,94 μ g/kg
Coefficient of variation ($n=5$)	21,26%

Uncorrected for recovery:

Concentration, arithmetic mean ($n=7$)	157,00 μ g/kg
Standard deviation ($n=7$)	33,46 μ g/kg
Coefficient of variation ($n=7$)	21,31%

Is not possible to provide assigned value for hexythiazox because the numbers of data are < 8.

Test material VF1770, lyophilized lettuce

Table 12: results of analyses performed on test material VF1770 (spiked sample): pesticides detection.

VF1770						
assigned value iprodion: 184,44 µg/kg (corrected for recovery)						
satisfactory range : 108,32-260,56 µg/kg						
assigned value iprodion: 162,19 µg/kg (uncorrected for recovery)						
satisfactory range : 93,94-230,43µg/kg						
Lab. code	Result corrected for recovery (µg/kg)	Result uncorrected for recovery (µg/kg)	Recovery %	z-score (corrected)	z-score (uncorrected)	LOQ (µg/kg)
1	250,0	235,1	94	1,72	2,14	2
2	161	156	103	-0,62	-0,18	10
5						
7	NS	NS				
8						
9	135,1	146,3	108,3	-1,30	-0,47	20
10						
12	NS					
13	243,48	168,00	69	1,55	0,17	10
14	158	147	93,0	-0,69	-0,45	10
15	160,81	154,72	103,94	-0,62	-0,22	10
16	-	<10				
17	170	153	90	-0,38	-0,27	10
22						
23	-	167			0,14	10
27	NS					
30	-	247	114		2,49	10
32						
39	-	177,18	135,1		0,44	10
41	-	167			0,14	10
45	185	148	80	0,01	-0,42	10
50	196,53	150,72	76,69	0,32	-0,34	10

Test material VF1770, lyophilized lettuce

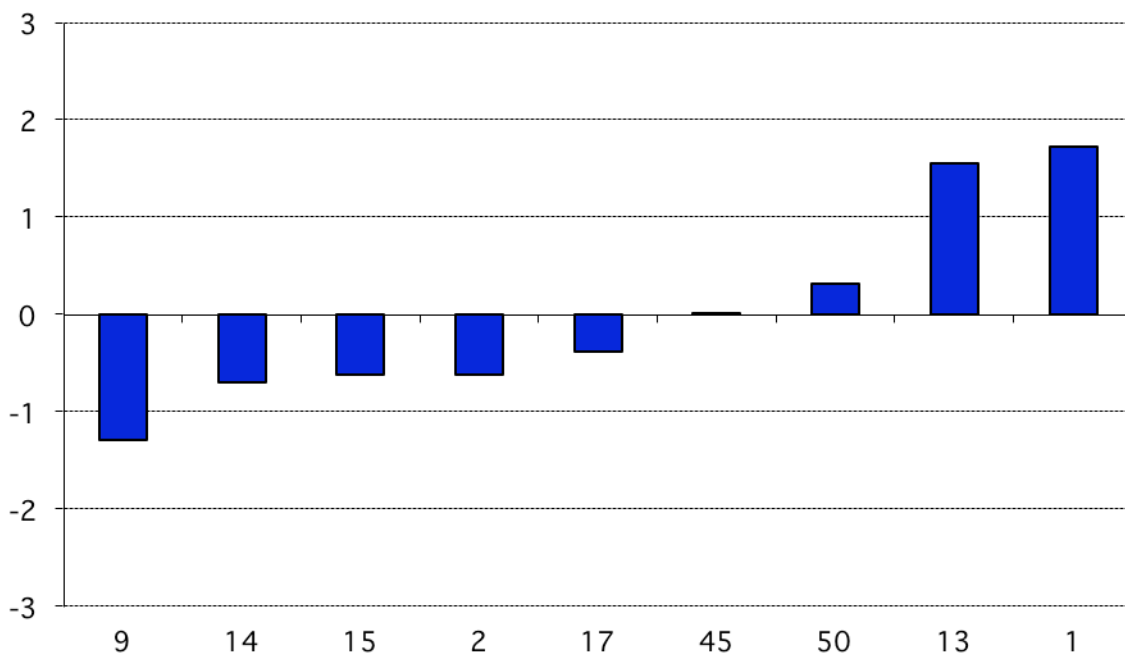
Corrected for recovery:
 Concentration, arithmetic mean ($n = 9$) 184,44 $\mu\text{g/kg}$
 Standard deviation ($n = 9$) 39,34 $\mu\text{g/kg}$
 Coefficient of variation ($n = 9$) 21,33%

Table 13: assigned value and standard deviations (corrected for recovery data).

Analyte	Assigned value ($\mu\text{g/kg}$)				Standard deviation for proficiency assessment		
	Data points, n	Mean from Algorithm A	SD	CV	Standard uncertainty $u(x_{pt})$	b	$\sigma_{pt} = b \cdot x_{pt}$
Iprodion	9	184,44	44,59	24,17	14,86	0,21	38,06

$0,1 < [u(x_{pt})]^2 / \sigma_{pt}^2 \leq 0,5\%$

Iprodion, assigned value: 184,44 $\mu\text{g/kg}$



$|z| \leq 2$ = satisfactory $2 < |z| \leq 3$ = questionable
 $|z| > 3$ = unsatisfactory * = outliers

Test material VF1770, lyophilized lettuce

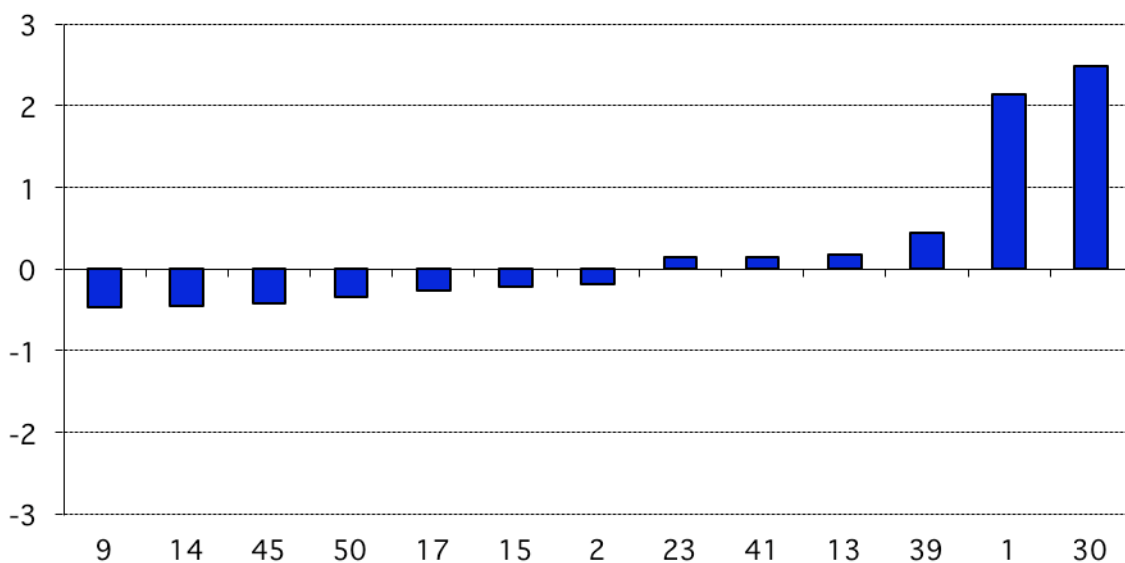
Uncorrected for recovery:
 Concentration, arithmetic mean ($n=13$) 170,54 $\mu\text{g}/\text{kg}$
 Standard deviation ($n=13$) 32,79 $\mu\text{g}/\text{kg}$
 Coefficient of variation ($n=13$) 19,23%

Table 14: assigned value and standard deviations (uncorrected for recovery data).

Analyte	Assigned value ($\mu\text{g}/\text{kg}$)				Standard deviation for proficiency assessment		
	Data points, n	Mean from Algorithm A	SD	CV	Standard uncertainty $u(x_{pt})$	b	$\sigma_{pt} = b \cdot x_{pt}$
Iprodion	13	162,19	16,38	10,10	4,54	0,21	34,12

$$[u(X_{pt})]^2 / \sigma_{pt}^2 \leq 0,1$$

Iprodion , assigned value: 162,19 $\mu\text{g}/\text{kg}$



$|z| \leq 2$ = satisfactory $2 < |z| \leq 3$ = questionable
 $|z| > 3$ = unsatisfactory * = outliers

Test material VF1770, lyophilized lettuce

Table 15: results of analyses performed on test material VF1770 (spiked sample): pesticides detection.

VF1770						
assigned value triadimenol: 75,94 µg/kg (corrected for recovery)						
satisfactory range : 40,12-111,75µg/kg						
assigned value triadimenol: 65,00 µg/kg (uncorrected for recovery)						
satisfactory range : 33,61-96,39 µg/kg						
Lab. code	Result corrected for recovery (µg/kg)	Result uncorrected for recovery (µg/kg)	Recovery %	z-score (corrected)	z-score (uncorrected)	LOQ (µg/kg)
1	98,8	84,0	85	1,28	1,21	3
2	68	87	78	-0,44	1,40	10
5						
7	NS					
8						
9	NS					
10						
12	NS					
13	NS					
14	64	65	101,5	-0,67	0,00	10
15	63,51	63,20	100,49	-0,69	-0,11	20
16	59,5	59	99,1	-0,92	-0,38	10
17	67	58	86	-0,50	-0,45	10
22						
23	-	140			4,78	10
27	136,0	129,5	105	3,35	4,11	2,5
30	-	59			-0,38	99
32						
39	-	97,23	101,16		2,05	10
41	NS					
45	81	64	79	0,28	-0,06	10
50	NS					

Test material VF1770, lyophilized lettuce

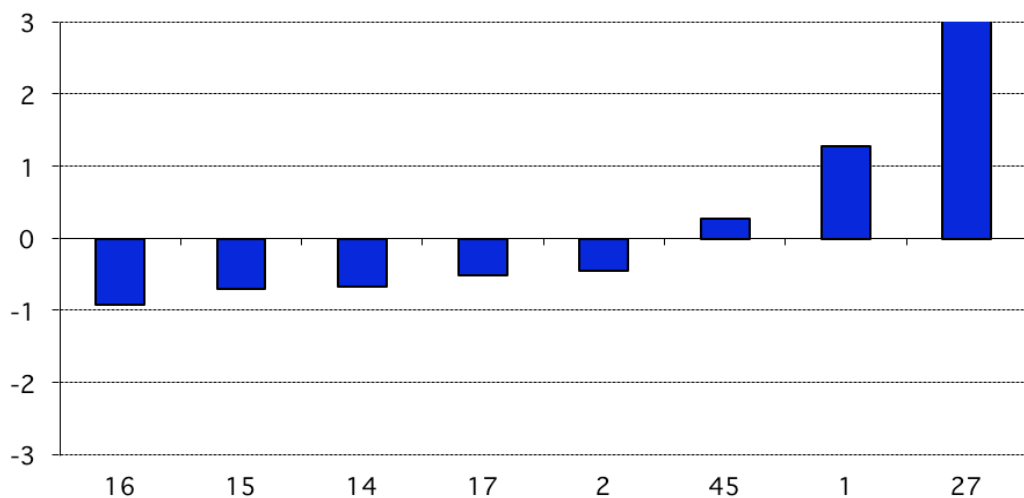
Corrected for recovery:
 Concentration, arithmetic mean ($n = 8$) 79,73 $\mu\text{g}/\text{kg}$
 Standard deviation ($n = 8$) 26,05 $\mu\text{g}/\text{kg}$
 Coefficient of variation ($n = 8$) 32,68%

Table 16: assigned value and standard deviations (corrected for recovery data).

Analyte	Assigned value ($\mu\text{g}/\text{kg}$)				Standard deviation for proficiency assessment		
	Data points, n	Mean from Algorithm A	SD	CV	Standard uncertainty $u(x_{pt})$	b	$\sigma_{pt} = b \cdot x_{pt}$
Triadimenol	8	75,94	19,83	26,11	7,01	0,24	17,91

$$0,1 < [u(x_{pt})]^2 / \sigma_{pt}^2 \leq 0,5\%$$

Triadimenol, assigned value: 75,94 $\mu\text{g}/\text{kg}$



$|z| \leq 2$ = satisfactory $2 < |z| \leq 3$ = questionable
 $|z| > 3$ = unsatisfactory * = outliers

Test material VF1770, lyophilized lettuce

Uncorrected for recovery:

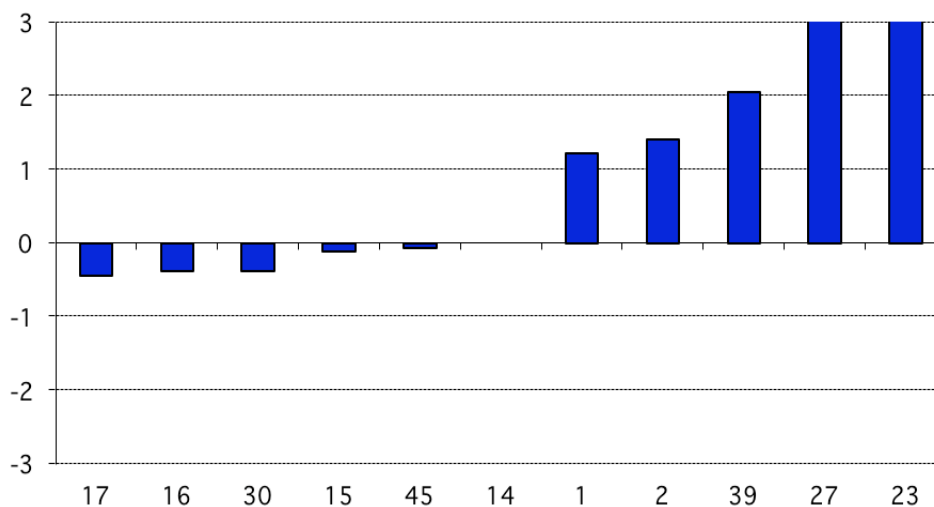
Concentration, arithmetic mean ($n=11$) 82,36 µg/kg
 Standard deviation ($n=11$) 29,12 µg/kg
 Coefficient of variation ($n=11$) 35,36%

Table 17: assigned value and standard deviations (uncorrected for recovery data).

Analyte	Assigned value (µg/kg)				Standard deviation for proficiency assessment		
	Data points, n	Median	MADe	CV	Standard uncertainty $u(x_{pt})$	b	$\sigma_{pt}=b \cdot x_{pt}$
Triadimenol	11	65,00	10,38	15,97	3,13	0,24	15,69

$$[u(X_{pt})]^2 / \sigma_{pt}^2 \leq 0,1$$

Triadimenol, assigned value: 65,00 µg/kg



$|z| \leq 2$ = satisfactory $2 < |z| \leq 3$ = questionable
 $|z| > 3$ = unsatisfactory * = outliers

Test material VF1770, lyophilized lettuce

Table 18: other compounds detected in the test material:

Lab cod	other compounds:
12	uncorrect: Acetochlor: 0,010 ppb – Azoxystrobin: 0,021 ppb – Carbofuran: 0,90 ppb - Pirimiphos-methyl: 0,31 ppb - Prochloraz: 0,022 ppb – Propoxur: 0,025 ppb
13	A few residue present were also detected in the blank sample at low concentrations close our LD 5 ug/kg. For example: Pyridaben.
30	Pyrifenox: > 10ppb – Fenamidone: >10ppb
50	Cimoxanil: corrected 174,88ppb - uncorrected 168,07ppb

ANNEX

ANALYTICAL METHODS USED

PESTICIDES IN LYOPHILIZED LETTUCE, VF1770

Is the method already accredited?

	Laboratory code
yes	01-02-07-13-14-15-16-17-27-30-39-41-45
no	09-12-23-50

Analytical methods used by participants

Methods	Laboratory code
HPLC/MS/MS	01-02-07-14-16-17-23-27-30-39-41-45-50
HPLC Fluorescenza	15
GC/MS/MS	01-12-13-14-15-17-27-30-39-41-45-50
GC/MS	02-16
GC-ELD	09
GC-NPD / GC-ECD	15
GC-uECD	12
GC-FPD	07

Is the analytical method a routine one?

	Laboratory code
Yes	01-09-13-14-15-16-17-27-30-39-41-45-50

Do you participate regularly to pesticides proficiency test (PT)?

	Laboratory code
Yes: one time per year	07-09-13-15-23-50
Yes: more than once per year	01-02-14-16-17-27-30-39-41-45
No	12

Number of replicates (1 replicate = 1 extraction)

	Laboratory code
2	02-07-12-13-14-15-16-17-23-27-30-41-45-50
3	09
4	39

Source of standards (only for detected molecule)

	Laboratory code
dr. Ehrenstorfer	02-07-09-12-16-17-30-50
Sigma-Aldrich	01-02-09-15-41-45
LGC	13-45
Chem -service	02-15
Lab instrument	23-39
Chebios	27
other	41

Percentage of recovery measured in the same analytical run than test material?

	Laboratory code
Yes	02-07-09-12-13-14-15-17-27-30-39-45-50
No	16-23

Blank sample

Blank sample used for spiking	Laboratory code
Blank supplied by PT provider	01-02-07-09-12-13-14-15-16-17-23-27-39-45-50
In house blank sample (lettuce)	09-41
Reagent blank and solvent	12

Sample preparation

Amount of test sample for the extraction (after reconstitution)

Sample volume (g)	Laboratory code
1	45
5	23
10	02-07-09-12-13-14-15-16-17-27-30-39-41-50
20	45
23,7	01

GC and HPLC sample treatment

	Laboratory code
Extraction solvent	
acetone	45
acetonitrile	02-07-09-12-13-14-15-16-17-23-27-30-39-41-45-50
ethyl acetate	45
cyclohexan	45
pH adjusted	
Yes	01-13-14-16-27-30
No	02-09-12-15-17-23-39-41-50
Extraction techniques	
QuEChERS	01-02-07-13-14-15-16-17-23-27-30-39-41-45-50
macerate at room temperature	09-12-30-41-45
Clean up	
solid phase extraction (SPE)	02-09-12-15-17-27-30
DPE	13
d-SPE	23-50
PSA/GCB	07
SEC	45

HPLC mobil phase components

	Laboratory code
acetonitrile	14-15-16-30
water	01-02-07-13-14-15-16-23-27-30-41-45
formic acid	01-13-23-27-30-45
methanol	01-02-07-13-23-27-41-45
ammonium acetate	07-13-16-23
ammonium formiate 5mM / 0,1% formic acid	17
ammonium formiate	45-50

Identification by mass spectrometry of detected molecules

	Laboratory code
Yes	01-07-12-13-14-15-16-17-23-27-30-39-41-45-50
No	02-09