

**relana[®]-Method-Ringtest
No. 02/2016
Metabolites of Pesticides**

Report



August 2016

Summary

The method ring test was designed and organised exclusively for members of the relana[®] quality circle. It offers the relana[®] laboratories the opportunity to test their analytical performance with respect to the quantification of relevant metabolites of pesticides in pears and tomatoes. The results of the method ring test are discussed in a subsequent relana[®] meeting and thus the relana[®] laboratories are offered the opportunity to exchange their knowledge and to identify current shortcomings and to further improve the applied analytical methods.

Ten relana[®] laboratories across six European countries took part in the method ring test.

Two test materials – pear and tomato - and the corresponding blank materials were provided to the participants. The test materials were prepared of organic pears and tomatoes, which were homogenised and spiked thereafter.

The test materials were spiked with **27 pesticide metabolites** at different concentration levels.

The report contains an assessment related to

- the trueness of the results. The trueness is expressed as the coverage of the spiked level in %. The coverage should be at least between 70 and 120 % of the spiked level.
- the comparability of the results. The evaluation of the comparability is based on the z-score model. The z-score should be at least $\leq |2|$.

Summary of the results:

- An **influence of the matrix** on the results is observed. In general, the mean recoveries (assigned values) are lower for the matrix pear compared to the matrix tomato.
- The most **challenging metabolites** are 3-OH-carbofuran, disulfoton-sulfone, fenthion-oxon and fenthion-sulfoxide.
- All laboratories reported comparable results for more than 70 % of the metabolites and both matrices.
- Test material **pear**: Six laboratories pass the comparability criterion for all metabolites, while seven laboratories pass the trueness criterion for > 75 % of the metabolites.
- Test material **tomato**: Four laboratories pass the comparability criterion for all metabolites, while four more laboratories quantified 26 out of 27 metabolites correctly. Two laboratories pass the trueness criterion for all parameters, while seven more laboratories quantified > 75 % of the metabolites within 70 to 120 % of the spiked levels.

Performance of the laboratories with respect to the matrix **pear**:

Pesticide metabolite	Spiked level [mg/kg]	Assigned value [mg/kg]	Total No of results	No of comparable results	No of true results
3-Hydroxy-carbofuran	0.0030	0.00254	8	8	5
BYI08330-enol	0.068	0.0517	10	10	8
BYI08330-enol-glucoside	0.13	0.101	10	10	9
BYI08330-keto-hydroxy	0.10	0.0880	10	9	8
BYI08330-mono-hydroxy	0.084	0.0690	10	10	9
Disulfoton-sulfone	0.038	0.0235	10	10	3
Disulfoton-sulfoxide	0.044	0.0361	10	10	9
DMPF	0.19	0.143	9	8	6
DMF	0.035	0.0278	9	9	9
Ethirimol	0.14	0.114	10	9	9
Fenthion-oxon	0.041	0.0214	10	10	1
Fenthion-oxon-sulfone	0.088	0.0719	10	9	8
Fenthion-oxon-sulfoxide	0.067	0.0636	10	10	9
Fenthion-sulfone	0.033	0.0250	10	10	9
Fenthion-sulfoxide	0.056	0.0393	10	10	5
Fipronil-sulfone	0.048	0.0370	10	10	8
FM-6-1	0.28	0.224	9	9	9
Methiocarb-sulfone	0.12	0.103	10	10	9
Methiocarb-sulfoxide	0.090	0.0816	10	10	10
Pentachloroaniline	0.066	0.0522	10	10	10
Phorate-sulfone	0.030	0.0257	9	9	9
Phorate-sulfoxide	0.046	0.0377	9	9	9
Phosmet-oxon	0.24	0.211	10	9	7
Phthalimide (PTI)	0.086	0.0838	10	10	10
TFNA	0.092	0.0702	10	9	7
TFNG	0.23	0.175	10	10	6
THPI	0.27	0.217	10	9	7



Performance of the laboratories with respect to the matrix **tomato**:

Pesticide metabolite	Spiked level [mg/kg]	Assigned value [mg/kg]	Total No of results	No of comparable results	No of true results
3-Hydroxy-carbofuran	0.0030	0.00268	8	8	6
BYI08330-enol	0.068	0.0643	10	10	10
BYI08330-enol-glucoside	0.13	0.110	10	10	8
BYI08330-keto-hydroxy	0.10	0.0946	10	9	8
BYI08330-mono-hydroxy	0.084	0.0799	10	10	10
Disulfoton-sulfone	0.038	0.0286	10	10	7
Disulfoton-sulfoxide	0.044	0.0401	10	10	10
DMPF (Amitraz metab.)	0.19	0.1731	9	9	8
DMF (Amitraz metab.)	0.035	0.0293	9	9	7
Ethirimol	0.14	0.127	10	9	9
Fenthion-oxon	0.041	0.0346	10	10	10
Fenthion-oxon-sulfone	0.088	0.0814	10	10	9
Fenthion-oxon-sulfoxide	0.067	0.0618	10	9	9
Fenthion-sulfone	0.033	0.0294	10	10	10
Fenthion-sulfoxide	0.056	0.0478	10	10	10
Fipronil-sulfone	0.048	0.0407	10	10	9
FM-6-1	0.28	0.245	9	9	9
Methiocarb-sulfone	0.12	0.120	10	10	10
Methiocarb-sulfoxide	0.090	0.0920	10	10	9
Pentachloroaniline	0.066	0.0576	10	10	10
Phorate-sulfone	0.030	0.0296	9	9	9
Phorate-sulfoxide	0.046	0.0440	9	9	9
Phosmet-oxon	0.24	0.238	10	10	6
Phthalimide (PTI)	0.086	0.0938	10	9	9
TFNA	0.092	0.0813	10	10	8
TFNG	0.23	0.191	10	10	10
THPI	0.27	0.244	10	10	9



The overall results of the test summarised as descriptive statistics as well as the spiked levels are presented in the tables above. The spiked levels are identical for both test materials.

The assigned values are in good accordance with the spiked levels for most of the metabolites in the two matrices. With respect to the test material tomato the assigned values of all metabolites are within 75 to 109 % of the spiked levels. With respect to the test material pear the assigned values of all but three metabolites are within 97 %. Metabolites with comparably low assigned values compared to the spiked levels are disulfoton-sulfone (62%), fenthion-oxon (52 %), and fenthion-sulfoxide (70 %). The assigned values are lower for the metabolites in the matrix pear compared to the assigned values in matrix tomato (exception: fenthion-oxon-sulfoxide).

Discussion of contingencies related to individual metabolites

3-Hydroxy-carbofuran

According to regulation (EC) No. 396/2005 the currently applicable MRLs of carbofuran are 0.001 mg/kg (pear) resp. 0.002 mg/kg (tomato). The residue definition of carbofuran is "sum of carbofuran (including any carbofuran generated from carbosulfan, benfuracarb or furathiocarb) and 3-OH carbofuran expressed as carbofuran".

The minimum requirements for analytical methods with respect to the reporting limits are defined by the currently applicable MRLs as defined by regulation (EC) No. 396/2005.

MRLs of carbofuran are 0.001 mg/kg for the matrix pear and 0.002 mg/kg for the matrix tomato. The laboratories thus should at least achieve a reporting limit of 0.001 for carbofuran as well as for the metabolite 3-OH-carbofuran.

7 out of 10 laboratories reported an inappropriate reporting limit of >0.001 mg/kg, four of them with a RL of 0.01 mg/kg, two with a RL of 0.02 mg/kg and one with a RL of 0.03 mg/kg. Only three laboratories are fit to verify samples for the compliance with the currently applicable MRL (at least for the matrix pear).

However, 8 out of 10 laboratories reported results even though they are below the reporting limits of some of the laboratories. Two laboratories were not able to quantify the spiked concentration level of 0.003 mg/kg 3-OH-carbofuran.

Eight out of ten laboratories reported the results with an accuracy of one significant figure, while two laboratories (labs 5, 10) reported two significant figures. As a consequence of the reporting, the results of those eight laboratories were either at 67 % of the spiked level or at 100 % of the spiked level.

Disulfoton-sulfone

The recoveries of disulfoton-sulfone are low for both matrices. The assigned values are slightly above (75 %) resp. slightly below (62 %) the lower side of the accepted range with respect to the trueness criterion. As a consequence, 7 out of 10 labs just passed the trueness criterion for the matrix tomato, while only three labs passed the trueness criterion for the matrix pear.

Fenthion-oxon

While the assigned value is at 84 % of the spiked level in the matrix tomato, the assigned value is at 52 % of the spiked level only in the matrix pear. Only one laboratory (lab 3) reported results within the accepted range of 70 to 120 % of the spiked level.

Fenthion-sulfoxide

Like described above for fenthion-oxon, the quantified concentration levels of fenthion-sulfoxide in the test material pear are much lower than the concentration levels in the test material tomato. The assigned value is at 70 % of the spiked value for the matrix pear.