Interlaboratory Comparison Measurement Pest-1
Final Report

02.06.2009

Report compiled by Koit Herodes and Ivo Leito

This report is available at the website of UT at http://www.ut.ee/katsekoda/ILC/
Testing Centre, University of Tartu

Tartu 2009

Table of Contents

1 The Aim of the Intercomparison

The aim of the Pest-1 intercomparison was to allow the participating laboratories to assess their performance in determining the following pesticide residues in tomato matrix:

1. Carbendazim
2. Thiabendazole
3. Imazalil
4. Methiocarb

2 Organization

2.1 General

The intercomparison measurement was organized by the Testing Centre of University of Tartu (below UT). Contact information of the organizer:

University of Tartu, Testing Centre
http://www.ut.ee/katsekoda
Jakobi 2, 51014 Tartu, Estonia
Contact person: Koit Herodes, koit.herodes@ut.ee

This report is publicly available via the website of UT at http://www.ut.ee/katsekoda/ILC/. The participants are listed in this report but the results are presented in random order, so that the results cannot be traced back to the participants. Every participant will receive a private letter revealing his/her result number and permitting assessment of performance.

2.2 The Samples

The samples – tomatoes – were bought from local supermarket. The tomatoes were not organically grown or otherwise guaranteed to be free from pesticide residues. Subsample was drawn and analyzed to confirm that the residues of target pesticides do not incur in the sample to any significant level. Target pesticides were spiked into homogenized sample and mixed well.
The samples were stored refrigerated (-60°C) and frozen samples were sent to participants. The laboratories received three random samples from the batch. Two of the samples were spiked at the same level and one was not spiked (blank).

2.3 Data Treatment

The evaluation of participant data was done at UT according to the ISO Guide 43-1. The z-score approach was used. The z-score for a particular measured value of a participant is calculated according to the following equation:

$$z = \frac{x - x_c}{s} \qquad (1)$$

where x is the participant's value, x_c is the consensus value and s is the target standard deviation. The consensus values are found as the mean values after elimination of outliers. The target standard deviation in our case is found as the real standard deviation of the participant values after elimination of outliers.
Elimination of outliers was done using the Cochran's and Grubbs tests[1].

Assessment of participant performance was carried out in two ways.

(1) Absolute values of z-scores (|z| values) are used for assessing the acceptability of the results as described in Table 1.

Table 1. Assessment of Acceptability of the Results Using z-Scores.

|z| Value	Acceptability of the Result	Required Action
$\|z\| \leq 2$	Acceptable result	No action is required
$2 < \|z\| < 3$	Doubtful result	Preventive action is required
$\|z\| \geq 3$	Unacceptable result	Corrective action is required

(2) Pairwise E_n values between participants presented as tables. This is done using the E_n numbers as described in ISO Guide 43-1:

$$E_n = \frac{C_{lab1} - C_{lab2}}{\sqrt{U_{lab1}^2 + U_{lab2}^2}} \qquad (2)$$

where C_{lab1} and C_{lab2} are the results of the two laboratories that are compared and U_{lab1} and U_{lab2} are their expanded uncertainties. Equation 2 is adequate, if between-sample variability is significantly (more than 5 times) lower than between-participant variability.

Agreement between two results is considered acceptable if $|E_n| \leq 1$.

[1] OFFICIAL METHODS OF ANALYSIS OF AOAC INTERNATIONAL Dr. William Horwitz, editor, CD-ROM edition: 17th ed., 2nd revision current through 2003, Gaithersburg (Md.) : AOAC International, 2003

3 Participants

The participants are listed in Table 2.

Table 2. Participants of Pest-1.

Institution	Country
Health Protection Inspectorate, Tartu laboratory	Estonia
Environmental Protection Institute	Slovenia
Agricultural Research Centre	Estonia
Finnish Customs Laboratory	Finland
Health Protection Inspectorate, Central laboratory	Estonia
Testing Centre of University of Tartu	Estonia

4 Results

4.1 Results of the Participants

Results of the participants are presented in Table 3. The results are presented with the same number of decimal digits as given by the participants. Some participants presented relative uncertainty; conversion was done by the organizer.

Table 3. Participant Results together with the Expanded Uncertainties and the Derived Consensus Values.

		Carbendazim		Thiabendazole		Imazalil		Methiocarb	
Part.	Samp	c, mg/kg	U, mg/kg (k=2)	c, mg/kg	U, mg/kg (k=2)	c, mg/kg	U, mg/kg (k=2)	c, mg/kg	U, mg/kg (k=2)
Blank samples									
P1	A29	<0.01		<0.01		<0.01		<0.01	
P2	n.r.	n.r.		n.r.		n.r.		n.r.	
P3	A26	0.013	0.000375	0.01	0.000181	0.006	8.18E-05	0.009	0.000257
P4	A23	<0.01		<0.01		<0.01		<0.01	
P5	A28	n.f.		n.f.		n.f.		n.f.	
P6	A30	<0.01		<0.01		<0.01		<0.01	
Spiked samples									
P1	A4	0.625	0.563	0.233	0.210	0.227	0.204	0.170 [b]	0.153
P1	A12	0.587	0.529	0.243	0.219	0.245	0.220	0.212 [b]	0.191
P2	A6	0.92 [b]	0.15	0.38 [b]	0.06	n.r.	n.r.	n.r.	n.r.
P2	A16	n.r.	n.r.	n.r.	n.r.	0.23 [b]	0.05	0.37 [b]	0.08
P3	A8	0.550	0.0682 [a]	0.413	0.043778 [a]	0.222	0.036852 [a]	0.300	0.0858 [a]
P3	A15	0.541	0.000375 [a]	0.414	0.000181 [a]	0.233	8.18E-05 [a]	0.296	0.000257 [a]
P4	A9	0.45	0.225 [a]	n.r.	n.r.	0.35	0.175 [a]	0.42	0.21 [a]
P4	A17	0.36	0.18 [a]	n.r.	n.r.	0.29	0.145 [a]	0.42	0.21 [a]
P5	A2	0.501	0.145	0.324	0.087	0.306	0.073	0.281	0.076
P5	A13	0.522	0.151	0.330	0.089	0.318	0.073	0.272	0.074
P6	A3	0.57	0.171 [a]	0.31	0.093 [a]	0.27	0.081 [a]	0.28	0.084 [a]
P6	A18	0.59	0.177 [a]	0.30	0.09 [a]	0.26	0.078 [a]	0.27	0.081 [a]
	x_c	0.5296		0.320875		0.2721		0.317	
	s	0.077602		0.067181		0.042951		0.064194	

Notes:
Part. – Participant code. (The participating laboratories are assigned random codes, the order is different from that in the table of participants.)
Samp. – Sample code.
n.r. – not reported by the participant
n.f. – residues reported as not found by the participant
x_c – consensus value
s – target standard deviation
[a] The uncertainties calculated form the relative uncertainty reported by the participant.
[b] Identified as outliers by Cochran's test and therefore excluded from the calculation of consensus value and target standard deviation.

5 Discussion

5.1 Elimination of Outliers Using the Cochran's and Grubbs Tests

Altogether 6 of the reported results were eliminated from consensus value and target standard deviation calculation based on the Cochran's test. Four results were excluded because respective results of parallel measurements were missing.

5.2 Assessment of the results of blank sample analysis

Four participants reported the results of blank (unspiked) sample analysis as <0.01 mg/kg. One participant gave verbal response "Not found". Only one participant reported numerical values to analyte concentrations along with the uncertainties.

5.3 Assessment of Participant Results by the z-Score Approach

For spiked samples in total 42 results were submitted. According to the z-score approach 39 of them (93%) were acceptable, 2 (5%) were doubtful and 1 (2%) was unacceptable (See Table 4). The standard deviations after outlier elimination are in the range of 14 .. 21% of the consensus value, which can be considered a good result for trace pesticide analysis, especially keeping in mind that:

1. All participants used different sample preparation methods.
2. The results are not corrected for the recovery (common practice in the field).

Table 4. Participant z-scores (absolute values).

Participant	Sample	Carbendazim	Thiabendazole	Imazalil	Methiocarb
P1	A4	1.2	1.3	1.1	2.3 [a]
P1	A12	0.7	1.2	0.6	1.6
P2	A6	5.0 [b]	0.9	n.r.	n.r.
P2	A16	n.r.	n.r.	1.0	0.8
P3	A8	0.3	1.4	1.2	0.3
P3	A15	0.1	1.4	0.9	0.3
P4	A9	1.0	n.r.	1.8	1.6
P4	A17	2.2 [a]	n.r.	0.4	1.6
P5	A2	0.4	0.0	0.8	0.6
P5	A13	0.1	0.1	1.1	0.7
P6	A3	0.5	0.2	0.0	0.6
P6	A18	0.8	0.3	0.3	0.7

Notes:
n.r. – result not reported by the participant
[a] Doubtful result
[b] Unacceptable result

Although according to the z-score approach most of the participants performed satisfactorily, it is of interest to compare the self-declared uncertainties of the participant results to the agreement between the participant results. The picture is quite uniform. In the case of all pesticides it is possible to find a value (not necessarily the consensus value) with which all the non-outlying participant uncertainty ranges overlap.

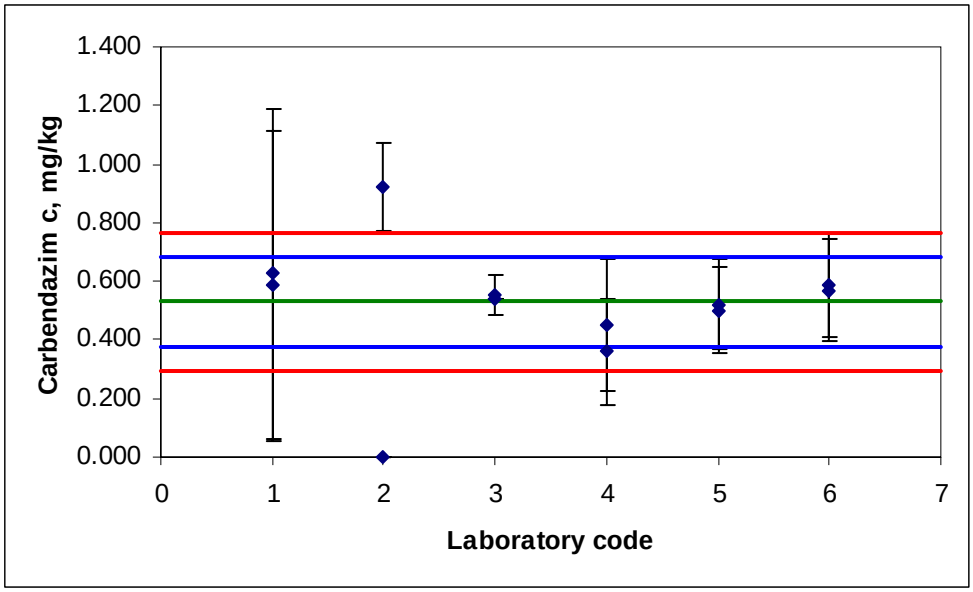

Figure 1. Results of participants for Carbendazim with the z-score boundaries.

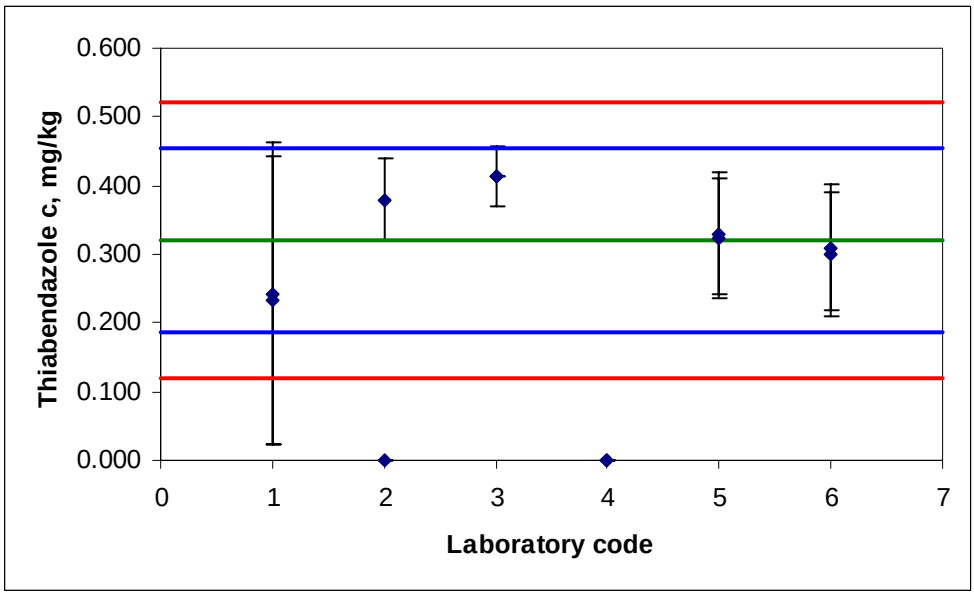

Figure 2. Results of participants for Thiabendazole with the z-score boundaries.

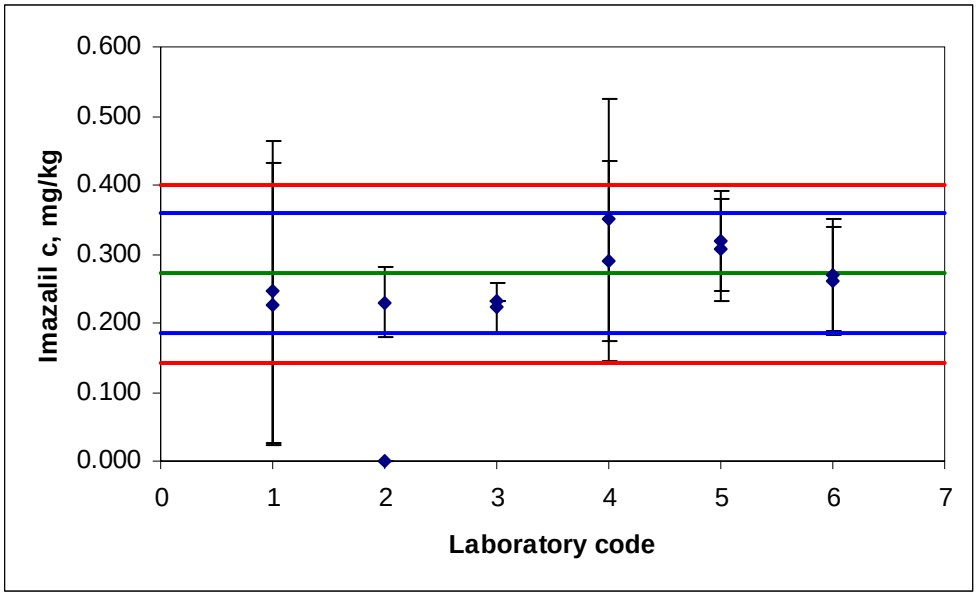

Figure 3. Results of participants for Imazalil with the z-score boundaries.

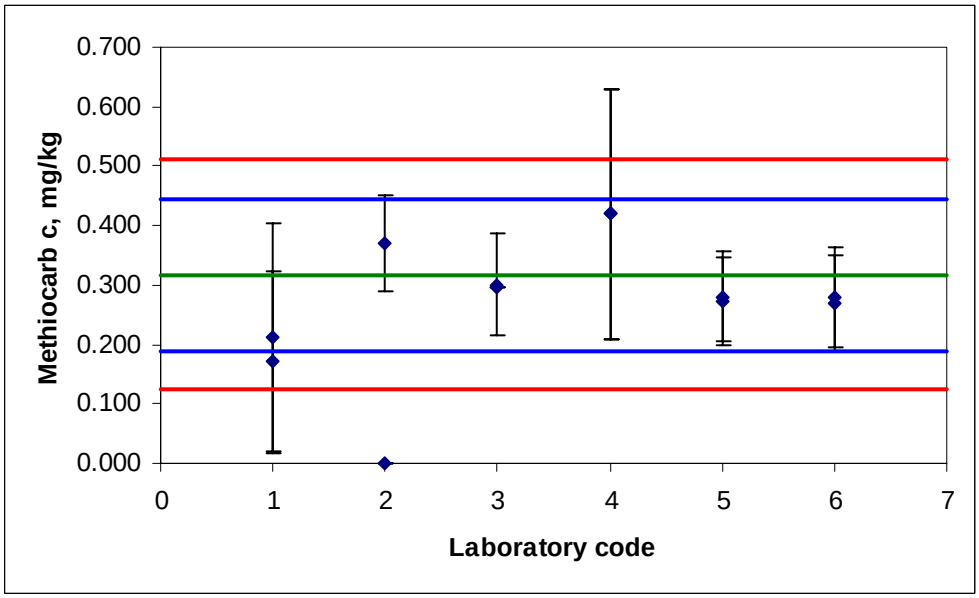

Figure 4. Results of participants for Methiocarb with the z-score boundaries.

5.4 Pair-wise Comparison of Participant Results

The paired comparisons are presented in Tables 5 to 8. The results are good. The worst case is Carbendazim determination, having four disagreeing pairs (all involving a particular participant). In the case of Thiabendazole and Imazalil there is only one disagreeing pair and in the case of Methiocarb the results of all laboratories mutually agree.

The uncertainties of the results have been in general estimated realistically.

Table 5. Pair-wise comparison of E_n values for Carbendazim measurement results.

Participant	P1	P2	P3	P4	P5	P6
P1	0.0	0.6	-0.1	-0.3	-0.2	0.0
P2	-0.6	0.0	-2.4	-2.0	-1.9	-1.5
P3	0.1	2.4	0.0	-0.7	-0.2	0.2
P4	0.3	2.0	0.7	0.0	0.4	0.7
P5	0.2	1.9	0.2	-0.4	0.0	0.3
P6	0.0	1.5	-0.2	-0.7	-0.3	0.0

Table 6. Pair-wise comparison of E_n values for Thiabendazole measurement results.

Participant	P1	P2	P3	P4	P5	P6
P1	0.0	0.6	0.8	n.r.	0.4	0.3
P2	-0.6	0.0	0.5	n.r.	-0.5	-0.7
P3	-0.8	-0.5	0.0	n.r.	-0.9	-1.1
P4	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
P5	-0.4	0.5	0.9	n.r.	0.0	-0.2
P6	-0.3	0.7	1.1	n.r.	0.2	0.0

n.r. – Not reported

Table 7. Pair-wise comparison of E_n values for Imazalil measurement results.

Participant	P1	P2	P3	P4	P5	P6
P1	0.0	0.0	0.0	0.3	0.3	0.1
P2	0.0	0.0	0.0	0.5	0.9	0.4
P3	0.0	0.0	0.0	0.6	1.1	0.4
P4	-0.3	-0.5	-0.6	0.0	0.0	-0.3
P5	-0.3	-0.9	-1.1	0.0	0.0	-0.4
P6	-0.1	-0.4	-0.4	0.3	0.4	0.0

Table 8. Pair-wise comparison of E_n values for Methiocarb measurement results.

Participant	P1	P2	P3	P4	P5	P6
P1	0.0	0.9	0.6	0.8	0.5	0.4
P2	-0.9	0.0	-0.7	0.2	-0.9	-0.8
P3	-0.6	0.7	0.0	0.6	-0.2	-0.2
P4	-0.8	-0.2	-0.6	0.0	-0.6	-0.6
P5	-0.5	0.9	0.2	0.6	0.0	0.0
P6	-0.4	0.8	0.2	0.6	0.0	0.0

The pair-wise agreement of participant results is good.