European Union Reference Laboratory
for Pesticide Residues using Single Residue Methods

EUPT–SRM5, 2010

Proficiency Test on Spiked Pesticides in Apple Purée

Final Report

Chemisches und Veterinär-
untersuchungsamt Stuttgart

EU PROFICIENCY TEST
EUPT-SRM5, 2010

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DG-SANCO PROFICIENCY TEST
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FINAL REPORT

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FOREWORD

Regulation 882/2004/EC [1] lays down the general tasks and duties of the EU Reference Laboratories (EURLs) for Food, Feed and Animal Health[1] including the organisation of comparative tests. These proficiency tests are carried out on an annual basis and aim to improve the quality, accuracy and comparability of the analytical results generated by EU Member States within the frame of the EU co-ordinated control and national monitoring programmes. At the same time laboratories can assess their analytical performance and scope and make a comparison with other participating laboratories, which will hopefully result in additional efforts for improvement.

According to Article 28 of Regulation 396/2005/EC on maximum residue levels of pesticides in or on food and feed of plant and animal origin [2], all laboratories analysing samples for the official controls of pesticide residues shall participate in the European Union Proficiency Tests (EUPTs) for pesticide residues on behalfof DG-SANCO as long as the scopes of the EUPT and the laboratory overlap.

The EURL for pesticides using Single Residue Methods (EURL-SRM) has so far conducted 4 EUPTs within the abovementioned frame; two in collaboration with the EURL for Pesticides in Fruit and Vegetables (EURL-FV) using apple juice and carrot homogenate as commodity (EUPT-SRM1, EUPT-SRM3) and two in collaboration with the EURL for Cereals and Feedingstuff (EURL-CF) using wheat and oat as commodity (EUPT-C1/SRM2, EUPT-C2/SRM4). The EURL-SRM furthermore organized two ad-hoc EUPTs, one in 2008 concerning pentachlorophenol (PCP) in guar gum in cooperation with the EURL for Food of Animal Origin (EURL-AO) and the other one concerning nicotine in dried Boletus mushroom, organized in 2009. The present PT (EUPT-SRM5) was organised in collaboration with the EURL-FV, which took care of purchase and spiking of the apple purée as well as of the shipment of the test material.

DG-SANCO will have access to all data of EUPTs including the lab-code/lab-name key. Same will apply for all NRLs concerning the laboratories belonging to their own network. The results of this EUPT may be further presented to the European Commission Standing Committee for Animal Health and the Food Chain.

[1] Formerly Community Reference Laboratories (CRLs)

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EUROPEAN COMMISSION –
EURL-PROFICIENCY TEST ON PESTICIDE RESIDUES
IN APPLE PURÉE USING SINGLE RESIDUE METHODS
EUPT-SRM5, 2010

INTRODUCTION

On the 11th of May, 2010 all EU-National Reference Laboratories for pesticides using Single Residue Methods (NRL-SRMs) as well as all EU-Official Laboratories (OfLs) analyzing pesticide residues in fruits and vegetables were invited to participate in the 5th European Commission's Proficiency Test on Apple Purée using Single Residue Methods (SRMs). Also invited were official laboratories from EFTA countries (Iceland, Norway and Switzerland) which also contribute data to the EU-coordinated community control programme, as well as official laboratories from EU-candidate countries (Croatia, FYROM, Turkey). To make sure that all relevant OfLs become aware of the EUPT, the NRLs were additionally asked to forward the invitation to the relevant laboratories within their countries.

Included in the invitation were a Specific Protocol, a Calendar as well as a Target Pesticides List including compounds that potentially could be present in the test material (**Appendix 7**). The Target Pesticides List included 11 compounds (pesticides, metabolites etc.) requiring the use of SRMs along with the minimum required reporting levels (MRRLs) for each compound. 9 of the compounds in the Target Pesticides List were marked with an asterisk, indicating that they would be considered in the overall-classification and performance-ranking of the participating labs. The “General Protocol” (see **Appendix 8**) containing information common to all EUPTs on pesticides was also distributed to the laboratories.

In total 89 laboratories representing 29 countries (25 EU member states, plus Croatia, Norway, Switzerland and Egypt) registered on-line for participation. 36 laboratories from 11 EU member states provided explanations for their non-participation as requested by DG-SANCO. Additional 5 laboratories from non-EU countries also provided such explanations on voluntary basis.

The test material, apple purée, was spiked with pesticides in cold, but not frozen condition and mixed thoroughly. Five pesticides were used for the treatment: Abamectin, ethephon, fluazifop and fenbutatin oxide were spiked using analytical standards and thiram using a commercial formulation.

Participating laboratories were provided with 400 g, or 800 g if required, of each ‘blank’ and ‘treated’ (Test Material). The test materials were shipped to the participants on the 13 September 2010, and the deadline for submission of results to the Organiser was the 15 October 2010 (the original deadline, 7 October 2010, was extended to account for delays in shipment).

The participants were asked to analyse the treated and ‘blank‘ materials and to report the concentrations of any pesticides found which were included in the Target Pesticide List. Additionally, the ‘blank’ material could be used for recovery experiments and, if necessary, for the preparation of matrix-matched standards for the pesticides found in the test material. Submission of results was performed on-line via a website. Finally 80 labs representing 28 countries submitted results.

The medians of the analytical data submitted were used to obtain the assigned values for each of the pesticide residues present. A fit-for-purpose target relative standard deviation (FFP-RSD) of 25 % was chosen to calculate the target standard deviations (σ) as well as the z-scores for each of the compounds present. The robust standard deviations (Qn-RSD) were also calculated for informative purposes.

For the assessment of the overall performance, the laboratories were classified in Category A and B, based on their scopes. Labs within Cat. A were further sub-classified into “good”, “satisfied” and “unsatisfied” based on the sum of weighted z-scores (SWZ).

1 TEST MATERIALS

1.1 Analytical methods

The following analytical methods, briefly described below, were employed by the organiser to conduct the homogeneity and stability tests:

For **fluazifop** (acidic pesticide): QuEChERS-method [3] involving extraction with acetonitrile, partitioning after addition of salts, and direct determinative analysis LC-MS/MS in the ESI-neg. mode.

For **avermectin B1a**: QuEChERS-method involving extraction with acetonitrile, partitioning after addition of salts, and direct determinative analysis by LC-MS/MS in the ESI-pos. mode.

For **ethephon**: Extraction following addition of methanol containing 1 % formic acid, centrifugation, filtration and direct determinative analysis by LC-MS/MS in the ESI-neg. mode.

For **fenbutatin oxide** (organotin compound): QuEChERS-method involving extraction with acetonitrile, partitioning after addition of salts, and direct determination by LC-MS/MS in the ESI-pos. mode using a gradient containing 1 % formic acid.

For **dithiocarbamates**: 1) method involving cleavage with HCl/$SnCl_2$, partitioning into isooctane and determination by GC-ECD; and for confirmtation 2) method according to EN12396-3 involving cleavage with HCl/$SnCl_2$ to release carbon disulfide which is separated and purified by distillation and collected in a methanol/potassium hydroxide solution where potassium xanthogenate is formed and spectrophotometrically determined.

For more details on the above methods used see **http://www.EURL-pesticides.eu**.

1.2 Selection of Pesticides for the Target Pesticide List

The pesticides to be included in the Target Pesticides List were selected by the Organiser and the Scientific Committee considering the present and upcoming scope of the EU-coordinated Community Control Programme and the EURL-pesticide priority list which ranks the pesticides according to their relevance and risk-potential. The overall capacity and capability of the laboratories within the EU, as assessed from previous PTs and surveys, was also taken into account. In some cases, the residue definitions valid for the test differed slightly from those in legislation to account for analytical difficulties. The approximate spiking levels were chosen by the Organizer following the recommendation by the Quality Control Group and taking the MRRLs into account. The minimum required reporting levels (MRRLs) were set at 0.01 mg/kg for all compounds except for dithiocarbamates, ethephon and amitrole where they were set at 0.02 mg/kg.

1.3 Preparation and distribution of the 'blank' and 'treated' test materials

The apple purée used for this PT was purchased in a supermarket in Almería, Spain. According to the label the commodity contained 14 % sugars.

'**Blank' test Material:** Following a through mixing of a large quantity of the material 400 g portions were weighed out into screw-capped polyethylene plastic bottles, sealed, and stored in a freezer at about -20 °C till distribution to participants.

'**Treated' test material':** 75 kg of apple purée were poured in a large container and spiked with five pesticides dissolved in water (**Table 1**). Four of the pesticides were employed as pure analytical standards and one in form of a commercial formulation. The material was spiked at room temperature, mixed thouroughly for 15 minutes, weighed out into screw-capped polyethylene plastic bottles (400 g in each), sealed, cooled down immediately and stored in a freezer at about -20 °C till distribution to participants. In a preliminary

small-scale application it was tested whether the spiking levels and the desired homogeneity could be achieved.

A thermoisolated box containing 1 bottle of each treated and 'blank' material and packed with dry ice was delivered to each lab. No dry ice was added in shipments to countries where dry ice was not permitted by the IATA – Dangerous Goods Regulations, using the transport means available to the shipping company. Labs that ordered two portions of test material were sent one thermoisolated box containing two bottles of treated materials and one bottle of 'blank' material during the first shipment with dry ice and an additional bottle of 'blank' material in a second shipment, packed in frozen state in a thermoisolated box, but without dry ice. Although in many cases the second shipment arrived in defrosted condition, no significant changes as regards the use of this material for spiking experiments or for matrix-matched calibrations was expected. This was also experimentally verified by the Organizers in a comparison study.

Prior to shipment, the homogeneity test of the test-materials was undertaken by the Organiser.

Table 1: Pesticides used for spiking the treated material for EUPT-SRM5

Pesticide	Spiking	Type	Dissolved in…
Abamectin	in laboratory	Analytical standard	Acetonitrile
Ethephon	in laboratory	Analytical standard	Acetonitrile
Fenbutatin oxide	in laboratory	Analytical standard	Acetonitrile
Fluazifop	in laboratory	Analytical standard	Acetonitrile
Thiram	in laboratory	Commercial formulation	Water

1.4 Homogeneity and Stability Tests

Prior to the tests, the content of each of the 10 randomly selected bottles, containing treated test-sample material, was thoroughly mixed and a sufficient number of portions were weighed-out, into the analytical vessels, to be used for the homogeneity test (2 portions from each of the 10 bottles per analytical method) and the stability tests (15 portions from the same bottle per analytical method). The homogeneity test and the first round of stability tests were performed immediately. The vessels containing the analytical portions for the stability test-rounds 2 and 3 were stored at -18 °C till they were needed. In the case of dithiocarbamates the 10 g portions for the stability test rounds 2 and 3 were not portioned immediately but taken from the bulk shortly before analysis.

1.4.1 Homogeneity Test

Analyses were performed on duplicate portions taken from each of the ten randomly chosen bottles with treated test material. The sequence of analyses was determined using a table of randomly generated numbers. The injection sequence of the 20 extracts was also random. Quantification was done using a 5-point calibration curve derived using matrix-matched standards.

The statistical evaluation of the results was performed according to the International Harmonized Protocol published by IUPAC, ISO and AOAC [4]. An overview of the statistical evaluation results of the homogeneity test is shown in **Table 2**. The individual residue data are given in **Appendix 2**.

According to therules, the test material can be considered as sufficiently homogenous and suitable for the proficiency test, if the sampling standard deviation of the population of samples does not exceed the allowable fraction of the target standard deviation. For this purpose the following criterion should be met: $s_{sam}^2 < c$, where s_{sam}^2 is the sampling variance (between bottles), and c is the critical value [3]. The term c contains the variable σ_{all} ("acceptable sampling variance") and is defined as $(0.3\,\sigma_p)^2$, with σ_p being the

"standard deviation for proficiency assessment" which is calculated by multiplying the mean concentration of each pesticide with the target fit-for-purpose relative standard deviation (25 %). Before analysis of variance the Cochran's variance test for detecting outlying differences between duplicate paires was also carried out [4].

As all pesticides passed the homogeneity test, the test material was considered to be sufficiently homogeneous and suitable for the EUPT-SRM5.

The portion size of 5 g was chosen for the homogeneity test in all cases except for dithiocarbamates, where 10 g were employed. It was expected that the vast majority of the labs would use analytical test portions ≥ 5 g or 10 g respectively. Indeed, 100 % of the labs used sample portions ≥ 5 g in the case of fluazifop, abamectin and fenbutatin oxide and all but one lab (96 %) in the case of ethephon. Furthermore all but 6 labs (90 %) employed sample portions ≥ 10 g in the case dithiocarbamates.

Table 2: Statistical evaluation data of homogeneity test (n = 20 analyses), see also **Appendix 2**.

	Fluazifop	Ethephon	Dithiocarbamates	Abamectin	Fenbutatin oxide
Analytical portions [g]	5	5	10	5	5
Mean [mg/kg]	0.274	0.332	0.294	0.382	0,276
s_{sam}^2	0.000	0.000	0.00103357	0.000092	0.000
c	0.001573	0.001277	0.00104697	0.002104	0.001455
passed / failed	passed	passed	passed	passed	passed

s_{sam}^2: sampling variance; ***c***: critical value

1.4.2 Stability tests

The analytical methods described briefly above (in section **1.1**) were also used for the stability tests.

The tests were carried out on three occasions as follows: 20 September 2010, 01 October 2010 and 19 October 2010. The analytical portions used to check the stability of a compound were always taken from the same bottle. The results of the stability tests are shown in **Table 3**. The tests did not show any significant decrease in the pesticide levels at -18 °C (the recommended storage temperature), indicating that under these storage conditions the pesticides present in the test material remained sufficiently stable for the entire duration of the EUPT.

In an additional test it was shown, however, that the levels of dithiocarbamates, determined as CS_2, decrease during storage of the test material at room temperature (in an open vessel) by 25 % within 5 h and by 47 % within 14 hours.

Table 3: Stability test results of SRM5-analytes in mg/kg (storage at -18 ºC), see also **Appendix 3**.

	Fluazifop	Ethephon	Dithiocarbamates	Abamectin	Fenbutatin oxide
	Storage at -18 ºC (mean values in mg/kg)				
Test 1: 20 Sept. 2010	0.295	0.342	0.297	0.403	0.295
Test 2: 01 Oct. 2010	0.293	0.350	0.299	0.387	0.293
Test 3: 19 Oct. 2010	0.263	0.331	0.330	0.375	0.313
% Deviation Test 3 vs. Test 1	**-10.92 %**	**-3.21 %**	**11.24 %**	**-6.97 %**	**5.96 %**
	Passed	**Passed**	**Passed**	**Passed**	**Passed**

1.5 Organisational details

1.5.1 Announcement / Invitation and EUPT-SRM5-Website

An Announcement/Invitation letter was sent on 11 May 2010 to all NRL-SRMs as well as to all official laboratories analyzing fruits and vegetables for pesticide resides within the frame of official controls. A list of laboratories that are obliged to participate in this EUPT according to Art. 28 of Reg. 396/2005/EU and Art 33 of Reg. 882/2005/EC, was constructed based on information submitted by the NRL-SRMs and the official laboratories themselves. The invitation was also sent to all official laboratories for which we did not receive any information as regards the scope they cover. NRLs were additionally prompted to carefully check the list of obliged laboratories within their network and asked to correct and complement it, where necessary, and to make sure that all obliged laboratories within their network become aware of this EUPT.

All documents relevant to this EUPT (Calendar, Target Pesticides List, Specific Protocol, General Protocol) were uploaded in the EURL-web-portal and the CIRCA/FIS-VL platform. An EUPT-SRM5-Website containing links to all these documents, was constructed within the EURL-web-portal **(http://www.eurl-pesticides.eu/docs/public/tmplt_article.asp?CntID=729&LabID=200&Lang=EN)**.

1.5.2 Registration and confidentiality

All obliged laboratories, regardless of whether they were intending to participate in this exercise or not, had to register within the EUPT-registration-website. Obliged laboratories that would not participate were asked to state the reasons for their non-participation. The participating labs were provided with a unique laboratory code as well as with unique login information to be used to enter the online result-submission-website. This ensured confidentiality throughout the entire duration of the PT.

1.5.3 Distribution of the test material

One bottle of treated test material (400 g) and one bottle of ‘blank’ material (400 g) were shipped on 13 September 2010 to each participant in thermoisolated polystyrene boxes containing dry ice. If double amount of test materials was ordered, the laboratories were send an additional bottle (400 g) of treated material within the same box. An additional bottle of ‘blank’ material (400 g) was shipped in a separate box in frozen condition but without dry ice. The laboratories were asked to check the state of the sample on receipt and to report to the organizer whether they accept the test material arrived and report any observations or complaints via the website.

An instruction on how to treat the test materials upon receipt was provided to the participating laboratories within the specific protocol (**Appendix 7**), which was released on June 4th, 2010.

1.5.4 Submission of results

An online submission tool allowed participants to submit their results via the Internet. All participants had access to the result-submission website from a week after the sample shipment until the result submission deadline (15 October 2010). Participants were asked not only to report their analytical results, but also to state their experience with the analysis of all pesticides within the Target Pesticides List. In addition, laboratories had to provide details about the methods employed and to indsicate their own reporting limits (RLs) for each of the pesticides.

2 EVALUATION RULES

2.1 False positives and negatives

2.1.1 False positives

In principle, any result indicating the presence of a pesticide listed in the Target Pesticides List which is (a) not used in the preparation of the test material, (b) not detected by the Organiser, even following a repeat analysis and (c) not detected by the overwhelming majority of the participants that tested for this compound, was treated as a false positive, if it was reported at a concentration at or above the respective Minimum Required Reporting Level (MRRL). Results lower than the MRRL were ignored by the Organisers and were not considered as false positives. No z-score values were calculated for any false positive result.

2.1.2 False negatives

These are results of pesticides reported as “Analyzed” but where no numerical values were given, although they were used by the Organiser to prepare the test material and were detected, at or above the MRRL, by the Organiser and the majority of participating laboratories. Z-Scores for false negatives were calculated using the MRRL as the result. Any laboratory reporting limits (RLs) higher than the MRRL were not taken into account.

2.2 Establishment of the assigned (consensus) values

To establish the assigned values, the median levels of all reported results, excluding outliers, were used.

2.3 Fixed target standard deviation (FFP-approach)

Based on previous experience from EU proficiency tests on fruit and vegetables a fixed fit-for-purpose relative standard deviation (FFP-RSD) of 25 % was applied in statistical evaluation. The target standard deviation (σ) for each individual pesticide was calculated by multiplying this FFP-RSD by the assigned value. In addition, the robust relative standard deviation (Qn-RSDs) was calculated for informative purposes only.

2.4 Z-Scores

A z-score for each combination of laboratory and pesticide (i) was calculated according to the following equation:

$$z_i = (x_i - \mu_i) / \delta_i$$

Where

- x_i is the result reported by the participant for the pesticide (i) or
  the respective minimum required reporting level (MRRL) for false negative results
- μ_i is the assigned value for the pesticide (i)
- δ_i is the target standard deviation for the pesticide (i), which equals 25 % of the assigned value (FFP-approach)

Any z-scores > 5 were set at “5” in calculations of summed z-scores (see below).

The z-scores were classified as follows:

$\|z\| \leq 2$	acceptable
$2 < \|z\| \leq 3$	questionnable
$\|z\| > 3$	unacceptable

For results considered as false negatives, z-scores were calculated using the MRRL or the RL, if RL < MRRL. No z-score were calculated for any false positive results.

2.5 Lab Categorization and Ranking

2.5.1 Category A and B classification

Based on the scope covered, laboratories were subdivided into Categories (A and B). To be classified into Category A a laboratory should have

a) sought for all 9 pesticides marked with an asterisk in the Target Pesticides List
b) reported concentration values for all 5 pesticides present in the treated test material,
c) not reported any false positive results.

2.5.2 Combined z-scores

In order to evaluate the overall performance of each laboratory combined z-scores were calculated as follows:

Sum of Weighted z-scores (SWZ)

The SWZ[2] is calculated only for laboratories within Category A using the following formula:

$$SWZ = \frac{\sum_{|Z_i| \leq 2} |z_i| \cdot 1 + \sum_{|Z_i| \leq 3} |z_i| \cdot 3 + \sum_{|Z_i| > 3}^{\infty} |z_i| \cdot 5}{n}$$

where “n” is the number of reported results from each lab.
For the calculation, any z-score > 5 was set at “5”.

The SWZ-scores were classified as follows:

SWZ ≤ 2 :	good
2 < SWZ ≤ 3:	satisfactory
SWZ > 3:	unsatisfactory

Average of Absolute z-scores (AAZ)

The AAZ is calculated for all laboratories using the following formula:

$$AAZ = \frac{\sum_{|Z_i| = 0}^{\infty} |z_i|}{n}$$

where “n” is the number of reported results from each lab.
For the calculation, any z-score > 5 was set at “5”.

[2] The SWZ formula actually describes the **average** of the weighted absolute z-scores. The term SWZ is still used in this report for the sake of consistency and to avoid confusion, but the Advisory Group may decide to change the nomenclature in future EUPT-reports.

Sum of squared z-scores (SZ^2)[3]

The SZ^2 is calculated for all laboratories using the following formula:

$$SZ^2 = \frac{\sum_{|Zi|=0}^{\infty} z_i^{\,2}}{n}$$

where “n” is the number of reported results from each lab.

For the calculation, any z-score > 5 was set at “5”.

This formula is used for the first time and is planned to replace the SWZ formula in all EUPTs from 2011 onwards.

[3] The SZ^2 formula actually describes the **average** of the squared z-scores. The Advisory Group may decide to change the nomenclature in future EUPT-reports.

3 PARTICIPATION

90 % (80 out of 89) of the laboratories that had originally registered for participation in the EUPT-SRM5 submitted at least one result. An overview is given in **Table 4**. A list of all individual laboratories that registered for this PT, including those that did not submit any results, is presented in **Appendix 1**.

Table 4: Number of the laboratories registered to EUPT-SRM5 and submitted results

Country	Registered		Submitted Results		Notes
	Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	
Austria	1	1	1	1	
Belgium	5	1	5*	1	*Includes 4 sub-contracted labs based in BE (2), NL and DE
Bulgaria	1	1	1	1	
Cyprus	1	1	1	1	
Czech Republic	2	1	2	1	
Denmark	2	1	2	1	
Estonia	2	1	2	1	
Finland	1	1	1	1	
France	6	–	6	–	Officially no NRL-SRM established
Germany	12	1	12	1	
Greece	4	2	4	2	
Hungary	3	1	3	1	
Ireland	1	1	1	1	
Italy	7	1	4	1	
Latvia	1	1	1	1	
Lithuania	1	1	1	1	
Luxembourg	–	–	–	–	
Malta	2	1	1*	–	*Sub-contracted lab based in IT representing NRL of MT
Poland	10	1	9	1	
Portugal	4	1	4	1	
Romania	–	–	–	–	
Slovakia	1	1	1	1	
Slovenia	3	1	3	1	
Spain	8	(1)*	6	(1)*	*NRL-SRM had been appointed natioally but not yet officially communicated to DG-SANCO
Sweden	1	–	1*	–	*Sub-contracted lab based in SE representing NRL
The Netherlands	1	1	1	1	
UK	4	1	3	1	
EU Total	**85**	**24**	**77**	**23**	
Croatia	1				
Egypt	1		1		
Norway	1	1	1	1	
Switzerland	1		1		
Overall Sum	**89**	**25**	**80**	**24**	

In total laboratories representing 29 countries registered for participation, with laboratories representing 28 countries submitting results. Out of the EU member states only from Luxembourg and Romania no results were received. As far as NRL-SRMs are concerned, no results were received from the following EU-MS: France, Luxembourg and Romania. In the case of France, no NRL-SRM had been assigned at the time of the present EUPT. The NRLs of Malta and Sweden were represented by sub-contracted laboratories based in Italy and Sweden respectively. In the case of Spain an NRL-SRM had been designated nationally, but this information had not been officially forwarded to DG-SANCO at the time of the test.

Upon inquiry, 8 of the 9 laboratories (3x IT, 2x ES, 1x HR, 1x MT, 1x UK, 1x PL), that initially did register but then failed to submit any results, provided explanations. One OfL from Spain did not provide any explanation.

In total, 206 EU-OfLs (including NRL-SRMs) were considered as obliged to participate in the present EUPT. These were all EU-OfLs entailing fruits and vegetables in their scope plus all NRL-SRMs not targeting fruits and vegetables (without taking into consideration the pesticide scope covered by these labs). Obliged labs had to either participate or to provide an explanation for their non-participation. 122 of those 206 obliged laboratories did not register for participation with 40 of them (from 13 EU member states) stating to the Organizer the reasons for non-participation. The most common reasons for non-participation provided by the labs were limitations in capacity (time personnel, instrument availability) as well as the non-overlap of the lab-scope with the scope of this EUPT. This information is forwarded to DG-SANCO as requested. **Table 5** gives an overview of all participating and non-participating EU-labs.

Table 5: Overview of labs obliged to participate in the EUPT-SRM5

Total obliged EU-labs*	**206**	**100 %**
Thereof ….		
- Registered for Participation	**85**	**41 %**
- Submitting results	77	37 %
- Not submitting results / and providing explanation for non-participation	7 / 6	3 %
- Not-Registered for Participation	**122**	**59 %**
- Providing explanations for non-participation	40	19 %
- No feedback	82	40 %

* Official labs (including NRLs) of EU-member states covering fruits and vegetables plus any NRL-SRMs not including fruits and vegetables in their scope.

4 RESULTS

4.1 Overview of results

An overview of the results reported for the pesticides present in the sample and for all other pesticides within the Target Pesticides List is shown in **Table 6** and **Table 7** respectively. **Table 8** gives an overview of all results submitted by each laboratory. For the individual results reported by the laboratories see **Table 13**. The detailed information about the analytical methods used by the laboratories is shown **Appendix 6**.

Table 6: Overview of results for the pesticides present in the Test Sample

Pesticides	MRRL [mg/kg]	Labs reporting results [1]		No. of reported concentrations > MRRL	No. of reported NDs[3]
		No.	% (Based on N = 80) [2]		
Compounds Present in Test Material					
***Abamectin**	0.01	53	66 %	53	
***Dithiocarbamates**	0.02	71	89 %	67 (+ 2 x "< RL") [4]	2 (1 judged as FN) [5]
***Ethephon**	0.02	29	36 %	28	1 (FN)
***Fenbutatin oxide**	0.01	35	44 %	35	
***Fluazifop**	0.01	51	64 %	51	

1) Including ND-results
2) 80 laboratories have submitted at least one result
3) ND = Not detected (i.e. possibly false negative, see next notes)
4) Two labs reported that they had "detected" dithiocarbamates, but instead of reporting a numerical concentration value they reported that the results were below their respective Reporting Limits (RLs) which were in both cases >> MRRL. Following the rules in the General Protocol these results had to be judged as false negatives. For the calculation of the z-scores the MRRL was used in these two cases.
5) In the case of dithiocarbamates two labs reported ND (not detected). One of those results was not considered as a false negative (FN) because the test material arrived the lab unfrozen (reason: remote location of the lab and the special shipment regulations prohibiting the use of dry ice).

Table 7: Overview of results for the pesticides not present in the Test Sample (see notes of Table 6)

Pesticides	MRRL [mg/kg]	Labs reporting results		No. of reported concentrations > MRRL	No. of reported NDs
		No.	% (Based on N = 80)		
Compounds <u>not</u> Present in Test Material					
***2,4-D**	0.01	52	65 %	1 (FP) [1]	51
Amitrol	0.02	14	18 %	3 (FP)	11
***Chlormequat**	0.01	54	68 %	1 (FP)	53
2,4-DP (Dichlorprop)	0.01	41	51 %		41
***Haloxyfop**	0.01	51	64 %		51
Mepiquat	0.01	53	66 %	1 (FP)	52

1) FP = False positive result

Table 8: Overview of results with laboratory scope

			2,4-D	Fluazifop	Haloxyfop	2,4-DP	Chlormequat	Ethephon	Mepiquat	Amitrole	Dithiocarbamates	Abamectin	Fenbutatin oxide	All compounds		Compounds with asterisk	
Compound with asterisk			Yes	Yes	Yes		Yes	Yes	Yes		Yes	Yes	Yes	analysed	Correctly found	analysed	Correctly found
Compound present in test material				Yes				Yes			Yes	Yes	Yes				
Lab-Code	NRL-SRM	Cat.															
SRM5-2		B					ND		ND		V			3	1	3	1
SRM5-3	x	B	ND	V	ND	ND	ND		ND			V		7	2	6	2
SRM5-4		A	ND	V	ND	ND	ND	V	ND	ND	V	V	V	11	5	9	5
SRM5-5	x	B	ND	V	ND	ND	ND		ND		<RL		V	8	2	7	2
SRM5-6		A	ND	V	ND	ND	ND	V	ND		V	V	V	10	5	9	5
SRM5-7	x	A	ND	V	ND	ND	ND	V	ND	ND	V	V	V	11	5	9	5
SRM5-8		B									V			1	1	1	1
SRM5-9		B									V			1	1	1	1
SRM5-10		A	ND	V	ND	ND	ND	V	ND	ND	V	V	V	11	5	9	5
SRM5-11		B	ND	V	ND	ND	ND		ND	ND	V	V	V	10	4	8	4
SRM5-12		A	ND	V	ND	ND	ND	V	ND	ND	V	V	V	11	5	9	5
SRM5-14	x	A	ND	V	ND	ND	ND	V	ND		V	V	V	10	5	9	5
SRM5-15		B		V	ND		ND		ND		V	V		6	3	6	3
SRM5-16		B						V				V		2	2	2	2
SRM5-17	x	A	ND	V	ND	ND	ND	V	ND		V	V	V	10	5	9	5
SRM5-18		A	ND	V	ND	ND	ND	V	ND		V	V	V	10	5	9	5
SRM5-19	x	B	ND	V	ND	ND	ND		ND		V	V		8	3	7	3
SRM5-20		B	ND	V	ND	ND	ND		ND		V	V	V	9	4	8	4
SRM5-22		B	ND	V	ND	ND	ND	V	ND		V	V		9	4	8	4
SRM5-23		B					ND		ND					2	0	2	0
SRM5-24	x	A	ND	V	ND	ND	ND	V	ND	ND	V	V	V	11	5	9	5
SRM5-25		B									V			1	1	1	1
SRM5-26	x	B	ND	V	ND		ND		ND		V	V	V	8	4	8	4
SRM5-27		B									V			1	1	1	1
SRM5-28	x	B	ND	V	ND	ND	ND	V	ND			V	V	9	4	8	4
SRM5-29	x	B	ND	V	ND	ND	ND		ND		V	V		8	3	7	3
SRM5-30	x	B	ND	V	ND	ND						V		5	2	4	2
SRM5-31		B	ND	V	ND	ND	ND		ND		V	V	V	9	4	8	4
SRM5-32		B	FP	V			FP		FP			V		5	2	5	2
SRM5-33		B									(FN*)			1	0	1	0
SRM5-35	x	B	ND	V	ND	ND	ND	V	ND		V	V		9	4	8	4
SRM5-36		B	ND			ND								2	0	1	0
SRM5-37	x	B					ND	V	ND		V			4	2	4	2
SRM5-39		B	ND	V	ND	ND	ND		ND		V	V	V	9	4	8	4
SRM5-40		B	ND	V	ND	ND	ND		ND		V	V	V	9	4	8	4
SRM5-41	x	B		V	ND		ND	V	ND		V	V		7	4	7	4
SRM5-42		B	ND	V	ND	ND	ND		ND		V	V	V	9	4	8	4
SRM5-43		A	ND	V	ND		ND	V	ND		V	V	V	9	5	9	5
SRM5-44		A	ND	V	ND	ND	ND	V	ND	ND	V	V	V	11	5	9	5
SRM5-46		B									V			1	1	1	1
SRM5-47		B									V			1	1	1	1
SRM5-48		B	ND	V	ND	ND	ND		ND		V	V	V	9	4	8	4
SRM5-49	x	B	ND	V	ND	ND	ND	V	ND		V	V		9	4	8	4
SRM5-50		B	ND	V	ND	ND	ND		ND		V	V	V	9	4	8	4
SRM5-51		B	ND		ND		ND		ND		V	V	V	7	3	7	3
SRM5-52		B	ND	V	ND	ND		V		FP	V	V	V	9	5	7	5
SRM5-53	x	A	ND	V	ND	ND	ND	V	ND		V	V	V	10	5	9	5

			2,4-D	Fluazifop	Haloxyfop	2,4-DP	Chlormequat	Ethephon	Mepiquat	Amitrole	Dithiocarbamates	Abamectin	Fenbutatin oxide	All compounds		Compounds with asterisk	
Compound with asterisk			Yes	Yes	Yes		Yes	Yes	Yes		Yes	Yes	Yes	analysed	Correctly found	analysed	Correctly found
Compound present in test material				Yes				Yes			Yes	Yes	Yes				
Lab-Code	NRL-SRM	Cat.															
SRM5-54		B			ND						V	V		3	2	3	2
SRM5-56	x	B	ND	V	ND		ND		ND		V			6	2	6	2
SRM5-57		B	ND	V	ND	ND	ND	V	ND		V	V		9	4	8	4
SRM5-58		A	ND	V	ND	ND	ND	V	ND		V	V	V	10	5	9	5
SRM5-59	x	A	ND	V	ND	ND	ND	V	ND		V	V	V	10	5	9	5
SRM5-60		B	ND			ND	ND		ND		V			5	1	4	1
SRM5-61		B	ND	V	ND		ND	FN	ND	ND	V	V	V	10	4	9	4
SRM5-62		B									V			1	1	1	1
SRM5-63		B		V				V			V	V		4	4	4	4
SRM5-64	x	A	ND	V	ND	ND	ND	V	ND	ND	V	V	V	11	5	9	5
SRM5-65		B	ND	V	ND	ND	ND	V	ND	FP	V	V		10	4	8	4
SRM5-67		B	ND	V	ND		ND		ND		V	V	V	8	4	8	4
SRM5-70	x	B	ND	V	ND	ND	ND		ND	ND	V	V	V	10	4	8	4
SRM5-71		B									V			1	1	1	1
SRM5-73		B									V			1	1	1	1
SRM5-74		B					ND		ND					2	0	2	0
SRM5-75	x	B									V			1	1	1	1
SRM5-76		B	ND	V	ND	ND	ND		ND			V	V	8	3	7	3
SRM5-77		B									<RL			1	0	1	0
SRM5-78	x	B	ND	V	ND	ND	ND		ND		V	V	V	9	4	8	4
SRM5-79		B	ND	V	ND	ND					V	V	V	7	4	6	4
SRM5-80		B									V			1	1	1	1
SRM5-81		B									FN			1	0	1	0
SRM5-82		B	ND	V	ND	ND	ND				V	V	V	8	4	7	4
SRM5-85		B									V			1	1	1	1
SRM5-86		B	ND	V	ND		ND		ND	ND	V	V		8	3	7	3
SRM5-87		B					ND		ND		V			3	1	3	1
SRM5-88		B	ND	V	ND		ND	V	ND	FP	V	V		9	4	8	4
SRM5-89		B									V			1	1	1	1
SRM5-92		B									V			1	1	1	1
SRM5-95		B									V			1	1	1	1
SRM5-96	x	B	ND	V	ND		ND		ND		V	V		7	3	7	3
SRM5-98		B	ND					V			V	V		4	3	4	3

FP = False Positive result
FN = False Negative result
(FN*) = test material sent without dry ice and arrived the lab unfrozen thus not regarded as False Negative
< RL = analysed, detected and reported as < RL with the RL being >> MRRL, these results had to be judged as false negatives (FNs)
ND = analysed and correctly not detected
V = Concentration Value > 0.01 mg/kg reported

The laboratories were asked to explain for each individual pesticide within the Target Pesticides List they did not analyze for, the reasons why this was the case. In the vast majority of cases the non-analyzed pesticides were out of the routine scope of the labs. In the few cases, where they were part of the routine scope the non-analysis was due to the lack of a standard or a faulty equipment.

4.2 Assigned concentrations, target standard deviations and outliers

All assigned concentrations are shown in **Table 9**. To establish the assigned values, the medians of all reported results with absolute z-scores ≤ 5 and excluding false negatives were used.

The target standard deviation was obtained using a fixed value of 25 % (FFP-RSD). In parallel, the robust standard deviation (Qn-RSD) was calculated for information only (see **Table 9**).

In general, the FFP-RSD matches well with the Qn-RSD with the exception of "dithiocarbamates". The results reported for dithiocarbamates showed a very broad distribution ranging from 0.03 mg/kg to 0.55 mg/kg and giving a Qn-RSD of 59 %.

The EUPT-Scientific Committee decided that the z-scores calculated for dithiocarbamates using the FFP-RSD of 25 % are to be considered as tentative and only for the purpose of information and not to be used for the calculation of combined z-scores for the purpose of laboratory ranking.

Reasoning: Given the extensively broad distribution of results (Qn-RSD = 59 %), the use of the FFP-target standard deviation of 25 % was deemed as inappropriate.This decision is in line with [4] according to which the Qn-RSD should not be higher than 1.5 times the target standard diviation. Using the FFP-target RSD of 25 % the Qn-RSD should thus not exceed the value of 37.5 %. Furthermore, it could not be excluded that this broad distribution was at least partly based on factors outside the responsibility of the laboratories. The histogram with the distribution of results in **Appendix 5** suggests a tentatively bimodal distribution the reasons of which remain unclear, as it was not recognized in the homogeneity test and could not be linked to the different methodologies employed by the laboratories either (see **Appendix 4**).

Table 9: Assigned values and RSDs for all SRM-pesticides present in the test material

Pesticide	MRRL [mg/kg]	Assigned Value[1)] [mg/kg]	FFP-RSD [%]	Qn-RSD [%]
Fluazifop	0.01	**0.262**	25	**19.8**
Ethephon	0.02	**0.350**	25	**23.0**
Dithiocarbamates	0.02	**0.251**	25	**58.9**
Abamectin	0.01	**0.360**	25	**24.3**
Fenbutatin oxide	0.01	**0.280**	25	**20.6**
Average [2)]				**21.9** [2)]

1) Median
2) Excluding the value for dithiocarbamates

4.3 Assessment of laboratory performance

4.3.1 False positives

Labs SRM5-52, SRM5-65 and SRM5-88 reported amitrol concentrations of 0.052 mg/kg, 0.068 mg/kg and 0.26 mg/kg respectively. Furthermore, lab SRM5-32 reported concentrations of 0.046 mg/kg, 0.029 mg/kg and 0.10 mg/kg for 2,4-D, chlormequat and mepiquat, respectively. All these submitted results exceeded the MRRL and were thus judged as false positive results (FPs).

Table 10: Overview of False Positive results

Pesticide	PT-Code	Reported Result [mg/kg]	RL [mg/kg]	MRRL [mg/kg]	Judgement
2,4-D	SRM5-32	0.046	0.01	0.01	**False Positive**
Amitrol	SRM5-52	0.052	0.01	0.02	**False Positive**
	SRM5-65	0.068	0.02		**False Positive**
	SRM5-88	0.26	0.01		**False Positive**
Chlormequat	SRM5-32	0.29	0.01	0.01	**False Positive**
Mepiquat	SRM5-32	0.10	0.01		**False Positive**

4.3.2 False negatives

One laboratory (SRM5-61) reported ND (analysed but not detected) for ethephon. As the assigned value of ethephon in this EUPT (0.350 mg/kg) was much higher than the MRRL (0.02 mg/kg), this result was judged as false negative (FN).

Two laboratories (Codes: SRM5-33 and SRM5-81) reported ND for dithiocarbamates with RLs of 0.2 mg/kg and 0.05 mg/kg respectively. The result of lab SRM5-81 was judged as a false negative. In the case of lab SRM5-33 the test materials arrived the lab unfrozen due to the remote lab location and the non-acceptance of dry ice in this route. As this may have resulted in a significant decrease of the determined CS_2 concentration in the test material, the result was not regarded as a false negative.

Two laboratories (Codes: SRM5-5 and SRM5-77) reported that they have detected dithiocarbamates but instead reporting numerical concentration values, they reported < 0.4 mg/kg and < 0.25 mg/kg respectively, with 0.4 and 0,25 mg/kg representing the respective laboratory-own RLs. Following the rules of the General Protocol, these results had to be also judged as false negatives as no numerical values were provided. The RLs of the labs, are not taken into account in the judgement of false negatives.

The MRRL for dithiocarbamates (0.02 mg/kg) is sufficiently far apart from the assigned value of 0.251 mg/kg, suggesting that the false negative results are most likely related to the elevated RLs of the respective labs rather than to spurious low results within the normal distribution range.

Table 11: Overview of False Negative results

Pesticide	PT-Code	Detected	Reported Result [mg/kg]	RL [mg/kg]	Assigned value [mg/kg]	MRRL [mg/kg]	Judgement
Ethephon	SRM5-61	no	–	0.05	0.350	0.02	**False Negative**
Dithiocarbamates	SRM5-5	yes	< 0.4	0.4	0,251	0,02	**False Negative**
	SRM5-33	no	–	0.2			**–***
	SRM5-77	yes	< 0.25	0.25			**False Negative**
	SRM5-81	no	–	0.05			**False Negative**

*: not judged as False Negative because Test Material was sent without dry ice and arrived the lab unfrozen.

4.3.3 Individual and combined z-scores – laboratory ranking

All individual z-scores were calculated using the FFP-RSD of 25 %. **The z-scores of the dithiocarbamates are to be considered as tentative and are given only for informative purposes.**

Table 12 shows the overall classification of the z-scores achieved by all laboratories. Disregarding dithiocarbamates, “Acceptable” z-scores (see classification rules in **Chapter 2.4**) were achieved in 89 – 94 % of the cases (92 % on average).

Table 12: Overall classification of z-scores

Pesticides	Acceptable		Questionable		Unacceptable[2)]		FNs
	No.	%	No.	%	No.	%	No.
Fluazifop	47	92	3	6	1	2	0
Ethephon	26	90	0	0	3	10	1
Dithiocarbamates [1)]	46	65	12	17	13	18	3 [3)]
Abamectin	50	94	2	4	1	2	0
Fenbutatin oxide	31	89	0	0	4	11	0
Overall (including dithiocarbamates)	**200**	**83.7**	**17**	**7.1**	**22**	**9.2**	
Overall (excluding dithiocarbamates)	**154**	**91.7**	**5**	**3.0**	**9**	**5.3**	

1) Only for informative purpose
2) Including false negatives (FN)
3) See notes in **Table 6**

A compilation of all individual results and z-scores for each laboratory is shown in **Table 13**. A graphical representation of the z-score distribution of each pesticide present in the test material can be seen in **Appendix 4**. The corresponding histograms showing the distribution of the reported results are shown in **Appendix 5**.

Although **the individual z-scores for each pesticide are considered as being more important**, combined z-scores, i.e. Sum of Weighted z-scores (SWZ) and Average of Absolute z-scores (AAZ), were also calculated for each laboratory as a measure of overall performance.

Table 14 shows the laboratories classified into Category A, ranked by the SWZ. The Average of Absolute z-scores (AAZ) and SZ^2 for each lab are also given for information. In **Figure 1** the laboratories within Category A are ordered and classified according to the SWZ achieved (SWZ ≤ 2 = "Good", SWZ > 3 = "Unsatisfactory").

In **Table 15** laboratories classified into Category B are ordered by their lab-codes. The rates of acceptable, questionable and unacceptable results reported by Category A and B labs are shown in **Figure 2**. Looking at the data including dithiocarbamates, laboratories classified into Category A performed slightly better than those in Category B (89 vs. 81 % acceptable results and 9 vs. 9 % unacceptable results). When excluding dithiocarbamates the percentage of acceptable results was similar for both categories ranging at roughly 92 %. It is obvious that labs classified in category B do not necessarily report results of inferior quality as regards the accuracy. In any case, laboratories classified into Category B should increase their efforts to expand their analytical scope.

Table 16 ranks laboratories having reported 3 or more results according to the AAZ-score achieved. Laboratories belonging to Category A ranging at the bottom of the table (e.g. SRM5-17, SRM5-59, SRM5-64, SRM5-14) should put more emphasis in improving the quality of their analytical results. Laboratories belonging to Category B but ranked at the top of the table (e.g. SRM5-76, SRM5-82) may have a limited scope but have demonstrated a good analytical quality at least in the present EUPT. Decision-makers are thus encouraged to provide laboratories within Category B, demonstrating good performance throughout EUPTs, with the resources needed to expand their analytical scope.

Table 13: SRM-Results reported by the laboratories and the respective z-scores calculated using the FFP-RSD of 25 %

Analyte				Fluazifop		Ethephon		Dithiocarbamates		Abamectin		Fenbutatin oxide	
Assigned Value [mg/kg]				0.262		0.350		0.251		0.360		0.280	
MRRL [mg/kg]				0.01		0.02		0.02		0.01		0.01	
Qn RSD				19.8%		23.0%		58.1%		24.3%		20.6%	
Lab-Code	NRL-SRM	No. of Pesticides analysed / correctly found	Category	Conc. [mg/kg]	z-score (FFP RSD = 25 %)	Conc. [mg/kg]	z-score (FFP RSD = 25 %)	Conc. [mg/kg]	z-score[1)] (FFP RSD = 25 %)	Conc. [mg/kg]	z-score (FFP RSD = 25 %)	Conc. [mg/kg]	z-score (FFP RSD = 25 %)
SRM5-2		3 / 1	B					0.263	0.191				
SRM5-3	Yes	7 / 2	B	0.256	-0.092					0.315	-0.500		
SRM5-4		11 / 5	A	0.225	-0.565	0.331	-0.217	0.358	1.705	0.225	-1.500	0.408	1.829
SRM5-5	Yes	8 / 2	B	0.203	-0.901			<0.4 (FN)	-3.681			0.245	-0.500
SRM5-6		10 / 5	A	0.296	0.519	0.366	0.183	0.320	1.100	0.376	0.178	0.265	-0.214
SRM5-7	Yes	11 / 5	A	0.253	-0.137	0.374	0.274	0.158	-1.482	0.364	0.044	0.318	0.543
SRM5-8		1 / 1	B					0.264	0.207				
SRM5-9		1 / 1	B					0.320	1.100				
SRM5-10		11 / 5	A	0.272	0.153	0.386	0.411	0.060	-3.044	0.403	0.478	0.292	0.171
SRM5-11		10 / 4	B	0.235	-0.412			0.174	-1.227	0.395	0.389	0.314	0.486
SRM5-12		11 / 5	A	0.270	0.122	0.372	0.251	0.154	-1.546	0.325	-0.389	0.248	-0.457
SRM5-14	Yes	10 / 5	A	0.212	-0.763	0.027	-3.691	0.201	-0.797	0.365	0.056	0.224	-0.800
SRM5-15		6 / 3	B	0.288	0.397			0.330	1.259	0.526	1.844		
SRM5-16		2 / 2	B			0.300	-0.571			0.342	-0.200		
SRM5-17	Yes	10 / 5	A	0.320	0.885	0.510	1.829	0.340	1.418	0.640	3.111	0.580	4.286
SRM5-18		10 / 5	B	0.300	0.580	0.410	0.686	0.330	1.259	0.398	0.422	0.321	0.586
SRM5-19	Yes	8 / 3	B	0.239	-0.351			0.103	-2.359	0.392	0.356		
SRM5-20		9 / 4	B	0.290	0.427			0.290	0.622	0.350	-0.111	0.170	-1.571
SRM5-22		9 / 4	B	0.270	0.122	0.220	-1.486	0.072	-2.853	0.280	-0.889		
SRM5-23		2 / 0	B										
SRM5-24	Yes	11 / 5	A	0.258	-0.061	0.291	-0.674	0.187	-1.020	0.368	0.089	0.341	0.871
SRM5-25		1 / 1	B					0.220	-0.494				

Analyte				Fluazifop		Ethephon		Dithiocarbamates		Abamectin		Fenbutatin oxide	
Assigned Value [mg/kg]				0.262		0.350		0.251		0.360		0.280	
MRRL [mg/kg]				0.01		0.02		0.02		0.01		0.01	
Qn RSD				19.8%		23.0%		58.1%		24.3%		20.6%	
Lab-Code	NRL-SRM	No. of Pesticides analysed / correctly found	Category	Conc. [mg/kg]	z-score (FFP RSD = 25 %)	Conc. [mg/kg]	z-score (FFP RSD = 25 %)	Conc. [mg/kg]	z-score[1)] (FFP RSD = 25 %)	Conc. [mg/kg]	z-score (FFP RSD = 25 %)	Conc. [mg/kg]	z-score (FFP RSD = 25 %)
SRM5-26	Yes	8 / 4	B	0.308	0.702			0.277	0.414	0.399	0.433	0.236	-0.629
SRM5-27		1 / 1	B					0.100	-2.406				
SRM5-28	Yes	9 / 4	B	0.217	-0.687	0.352	0.023			0.192	-1.867	0.250	-0.429
SRM5-29	Yes	8 / 3	B	0.116	-2.229			0.426	2.789	0.285	-0.833		
SRM5-30	Yes	5 / 2	B	0.209	-0.809					0.340	-0.222		
SRM5-31		9 / 4	B	0.370	1.649			0.249	-0.032	0.230	-1.444	0.241	-0.557
SRM5-32		5 / 2	B	0.186	-1.160					0.100	-2.889		
SRM5-33		1 / 0	B					ND (not FN)	-3.681				
SRM5-35	Yes	9 / 4	B	0.218	-0.672	0.234	-1.326	0.189	-0.988	0.222	-1.533		
SRM5-36		2 / 0	B										
SRM5-37		4 / 2	B			0.394	0.503	0.284	0.526				
SRM5-39		9 / 4	B	0.288	0.397			0.158	-1.482	0.411	0.567	0.255	-0.357
SRM5-40		9 / 4	B	0.262	0.000			0.462	3.363	0.464	1.156	0.292	0.171
SRM5-41	Yes	7 / 4	B	0.122	-2.137	0.313	-0.423	0.205	-0.733	0.310	-0.556		
SRM5-42		9 / 4	B	0.169	-1.420			0.288	0.590	0.375	0.167	0.270	-0.143
SRM5-43		9 / 5	A	0.273	0.168	0.308	-0.480	0.430	2.853	0.384	0.267	0.285	0.071
SRM5-44		11 / 5	A	0.270	0.122	0.350	0.000	0.150	-1.610	0.473	1.256	0.300	0.286
SRM5-46		1 / 1	B					0.110	-2.247				
SRM5-47		1 / 1	B					0.300	0.781				
SRM5-48		9 / 4	B	0.235	-0.412			0.453	3.219	0.329	-0.344	0.227	-0.757
SRM5-49	Yes	9 / 4	B	0.242	-0.305	0.397	0.537	0.251	0.000	0.270	-1.000		
SRM5-50		9 / 4	B	0.319	0.870			0.182	-1.100	0.492	1.467	0.309	0.414
SRM5-51		7 / 3	B					0.378	2.024	0.289	-0.789	0.218	-0.886

Analyte				Fluazifop		Ethephon		Dithiocarbamates		Abamectin		Fenbutatin oxide	
Assigned Value [mg/kg]				0.262		0.350		0.251		0.360		0.280	
MRRL [mg/kg]				0.01		0.02		0.02		0.01		0.01	
Qn RSD				19.8%		23.0%		58.1%		24.3%		20.6%	
Lab-Code	NRL-SRM	No. of Pesticides analysed / correctly found	Category	**Conc.** [mg/kg]	**z-score** (FFP RSD = 25 %)	**Conc.** [mg/kg]	**z-score** (FFP RSD = 25 %)	**Conc.** [mg/kg]	**z-score**[1)] (FFP RSD = 25 %)	**Conc.** [mg/kg]	**z-score** (FFP RSD = 25 %)	**Conc.** [mg/kg]	**z-score** (FFP RSD = 25 %)
SRM5-52		9 / 5	B	0.292	0.458	0.382	0.366	0.212	-0.622	0.318	-0.467	0.334	0.771
SRM5-53	Yes	10 / 5	A	0.246	-0.244	0.350	0.000	0.167	-1.339	0.451	1.011	0.259	-0.300
SRM5-54		3 / 2	B					0.445	3.092	0.455	1.056		
SRM5-56	Yes	6 / 2	B	0.110	-2.321			0.160	-1.450				
SRM5-57		9 / 4	B	0.234	-0.427	0.305	-0.514	0.253	0.032	0.291	-0.767		
SRM5-58		10 / 5	A	0.262	0.000	0.362	0.137	0.151	-1.594	0.408	0.533	0.282	0.029
SRM5-59	Yes	10 / 5	A	0.298	0.550	0.749	4.560	0.586	5.339	0.437	0.856	0.314	0.486
SRM5-60		5 / 1	B					0.500	3.968				
SRM5-61		10 / 4	B	0.150	-1.710	ND (FN)	-3.771	0.420	2.693	0.480	1.333	0.045	-3.357
SRM5-62		1 / 1	B					0.350	1.578				
SRM5-63		4 / 4	B	0.330	1.038	0.250	-1.143	0.300	0.781	0.310	-0.556		
SRM5-64	Yes	11 / 5	A	0.229	-0.504	0.334	-0.183	0.373	1.944	0.325	-0.389	1.580	18.571 [2)]
SRM5-65		10 / 4	B	0.298	0.550	0.361	0.126	0.269	0.287	0.415	0.611		
SRM5-67		8 / 4	B	0.255	-0.107			0.143	-1.721	0.417	0.633	0.518	3.400
SRM5-70	Yes	10 / 4	B	0.240	-0.336			0.626	5.976	0.339	-0.233	0.225	-0.786
SRM5-71		1 / 1	B					0.182	-1.100				
SRM5-73		1 / 1	B					0.210	-0.653				
SRM5-74		2 / 0	B										
SRM5-75	Yes	1 / 1	B					0.116	-2.151				
SRM5-76		8 / 3	B	0.267	0.076					0.341	-0.211	0.259	-0.300
SRM5-77		1 / 0	B					<0.25 (FN)	-3.681				
SRM5-78	Yes	9 / 4	B	0.310	0.733			0.558	4.892	0.095	-2.944	0.278	-0.029
SRM5-79		7 / 4	B	0.351	1.359			0.032	-3.490	0.416	0.622	0.380	1.429

Analyte				Fluazifop		Ethephon		Dithiocarbamates		Abamectin		Fenbutatin oxide	
Assigned Value [mg/kg]				0.262		0.350		0.251		0.360		0.280	
MRRL [mg/kg]				0.01		0.02		0.02		0.01		0.01	
Qn RSD				19.8%		23.0%		58.1%		24.3%		20.6%	
Lab-Code	NRL-SRM	No. of Pesticides analysed / correctly found	Category	Conc. [mg/kg]	z-score (FFP RSD = 25 %)	Conc. [mg/kg]	z-score (FFP RSD = 25 %)	Conc. [mg/kg]	z-score[1)] (FFP RSD = 25 %)	Conc. [mg/kg]	z-score (FFP RSD = 25 %)	Conc. [mg/kg]	z-score (FFP RSD = 25 %)
SRM5-80		1 / 1	B					0.103	-2.359				
SRM5-81		1 / 0	B					ND (FN)	-3.681				
SRM5-82		8 / 4	B	0.293	0.473			0.288	0.590	0.360	0.000	0.291	0.157
SRM5-85		1 / 1	B					0.110	-2.247				
SRM5-86		8 / 3	B	0.272	0.153			0.160	-1.450	0.323	-0.411		
SRM5-87		3 / 1	B					0.161	-1.434				
SRM5-88		9 / 4	B	0.060	-3.084	0.192	-1.806	0.331	1.275	0.306	-0.600		
SRM5-89		1 / 1	B					0.391	2.231				
SRM5-92		1 / 1	B					0.200	-0.813				
SRM5-95		1 / 1	B					0.180	-1.131				
SRM5-96	Yes	7 / 3	B	0.303	0.626			0.450	3.171	0.370	0.111		
SRM5-98		4 / 3	B			0.310	-0.457	0.310	0.940	0.230	-1.444		

1) The z-scores for dithiocarbamates are given only for informative purposes
2) According to Lab 64 the very high result for fenbutatin oxide was due to the use of an incorrectly prepared standard

Table 14: Category A laboratories[1)] ranked by the Sum of Weighted z-Scores (SWZ)

Pos.	Lab-Code	NRL-SRM	No. of Pesticides analysed / correctly found	z-scores				SWZ [2)]	SZ [2)]	AAZ [2)]	z-scores of dithiocarbamates (for information only) [3)]
				Fluazifop	Ethephon	Abamectin	Fenbutatin oxide				
1	58		10 / 5	0.000	0.137	0.533	0.029	0.175	0.175	0.076	-1.594
2	43		9 / 5	0.168	-0.480	0.267	0.071	0.247	0.247	0.084	2.853
3	7	Yes	11 / 5	-0.137	0.274	0.044	0.543	0.250	0.250	0.098	-1.482
4	6		10 / 5	0.519	0.183	0.178	-0.214	0.274	0.274	0.095	1.100
5	10		11 / 5	0.153	0.411	0.478	0.171	0.303	0.303	0.113	-3.044
6	12		11 / 5	0.122	0.251	-0.389	-0.457	0.305	0.305	0.110	-1.546
7	53	Yes	10 / 5	-0.244	0.000	1.011	-0.300	0.389	0.389	0.293	-1.339
8	44		11 / 5	0.122	0.000	1.256	0.286	0.416	0.416	0.418	-1.610
9	24	Yes	11 / 5	-0.061	-0.674	0.089	0.871	0.424	0.424	0.306	-1.020
10	18		10 / 5	0.580	0.686	0.422	0.586	0.568	0.568	0.332	1.259
11	4		11 / 5	-0.565	-0.217	-1.500	1.829	1.028	1.028	1.490	1.705
12	14	Yes	10 / 5	-0.763	-3.691	0.056	-0.800	5.019	1.328	3.713	-0.797
13	59	Yes	10 / 5	0.550	4.560	0.856	0.486	6.173	1.613	5.516	5.339
14	64	Yes	11 / 5	-0.504	-0.183	-0.389	18.571 [4)]	6.519	1.519	6.360	1.944
15	17	Yes	10 / 5	0.885	1.829	3.111	4.286	9.925	2.528	8.044	1.418

1) This table includes only laboratories that a) have analysed all 9 pesticides marked with an asterisk in the Target Pesticides List, b) have reported concentration values for all 5 pesticides present in the treated test material, and c) have not reported any false positive results.
2) SWZ: Sum of Weighted z-Scores; SZ : Average of squared z-scores; AAZ: Average of absolute z-scores
3) The z-scores for dithiocarbamates are given only for informative purposes and were not taken into account in the calculation of the SWZ and AAZ.
4) The z-score for fenbutatin oxide of this laboratory was lowered to 5 for the calculation of the SWZ, AAZ and SZ^2.
5) According to the lab the very high result for fenbutatin oxide was due to the use of an incorrectly prepared standard

Figure 1: Category A laboratories ranked according to the Sum of Weighted z-scores (SWZ)

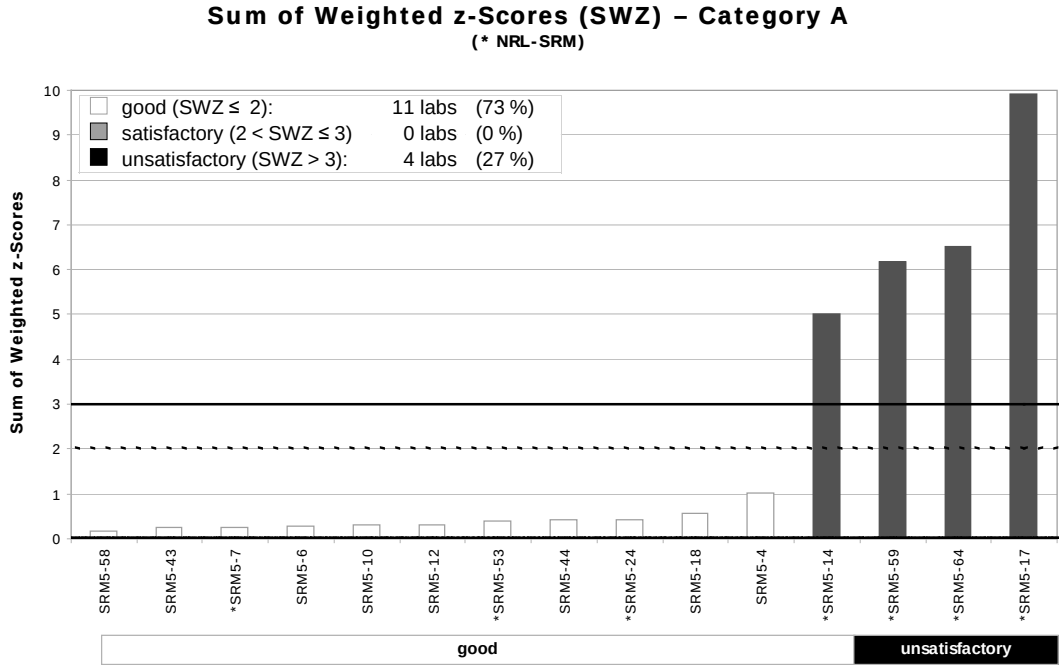


Table 15: Category B laboratories ordered by their Lab-ID

LabCode	NRL-SRM	z-scores					False positives
		Fluazifop	Ethephon	Abamectin	Fenbutatin oxide	Dithiocarbamates (only informative) [1]	
2						0,191	
3	Yes	-0,092		-0,500			
5	Yes	-0,901			-0,500	**-3.681** (FN) [2]	
8						0,207	
9						1,100	
11		-0,412		0,389	0,486	-1,227	
15		0,397		1,844		1,259	
16			-0,571	-0,200			
19	Yes	-0,351		0,356		**-2,359**	
20		0,427		-0,111	-1,571	0,622	
22		0,122	-1,486	-0,889		**-2,853**	
23 [5]							
25						-0,494	
26	Yes	0,702		0,433	-0,629	0,414	
27						**-2,406**	
28	Yes	-0,687	0,023	-1,867	-0,429		
29	Yes	**-2,229**		-0,833		**2,789**	
30	Yes	-0,809		-0,222			
31		1,649		-1,444	-0,557	-0,032	
32		-1,160		**-2,889**			3
33						**-3.681** (ND) [3]	
35	Yes	-0,672	-1,326	-1,533		-0,988	
36 [4]							
37	Yes		0,503			0,526	
39		0,397		0,567	-0,357	-1,482	
40		0,000		1,156	0,171	**3,363**	
41	Yes	**-2,137**	-0,423	-0,556		-0,733	
42		-1,420		0,167	-0,143	0,590	
46						**-2,247**	
47						0,781	
48		-0,412		-0,344	-0,757	**3,219**	
49	Yes	-0,305	0,537	-1,000		0,000	
50		0,870		1,467	0,414	-1,100	
51				-0,789	-0,886	**2,024**	
52 [6]		0,458	0,366	-0,467	0,771	-0,622	1
54				1,056		3,092	
56	Yes	**-2,321**				-1,450	
57		-0,427	-0,514	-0,767		0,032	
60						**3,968**	
61		-1,710	**-3,771** (ND)	1,333	**-3,357**	**2,693**	
62						1,578	
63		1,038	-1,143	-0,556		0,781	

LabCode	NRL-SRM	z-scores					False positives
		Fluazifop	Ethephon	Abamectin	Fenbutatin oxide	Dithiocarbamates (only informative) [1]	
65 [6]		0,550	0,126	0,611		0,287	1
67		-0,107		0,633	3,400	-1,721	
70	Yes	-0,336		-0,233	-0,786	**5,976**	
71						-1,100	
73						-0,653	
74 [5]							
75	Yes					-2,151	
76		0,076		-0,211	-0,300		
77						**-3.681** (FN) [2]	
78	Yes	0,733		**-2,944**	-0,029	**4,892**	
79		1,359		0,622	1,429	**-3,490**	
80						**-2,359**	
81						**-3.681** (FN) [7]	
82		0,473		0,000	0,157	0,590	
85						**-2,247**	
86		0,153		-0,411		-1,450	
87						-1,434	
88 [6]		**-3,084**	-1,806	-0,600		1,275	1
89						**2,231**	
92						-0,813	
95						-1,131	
96	Yes	0,626		0,111		**3,171**	
98			-0,457	-1,444		0,940	

1) The z-scores for dithiocarbamates are given only for informative purposes
2) Analyzed and detected, but reported as "< RL", with the RLs in both cases being much higher than the MRRL for dithiocarbamates stated in the Target Pesticides List.
1) Analysed but not detected (ND). Not considered as a false negative as the test material arrived this lab unfrozen.
2) Lab 36 has only analyzed for 2,4-D and 2,4-DP (not added to the test material)
3) Lab 23 and 74 have only analyzed for chlormequat and mepiquat (not added to the test material)
4) Labs 52, 65 and 88 had a sufficient scope, but were classified in Category B because of false positive results.
5) Analysed but not detected (ND). Judged as false negative (FN). As the MRRL was very distant to the assigned value these results were regarded as false negatives and the (informative) z-scores were calculated based on the MRRL.

Figure 2: Distribution of results reporded by labs classified into Category A and B.

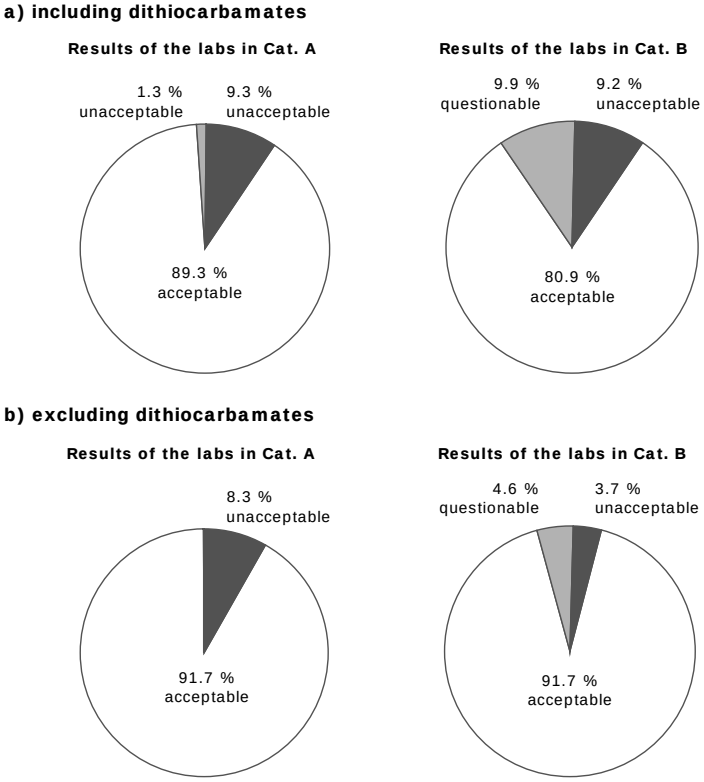


Table 16: Laboratories having reported 3 or more results ranked by the average of absolute z-scores (AAZ)

Lab-Code SRM5-	NRL-SRM	Cate-gory	Pesticides analysed / correctly found	z-scores				AAZ	False positives
				Fluazifop	Ethephon	Abamectin	Fenbutatin oxide		
58		A	10 / 5	0.000	0.137	0.533	0.029	**0.175**	
76		B	8 / 3	0.076		-0.211	-0.300	**0.196**	
82		B	8 / 4	0.473		0.000	0.157	**0.210**	
43		A	9 / 5	0.168	-0.480	0.267	0.071	**0.247**	
7	Yes	A	11 / 5	-0.137	0.274	0.044	0.543	**0.250**	
6		A	10 / 5	0.519	0.183	0.178	-0.214	**0.274**	
10		A	11 / 5	0.153	0.411	0.478	0.171	**0.303**	
12		A	11 / 5	0.122	0.251	-0.389	-0.457	**0.305**	
53	Yes	A	10 / 5	-0.244	0.000	1.011	-0.300	**0.389**	
44		A	11 / 5	0.122	0.000	1.256	0.286	**0.416**	
24	Yes	A	11 / 5	-0.061	-0.674	0.089	0.871	**0.424**	
65		B	10 / 4	0.550	0.126	0.611		**0.429**	1
11		B	10 / 4	-0.412		0.389	0.486	**0.429**	
39		B	9 / 4	0.397		0.567	-0.357	**0.440**	
40		B	9 / 4	0.000		1.156	0.171	**0.442**	
70	Yes	B	10 / 4	-0.336		-0.233	-0.786	**0.452**	
48		B	9 / 4	-0.412		-0.344	-0.757	**0.505**	
52		B	9 / 5	0.458	0.366	-0.467	0.771	**0.515**	1
18		A	10 / 5	0.580	0.686	0.422	0.586	**0.568**	
57		B	9 / 4	-0.427	-0.514	-0.767		**0.569**	
42		B	9 / 4	-1.420		0.167	-0.143	**0.576**	
26	Yes	B	8 / 4	0.702		0.433	-0.629	**0.588**	
49	Yes	B	9 / 4	-0.305	0.537	-1.000		**0.614**	
20		B	9 / 4	0.427		-0.111	-1.571	**0.703**	

Lab-Code SRM5-	NRL-SRM	Cate-gory	Pesticides analysed / correctly found	z-scores				AAZ	False positives
				Fluazifop	Ethephon	Abamectin	Fenbutatin oxide		
28	Yes	B	9 / 4	-0.687	0.023	-1.867	-0.429	**0.751**	
22		B	9 / 4	0.122	-1.486	-0.889		**0.832**	
63		B	4 / 4	1.038	-1.143	-0.556		**0.912**	
50		B	9 / 4	0.870		1.467	0.414	**0.917**	
4		A	11 / 5	-0.565	-0.217	-1.500	1.829	**1.028**	
41	Yes	B	7 / 4	**-2.137**	-0.423	-0.556		**1.039**	
79		B	7 / 4	1.359		0.622	1.429	**1.137**	
35	Yes	B	9 / 4	-0.672	-1.326	-1.533		**1.177**	
31		B	9 / 4	1.649		-1.444	-0.557	**1.217**	
78	Yes	B	9 / 4	0.733		-2.944	-0.029	**1.235**	
14	Yes	A	10 / 5	-0.763	-3.691	0.056	-0.800	**1.328**	
67		B	8 / 4	-0.107		0.633	**3.400**	**1.380**	
64	Yes	A	11 / 5	-0.504	-0.183	-0.389	**18.571** [1)]	**1.519**	
59	Yes	A	10 / 5	0.550	**4.560**	0.856	0.486	**1.613**	
88		B	9 / 4	**-3.084**	-1.806	-0.600		**1.830**	1
17	Yes	A	10 / 5	0.885	1.829	**3.111**	**4.286**	**2.528**	
61		B	10 / 4	-1.710	**-3.771**	1.333	**-3.357**	**2.543**	

1) The z-score for fenbutatin oxide of this laboratory was lowered to 5 for the calculation of the AAZ.

4.4 Analytical methods used

Detailed information about the analytical methods used by the laboratories can be found in **Appendix 6.**

4.4.1 Extraction and determinative analysis

Abamectin (avermectin B1a) was analyzed by 53 laboratories with all of them providing information about the method-type used. 43 labs (81 %) employed methods based on acetonitrile extraction, with the majority of them (41 labs = 77 % overall) employing QuEChERS-based methods. 5 labs (10 %) employed ethylacetate-based methods, 4 labs methods based on methanol extraction (1 of them the ChemElut method) and 1 lab a method based on acetone (S19 / Luke type).

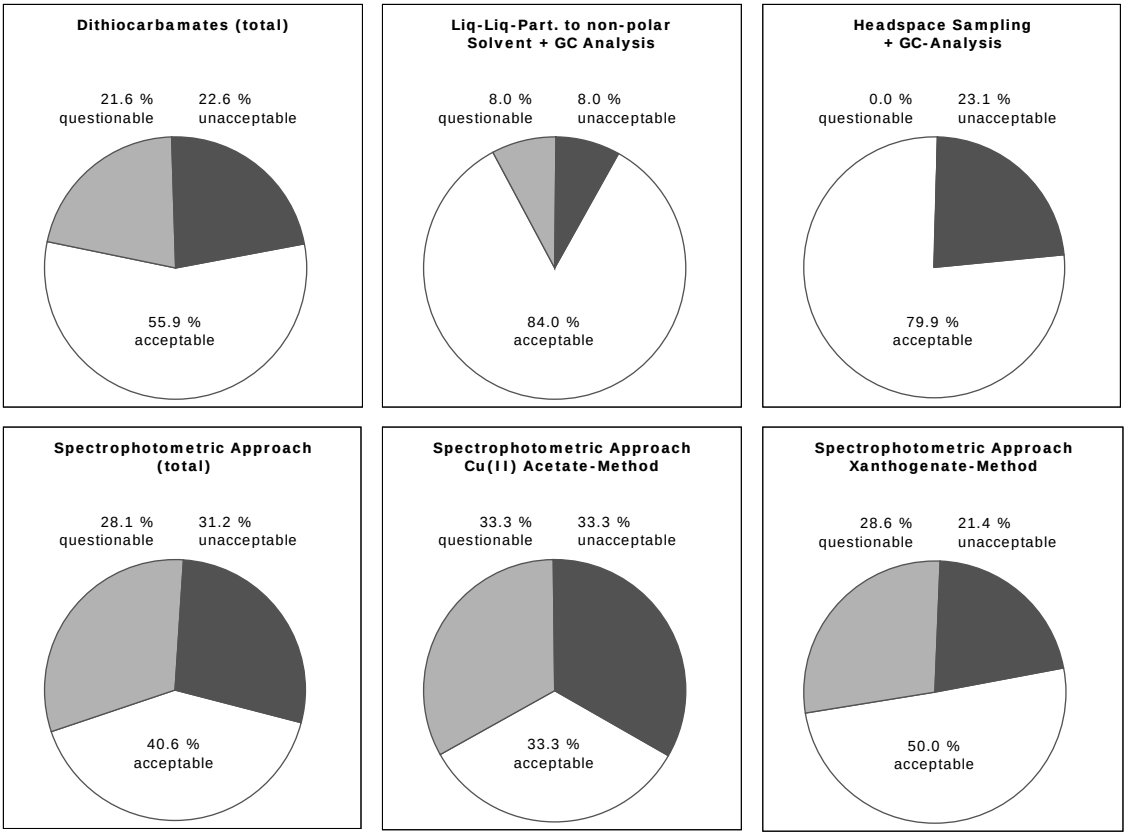
Determination of Avermectin B1a was conducted by LC-MS/MS in 47 out of the 51 participants that provided information this regarding (92 %). 3 labs employed LC with fluorescence detector following derivatization with methylimidazol and trifluoroacetic anhydride or acetic acid anhydride. 1 lab employed LC-DAD.

Dithiocarbamates were analyzed by 71 laboratories with 67 of them reporting a concentration value and all 71 providing information about the methodology used. Out of these labs 32 (45 % overall) employed methods involving cleavage to CS_2 followed by its derivatization and spectrophotometric detection. Out of this group 14 labs indicated the derivatization with MeOH/KOH to xanthogenate (EN-12396-3 -type methods) and 18 the derivatization with copper-(II)-acetate in diethanolamine and ethanol (EN-12396-1 -type methods). 26 laboratories (37 % overall) indicated the use of methods involving cleavage to CS2 and partitioning to isooctane (25 cases) or toluene (1 case) followed by GC-analysis in combination with MSD (10 cases), FPD (9 cases) or ECD (6 cases) detectors. 14 laboratories (20 % overal) employed methods involving cleavage to CS_2, headspace sampling and GC-analysis (EN-12396-2 -type methods). One of these labs employed SPME for headspace sampling.

Among the 70 labs giving information about the determinative technique used, 32 labs employed spectrophotometers, 15 labs GC-MSD, 12 GC-FPD, 10 GC-ECD and 1 GC-ITD.

Looking at the correlation between analytical approach and analytical performance, as reflected by the (informative) z-scores, it becomes apparent that laboratories using spectrophotophotometric approaches (EN-12396-1 and EN-12396-3 -type) reported poor results more frequently than those using the other types of methods. Nevertheless, these poor results do not show any clear trend towards over- or underestimation as the corresponding z-scores are distributed both in the negative and the positive end of the scale (see **Appendix 4** and **Figure 3**). The number of unacceptable z-scores (< 3) were 8 (44 %) for the EN-12396-1 type methods, 7 (50 %) EN-12396-3 type methods compared to 3 (21 %) for the EN-12396-2 type methods and just 2 (7 %) for the methods involving liquid-liquid-partitioning into non-polar solvents and GC-analysis. The EUPT-Scientific Committee therefore advices laboratories still employing spectrophotometric approaches (especially those using EN-12396-1 type methods) to switch to other type of methodologies involving determination by GC.

Figure 3: Distribution of results reported for dithiocarbamates, sorted by methods used



Ethephon was analyzed by 29 laboratories with one of them reporting a false negative result. 28 laboratories (N) gave information about the method-type used. Out of these labs 21 (75 % of N) employed methods involving extraction/dilution with a water-miscible solvent followed by LC-MS/MS determination. 15 labs thereof (54 % of N) followed the protocol published by the EURL-SRM. 6 (21 %) labs employed methods involving cleavage to ethylene at alkaline conditions followed by headspace sampling and GC-FID analysis. 2 labs employed methods involving derivatization of ethephon (with BSTFA in one case and diazomethane in the other) followed by GC-analysis.

19 (68 %) out of the 28 labs that provided information about the determinative analysis technique employed indicated the use of LC-MS/MS and 9 (32 %) the use of GC-techniques, thereof 6 (21 %) in combination with headspace sampling.

9 labs indicated the use of isotopically labelled ethephon and one lab the use of isotopically labelled glyphosate. 15 of the labs reported that they did not employ any internal standard and further 4 labs did not

provide any information this regarding. Out of the 15 labs not employing ISTDs 10 employed matrix-matched calibrations using the blank test material provided by the Organizer, 2 labs employed the standard additions approach and further 2 labs calibration standards based on pure solvent. 1 lab did not provide any information this regarding.

Fenbutatin oxide was analyzed by 35 laboratories with none of them reporting any false negative result and all of them giving information about the method-type used. 30 of the labs (86 %) employed methods involving acetonitrile extraction with 29 labs (83 % overall) employing a QuEChERS-type methodology. 2 labs (10 % of N) employed methods involving extraction with methanol (1 of them the ChemElut method) and 1 lab (4 % of N) methods based on acetone (S19 / Luke type) and 2 labs (6 %) employed extraction with a non-polar solvent (isooctane or isooctane/hexane) along with a derivatization step (using Grignard reagent) followed by GC-analysis. Derivatization was also performed by one laboratory using the QuEChERS-methodology.

31 (89 %) of the 35 labs, that provided information about the determinative analysis technique used, indicated the use of LC-techniques; thereof 29 (83 %) LC-MS/MS, 1 LC-MS and 1 LC-ITD. 2 labs (6 %) employed GC-techniques.

Fluazifop was analyzed by 51 laboratories with none of them reporting any false negative result. All laboratories gave information about the method-type used. Out of these labs 41 (80 %) employed methods involving acetonitrile extraction with 39 labs (75 % overall) employing a QuEChERS-type methodology. 5 labs (10 %) employed methods involving extraction with methanol (3 of them the ChemElut method); 3 labs (6 %) employed ethyl acetate-based methods and 2 labs (4 %) methods based on acetone (S19 / Luke type).

Although only the free acid was included in the Pesticides Target List, implying that no cleavage step is necessary, 3 labs employed alkaline hydrolysis, and one lab acidic hydrolysis. Nevertheless, as fluazifop was not present as an incurred residue (it was spiked to the homogenate), no covalently-bound fluazifop residues were expected in the test-material. Furthermore 3 labs employed dispersive SPE cleanup using PSA, which is not recommended as PSA removes acids from the extracts (see discussion under **4.4.4** concerning recovery correction).

45 (94 %) of the 48 labs that provided information about the determinative analysis technique used, indicated the use of LC-MS/MS. 3 labs (6 %) employed GC-techniques following derivatization with diazomethane, PFB-Br or trimethylsulfonium hydroxide.

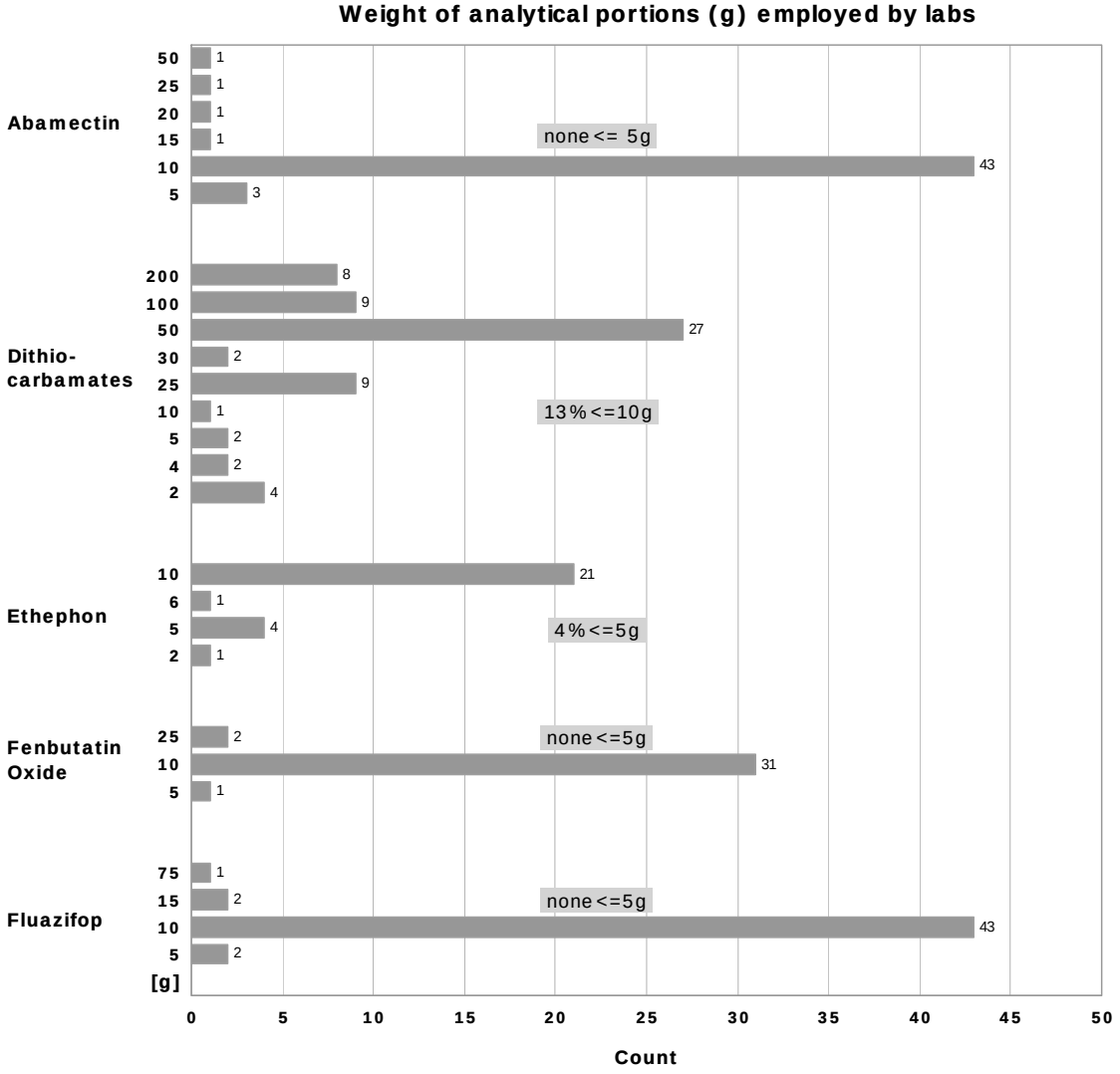
4.4.2 Size of analytical portions (sample amounts employed)

The amounts of test material (analytical portions) employed by the participants ranged between 2 g and 10 g for ethephon, 5 g and 25 g for fenbutatin oxide, 5 g and 50 g for abamectin, 5 g and 75 g for fluazifop and 2 g and 200 g for dithiocarbamate analyses (**Figure 4**). It should be noted that the homogeneity test was performed using 5 g sample portions in all cases except for dithiocarbamates, where 10 g were employed. Only 1 lab in the case of ethephon and 8 labs in the case of dithiocarbamates employed analytical portions smaller than 5 g and 10 g respectively. Higher sub-sampling variations are to be expected when smaller sample amounts are used. **Figure 4** shows the analytical portions employed by the labs for their dithiocarbamates-analyses. 17 labs employed 50 g or more. Most of these labs requested for additional test material, which increased the administrative effort as well as the costs for the labs.

Analytical methods for dithiocarbamates typically entail the use of non-homogenized material (e.g. fruit-segments, whole leafs) in large portions (e.g. 50 – 200 g) in order to minimize the degradation of the superficially located dithiocarbonates upon contact with the commodity juices and to ensure that the analytical portions are representative to the laboratory sample. As the EUPT test materials are already homogenized the use of such large portions in the case of EUPTs is only indispensable if the sensitivity of the procedure

is the limiting factor. Indeed, sensitivity seems to be a limiting factor for methodologies based on EN-12396-1 (derivatization with copper-(II)-acetate in diethanolamine and ethanol followed by spectrophotometric analysis) with 13 of the 15 labs having reported RL ≥ 0.1 mg/kg employing this method. The analytical portions employed by the laboratories using this method ranged between 50 g and 200 g with none of these labs reaching RLs lower than 0.05 mg/kg. For comparison, all 14 laboratories employing methods based on EN-12396-3 (xanthogenate approach) reported RLs ≤ 0.05 mg/kg and half of them stated RLs ≤ 0.02 = MRRL.

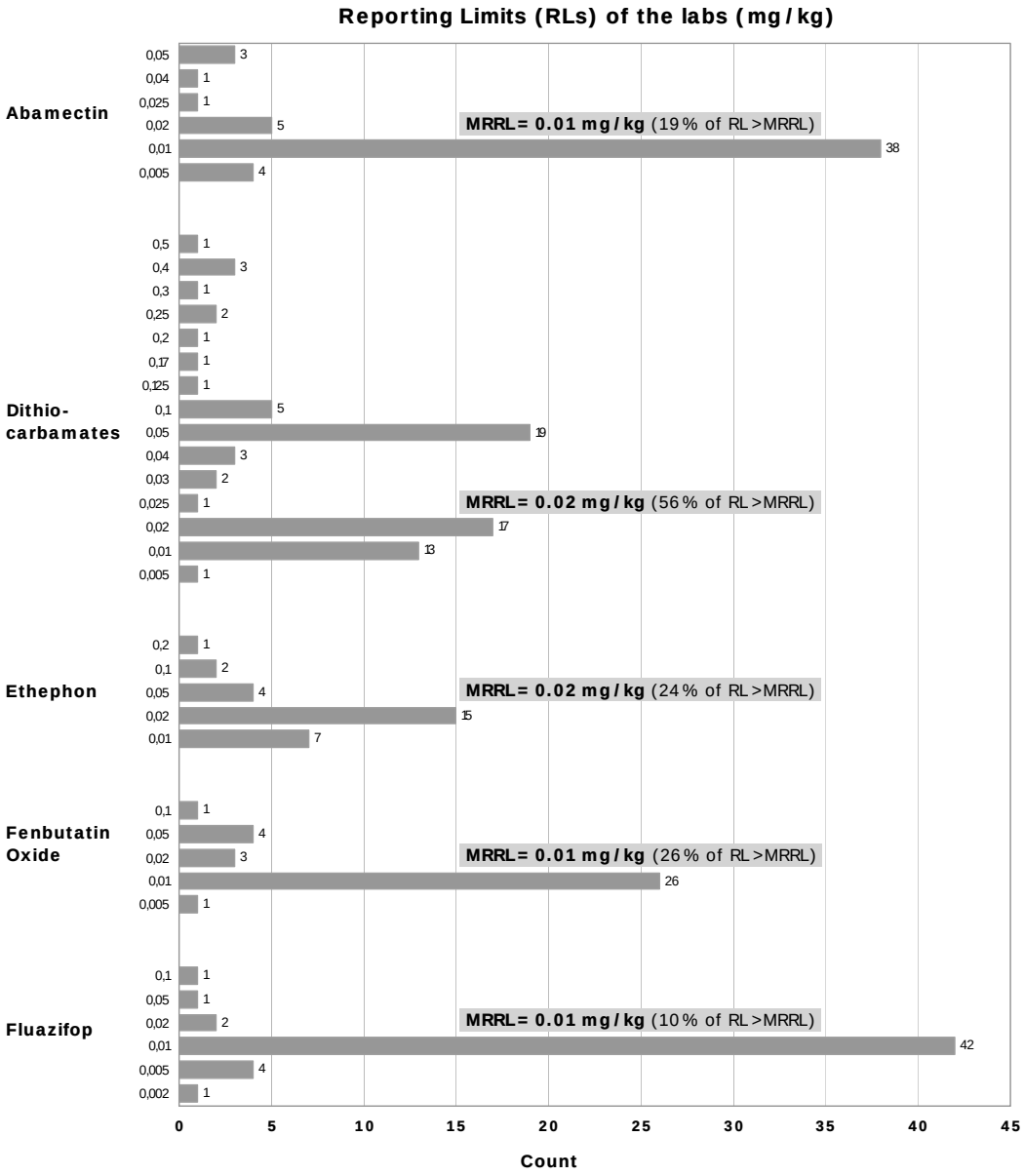
Figure 4: Size of sample portion used for analysis



4.4.3 Reporting Limits (RLs)

In the majority of the cases the laboratories were able to reach the required MRRLs (**Figure 5**). The MRRLs were not met in 10 % of the cases for fluazifop (MRRL = 0.01 mg/kg); 26 % of the cases for fenbutatin oxide (MRRL = 0.01 mg/kg); 24 % of the cases for ethephon (MRRL = 0.02 mg/kg), 19 % of the cases for abamectin (MRRL = 0.01 mg/kg) and in 56 % of the cases for dithiocarbamates (MRRL = 0.02 mg/kg). In only 5 cases, all of them concerning dithiocarbamates, the RLs submitted by the labs were even higher that the assigned value of 0.251 mg/kg. In all other cases the RLs were lower than the assigned values.

Figure 5: Labs' Reporting Limits (mg/kg)



4.4.4 Calibration approaches

Matrix-matched calibrations were employed in 64 % of the cases (including 8 % of the cases where standard additions approach was used). In 36 % of the cases solvent-based calibration solutions were employed by the participants.

Furthermore, 75 % of the results were generated using multi-level calibration versus 25 % of the cases where single level calibrations were used.

4.4.5 Impact of recovery correction

Recovery correction was applied in 11 % of all results (25 cases). In most cases recovery correction was a result of the procedure, i.e. standard additions approach (14 reported cases = 6 % overall); use of isotopically labelled ISTDs (7 reported cases = 6 %); and a combination of both (2 cases = 1 %). Recovery correc-

tion using the reported recovery figure was applied in just 2 cases with the respective recovery experiments being conducted within the same batch using the blank material provided by the Organizers.

In 89 % of the cases labs reported no recovery correction, independent of the recovery figures obtained. We have still used all reported recovery figures to create populations of recovery-corrected and non-recovery-corrected results to observe the impact of recovery-correction on result distribution (Qn-RSD).

It should be noted that the populations of the laboratories do only partly overlap (see **Table 17**). This is because many labs did not report either a) the recovery figures or b) whether a recovery-based correction was applied or not. Due to this inhomogeneity and the small population of data, any conclusions should be observed with reservation. An additional uncertainty results from the fact that 49 % of the recovery figures were obtained from just one experiment. 33 % concerned two replicates, 14 % 3 replicates, and just 5 % 4 or more replicates (see **Figure 6**). On the other hand 86 % of the recovery figures were obtained within the same batch as the test samples and using the EUPT-blank-matrix for spiking, versus 11 % that were obtained within the same batch but using a different matrix and 3 % using old QC-validation data.

Figure 6: Number of replicate recoveries behind the recovery figures reported by the participants

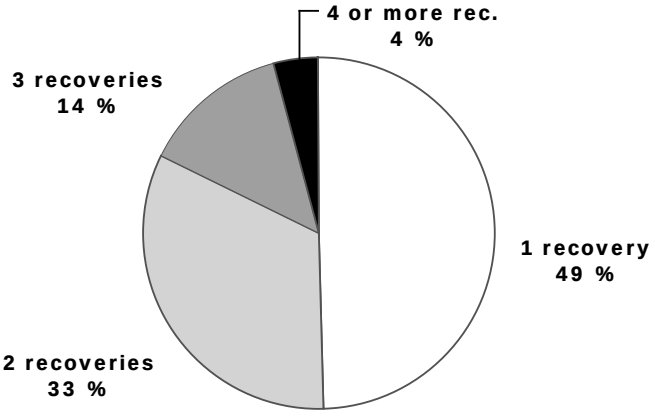


Table 17: Comparison Qn-RSDs with and without recovery correction using recovery figures reported by the labs.

Compound		All Results as reported by labs	Recovery-Corrected Results	Non-Recovery-Corrected Results
Fluazifop	**No. of Results**	51	40	32
	Qn-RSD	**19.8 %**	**16.6 %**	**31.3 %**
Ethephon	**No. of Results**	29	24	22
	Qn-RSD	**23.0 %**	**18.8 %**	**26.0 %**
Dithiocarbamtes	**No. of Results**	71	52	63
	Qn-RSD	**58.2 %**	**51.3 %**	**55.8 %**
Abamectin	**No. of Results**	53	43	49
	Qn-RSD	**24.3 %**	**24.9 %**	**23.9 %**
Fenbutatin oxide	**No. of Results**	35	31 [1)]	31 [1)]
	Qn-RSD	**20.6 %**	**24.9 %**	**20.9 %**

1) Despite the same number of labs, the two populations are slightly different.

As shown in **Table 17**, recovery-based correction did not have any significant impact in the Qn-RSDs in the case of abamectin, dithiocarbamates, and fenbutatin oxide. A clearly positive impact was, however, noticed in the case of fluazifop (Qn-RSD shifted from 31 % to 17 %) and of ethephon (from 26 to 19 %). In the case of fluazifop substantially low recoveries (< 70 %) correlating with substantially underestimated results were reported in 4 cases (labs SRM5-29, -42, -56 and -61), all of them employing the QuEChERS method and reporting the non-recovery corrected results. Applying recovery correction in these cases results in z-score shifts from -2.2, -1.4, -2.3 and -1.8 to -0.6, -0.2, -0.8 and -0.2 respectively. Based on the reported methodology data the low fluazifop recoveries could be in three of those cases linked to the use of PSA sorbent in DSPE cleanup (labs SRM5-29, -42 and 56). PSA sorbent is well known to be binding compounds with acidic groups and its use is not recommended when analyzing acidic pesticides such as fluazifop. **Figure 8** shows the correlation between the reported recovery figures and the reported results (expressed as percentage of the assigned value). In case of a good correlation the datapoints should be located along the 45° axis. Looking at the trendlines the best correlation in this respect is noticed for fluazifop, fenbutatin oxide and ethephon whereas in the cases of abamectin and dithiocarbamates the correlation is very bad showing that in these cases the variations in the reported results are rather based on spurious than on systematic factors.

Overall, 49 % of the recovery figures reported layed between 90 and 110 % and 79 % between 80 and 120 %. Just 9 % of the reported recovery figures ranged between 70 and 80 %, 8 % between 50 and 70 % and 4 % between 120 and 140 %. No recovery figures below 50 % or above 140 % were reported (**Figure 7**). Looking at the individual compounds the percentages of recovery figures laying between 80 and 120 % were 76 % for fenbutatin oxide, 78 % for dithiocarbamates, 80 % for avermectin B1a, 81 % for fluazifop and 85 % for ethephon. Recoveries below 70 % were reported for dithiocarbamates (6 cases), fluazifop (4 cases) and for fenbutatin oxide, ethephon and abamectin (in 1 case each). In the case of dithiocarbamates the low recoveries seemed to be spurious not necessarily correlating with underestimated results for the spiked test material.

Figure 7: Overview of recovery figures reproted by labs

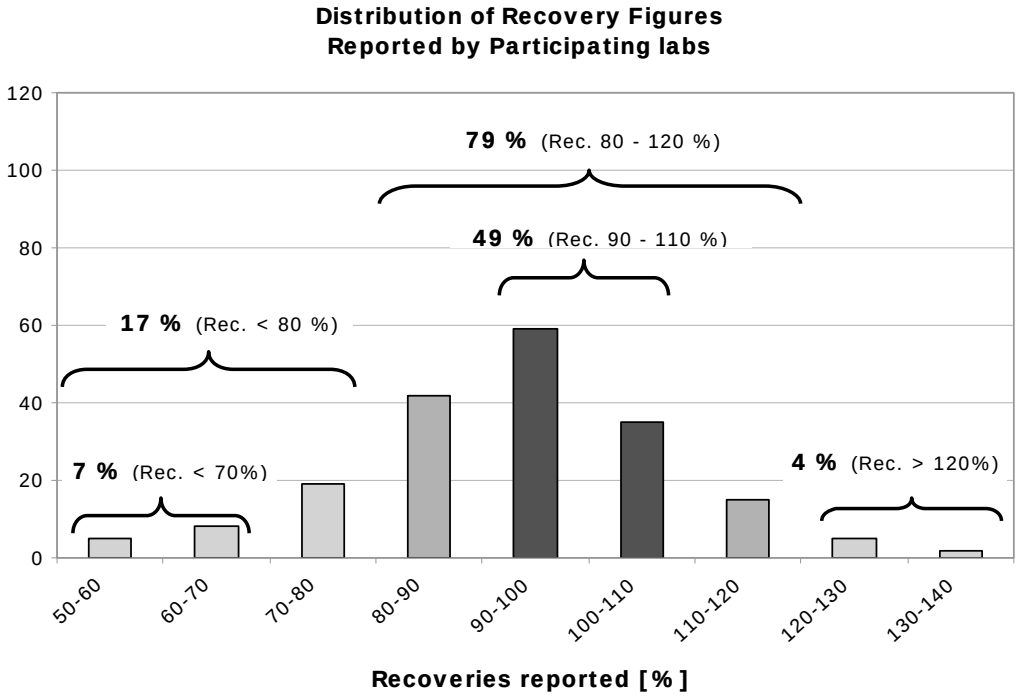
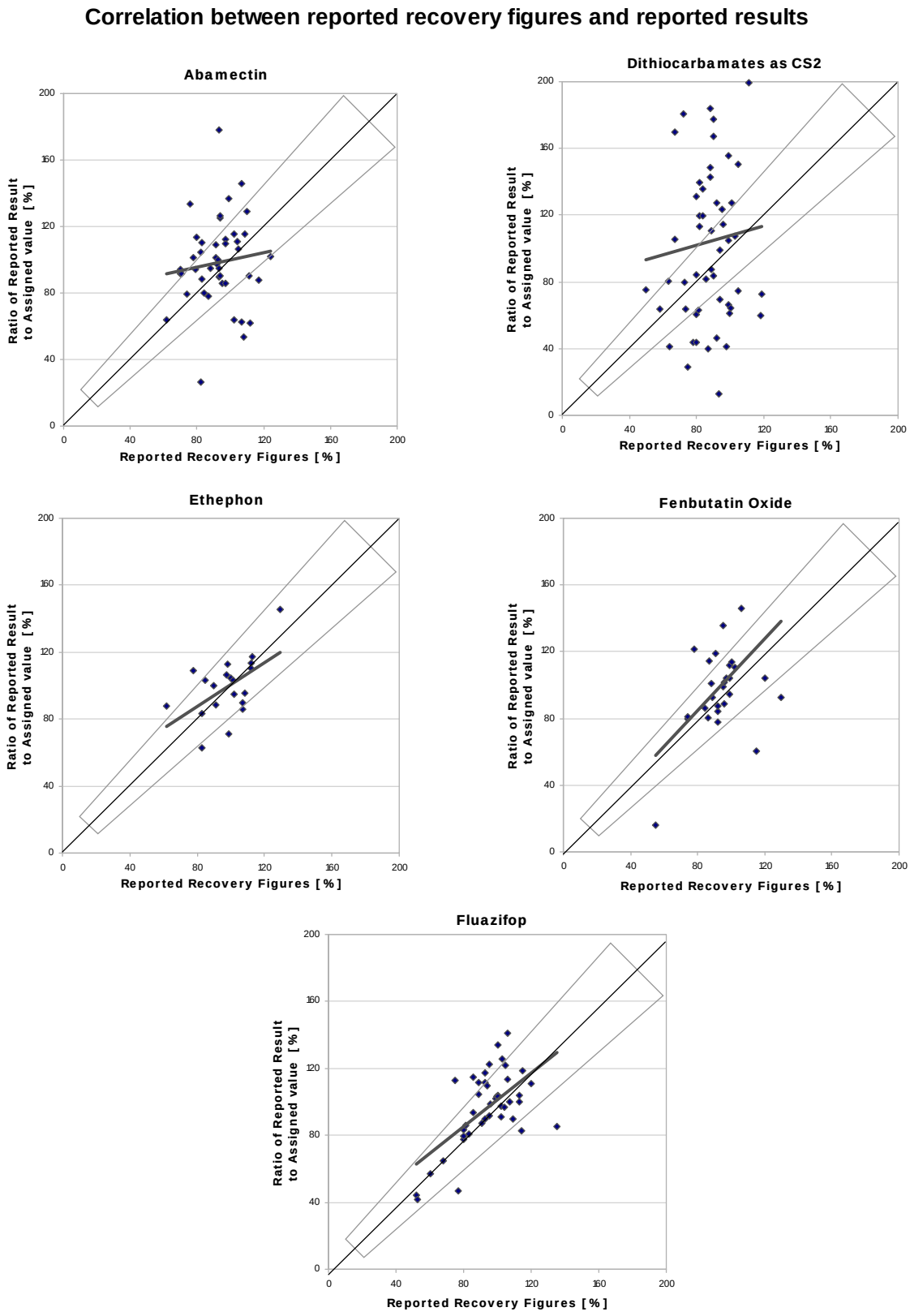


Figure 8: Correlation between reported recovery figures and reported results



4.4.6 Routine analysis of compounds by the labs

As can be seen in **Table 18** dithiocarbamates are more frequently included in the routine scope of the laboratories than any other compound (86 % of the 80 labs submitting results). Next in frequency are haloxyfop (59 %), fluazifop and 2,4-D (54 %), abamectin (51 %) and chlormequat (48 %). The least frequently targeted compounds are fenbutatin oxide (18 %), ethephon (15 %) and amitrole (5 %). The percentages were calculated assuming that labs not answering this question do not routinely target these compounds.

Table 18: Routine analysis of compounds by the labs

Compound	Within routine scope of lab	Analyzed for in this EUPT	Not analyzed for in this EUPT	Sum
Abamectin	Yes	41	0	**41 (51 %)**
	No	11	13	**24**
	No Data	1	14	**15**
	Sum	**53**	**27**	**80**
Dithiocarbamates	Yes	66	3	**69 (86 %)**
	No	3	5	**8**
	No Data	2	1	**3**
	Sum	**71**	**9**	**80**
Ethephon	Yes	12	0	**12 (15 %)**
	No	17	32	**49**
	No Data		19	**19**
	Sum	**29**	**51**	**80**
Fenbutatin oxide	Yes	14	0	**14 (18 %)**
	No	21	24	**45**
	No Data		21	**21**
	Sum	**35**	**45**	**80**
Fluazifop	Yes	42	1	**43 (54 %)**
	No	9	13	**22**
	No Data		15	**15**
	Sum	**51**	**29**	**80**
2,4-D	Yes	42	1	**43 (54 %)**
	No	10	14	**24**
	No Data		13	**13**
	Sum	**52**	**28**	**80**
2,4-DP	Yes	32	1	**33 (41 %)**
	No	9	21	**30**
	No Data		17	**17**
	Sum	**41**	**39**	**80**
Haloxyfop	Yes	46	1	**47 (59 %)**
	No	5	14	**19**
	No Data		14	**14**
	Sum	**51**	**29**	**80**
Amitrol	Yes	2	2	**4 (5 %)**
	No	12	43	**55**
	No Data		21	**21**
	Sum	**14**	**66**	**80**
Chlormequat	Yes	38	0	**38 (48 %)**
	No	15	14	**29**
	No Data	1	12	**13**
	Sum	**54**	**26**	**80**
Mepiquat	Yes	36	0	**36 (45 %)**
	No	16	15	**31**
	No Data	1	12	**13**
	Sum	**54**	**26**	**80**

All labs having abamectin, ethephon and fenbutatin oxide, chlormequat and mepiquat included in their routine scope have also analyzed for these compounds in this EUPT. Only 1 laboratory in the cases of fluazifop, haloxyfop, 2,4-D; 2,4-DP; 2 laboratories in the case of amitrole and 3 in the case of dithiocarbamates have not targeted the respective pesticides despite being part of their routine scope. In 128 cases overall (61 cases concerning compounds present in the sample) laboratories analyzed for compounds within this EUPT despite not being part of their routine scope.

4.4.7 Analytical experience of labs

Overall, more than half (53 %) of the labs indicated that they have > 2 years experience with the analysis of the compounds they have reported concentration values for (**Figure 9**). 18 % of the labs indicated that they had 1 – 2 years experience, 18 % < 1 year experience and 8 % no experience. Interestingly the experience of the labs did not seem to have had a decisive influence on the quality of the results (**Figure 10Fehler! Verweisquelle konnte nicht gefunden werden.**).

It should be highlighted, that the laboratories were only asked to indicate their experience with the analysis of the compounds in the Target Pesticide List. The answers do thus not always reflect the experience of the labs with the analysis of the compounds using the methodology employed in the present EUPT.

Among the 53 labs that provided data regarding the experience with the analysis of **Abamectin** 22 (42 %) indicated that they have a long experience (> 2 years), 14 labs (26 %) a short experience (1 – 2 years) and 11 labs (21 %) a very short experience (< 1 year). Further 5 labs (9 %) indicated that they had “no experience” with the analysis of this compound (**Figure 10**).

Among the 29 labs that provided data regarding the experience with the analysis of **Ethephon** 7 (24 %) indicated having > 2 years experience with analyzing this compound. 5 labs (17 %) indicated that they had 1 – 2 years experience and 8 labs (28 %) < 1 year experience (very short). 9 labs (31 %) indicated that they had “no experience” with the analysis of ethephon. Ethephon is thus the compound where the labs have the least experience with its analysis.

Out of the 35 labs providing information about their experience with the analysis of **Fenbutatin oxide**, 10 (29 %) indicated having > 2 years experience with analyzing this compound. 4 labs (11 %) indicated that they had 1 – 2 years experience and 12 labs (34 %) < 1 year experience (very short). Further 9 labs (26 %) indicated that they had “no experience” with the analysis of Fenbutatin oxide.

Figure 9: Overview of labs’ experience with the pesticides included in the target pesticides list

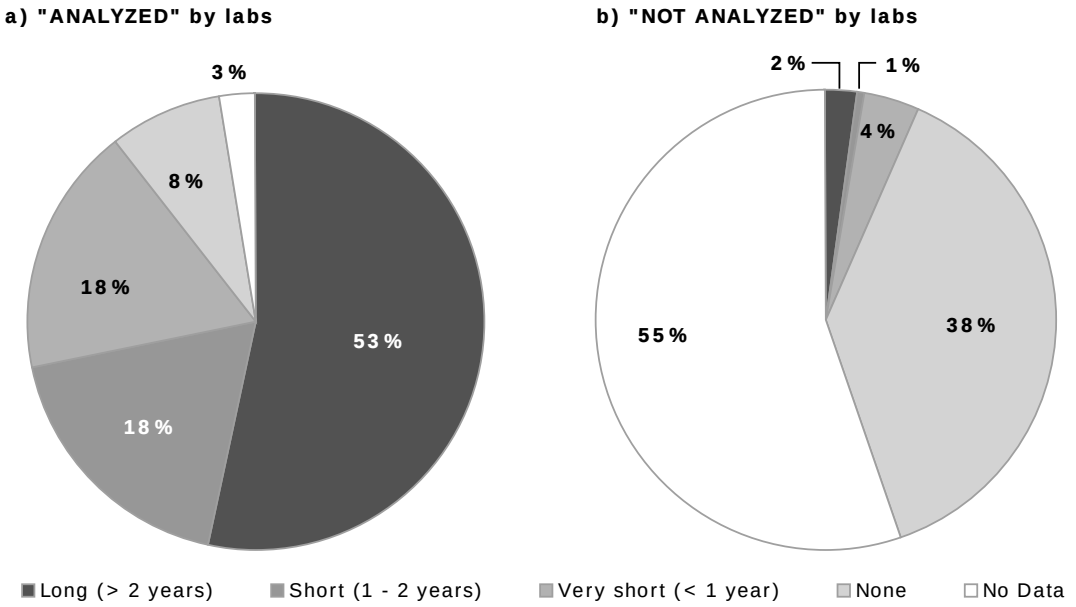
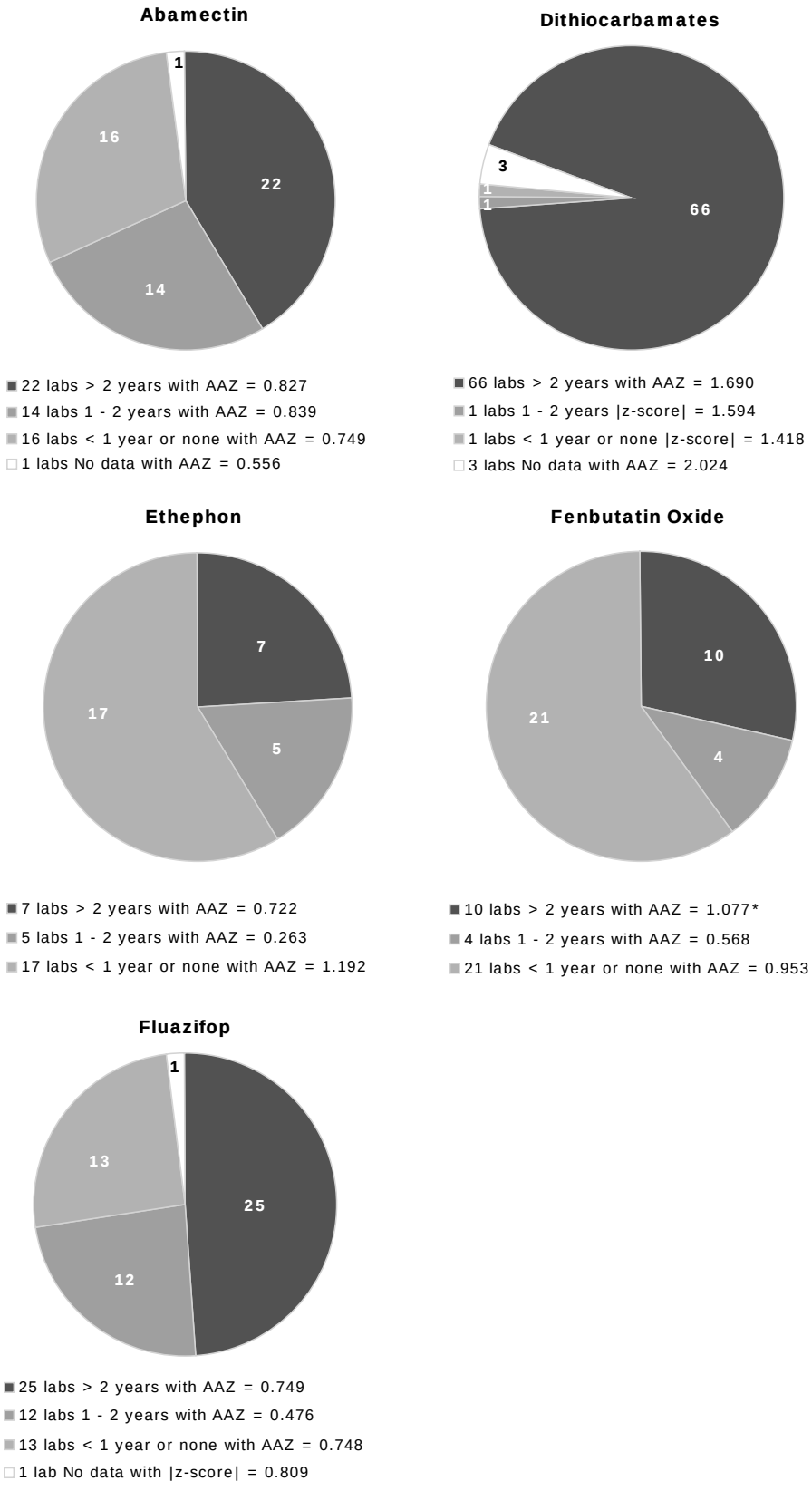


Figure 10: Labs' experience with each of the pesticides present in the test material and performance quality on average



Note: Results reported as ND were not included for the calculation of the mean absolute z-score. For the calculation "5" was used for all absolute z-scores higher than 5.

Out of the 50 labs providing information about their experience with the analysis of **Fluazifop**, 25 (50 %) indicated having > 2 years experience with analyzing this compound. 12 labs (24 %) indicated that they had 1 – 2 years experience, 11 labs (22 %) < 1 year experience (very short) and 2 labs (4 %) "no experience".

Out of the 68 labs providing information about their experience with the analysis of **Dithiocarbamates**, 66 (88 %) indicated having > 2 years experience with analyzing this compound. 1 lab each reported having 1 – 2 years experience, < 1 year experience (very short) and "no experience". Dithiocarbamates are thus not only the compounds most frequently analyzed by the labs but also those where the labs have the most experience with.

4.5 Summary, Conclusions and Prospects for the SRM pesticides

The EUPT-SRM5 was the fifth scheduled EUPT focusing on compounds requiring single residue methods and the third organized collaboratively between the EURL-SRM and the EURL-FV.

In total 89 laboratories registered for the EUPT-SRM5 with 80 of them, representing 28 countries (25 EU-MS plus Switzerland, Norway and Egypt) submitting results.

Compared to previous EUPTs organized by the EURL-SRM the participation clearly increased. In the previous two EUPT-SRMs, focusing on fruits and vegetables, the laboratories submitting results were 24 from 14 countries (13 EU-MS) at the EUPT-SRM1 (in 2006) and 66 from 23 countries (21 EU-MS) at the EUPT-SRM3 (in 2008). A notable positive trend was not only noticed as regards the number of participants but also as regards the number of labs analyzing individual compounds. The number of participants analyzing for ethephon, avermectin B1a, fluazifop and dithiocarbamates has increased from 4, 24, 35 and 59 in EUPT-SRM3 to 30, 53, 51 and 71 in EUPT-SRM5 respectively. For fenbutatin oxide the increase was from 10 labs in EUPT-SRM1 to 35 in the present test. This positive trend is surely based upon many factors such as the increased use of LC-MS/MS instrumentation by the laboratories, the implementation of simple methodologies including those developed and distributed by the EURL-SRM as well as the strengthening of the network of official laboratories within the EU and the information flow within it. Another important factor contributing in this direction was the fact that EUPT-participation became compulsory for official laboratories within the EU. It should be further noted, that in the case of EUPT-SRM3 and 5 the increased participation was also related to the inclusion of dithiocarbamates in the scope, which are routinely analysed by a high percentage of laboratories, as analysis does not involve the use of LC-MS technology.

The EU-member states from which no laboratory participated in EUPT-SRM5 were Romania and Luxembourg. Malta subcontracted a commercial laboratory based in Italy. Among the countries where NRL-SRMs did not submit any results were Romania, Luxembourg and France. The latter had not appointed any NRL-SRM at the time the PT was undertaken. Spain had appointed an NRL-SRM internally but had not communicated this information officially to DG-SANCO.

The target pesticide list, distributed to the laboratories well in advance to the test, contained in total 11 SRM-compounds with 9 of them being marked with an asterisk and considered in lab classification and lab ranking. The test material itself contained 5 pesticides namely; abamectin, ethephon, fenbutatin oxide, fluazifop and dithiocarbamates (thiram) all of them marked with an asterisk. All pesticides contained in the sample were spiked by the Organizer.

For each laboratory/pesticide combination, z-scores based on the FFP-RSD of 25 % were calculated and classified into 'acceptable', 'questionable' and 'unacceptable' according to the agreed rules. Overall, the quality of the results was good with 47 out of 51 laboratories (92 %) reporting results within the acceptable z-score-range in the case of fluazifop, 26 out of 29 (90 %) in the case of ethephon, 50 out of 53 (94 %) in the case of avermectin B1a and 31 out of 35 (89 %) for fenbutatin oxide. For dithiocarbamates the picture

was different, with only roughly two out of three labs (46 out of 71) achieving acceptable results when applying the FFP target standard deviation of 25 %.

The robust standard deviation (Qn-RSD), reflecting the result-distribution, was also calculated for each pesticide. Qn-RSD-levels were very satisfactory for fluazifop (20 %), ethephon (23 %), avermectin B1a (24 %) and fenbutatin oxide (21 %) fully justifying the use of the generic FFP target standard deviation. For dithiocarbamates, however, the Qn-RSD was at 59 % and thus well above what is acceptable when using the 25 % FFP-target standard deviation. For this reason, the quantitative results for dithiocarbamates were not included in the overall evaluation and the z-scores calculated using the FFP-RSD of 25 % are given for information only. Dithiocarbamates were, however, still considered from the qualitative point of view, i.e. inclusion in the scope and detection was considered in lab classification and ND results were judged as false negatives (as the MRRL was very distant from the assigned value).

False negative results concerned dithiocarbamates (3x) and ethephon (1x). False positives concerned amitrole (3x) as well as 2,4-D (1x), chlormequat (1x) and mepiquat (1x). The latter three false positives were reported by the same lab.

Laboratories were classified based on their scope and ranked based on their overall performance always considering the pesticides marked with an asterisk in the target pesticide list. In total 15 laboratories (19%) were classified into Category A with 7 of them being NRL-SRMs. 11 (73 %) of the Category A labs were classified as “Good” ($SWZ \leq 2$), none as “Satisfactory” ($SWZ\ 2-3$) and 4 (27 %) as “Unsatisfactory” ($SWZ > 3$). The other 65 laboratories (including 16 NRL-SRMs) were included in Category B because of insufficient scope or because of false positive results. In general NRL-SRMs performed better than the other laboratories in terms of scope but slightly worse as regards result accuracy as reflected by the z-scores. Overall 33 labs have reported results for at least 4 of the analytes present in the samples and 49 labs for at least 3 of those compounds.

The 77 EU labs that finally participated in this EUPT represent only 37% of all 206 labs that routinely analyze for pesticide residues in fruits and vegetables. This figure needs to be increasedin the future. To encourage laboratories to further increase their scope and decrease their reporting levels the EUPT-Scientific Committee strongly recommends laboratories to get equipped with LC-MS/MS, as most of the SRM-pesticides can only be analysed, with the efficiency required for routine analyses, via liquid chromatographic techniques. The aim is that laboratories continue to increase their scope of analytes in their methods in order to be able to fully enforce EU legislation and to improve their overall performance, both in terms of correctly detecting the pesticides present as well as accurately determining the residue levels.

Furthermore the Scientific Committee recomments laboratories that use extensively large analytical portions (> 50 g) to scale-down where possible their dithiocarbamates methods to (e.g. 10 - 50 g) as the material provided in EUPT is homogeneous. It is also recommended that labs using spectrophotometric methods, and particularly the method based on EN-12396-1 involving derivatisation with Cu(II) acetate, to switch to other types of methods allowing for lower reporting limits (RLs) and better accuracy.

The EURL-SRM will continue monitoring the performance of laboratories as regards the analysis of dithiocarbamates as well as the expansion of the scope of official labs by SRM-Analytes. To promote the latter, the EURL-SRM will further continue developing, validating and distributing simple-to-use, fast and cheap methodologies for compounds not amenable to multiresidue methods. In future PTs, the selection of pesticides will continue to focus on pesticides included in the scope of the coordinated control programmes as well as on additional pesticides of relevance.

5 ACKNOWLEDGEMENTS

The Organisers wishes to thank the members of the Scientific Committee (Quality Control Group and Advisory Group) for their valuable advice.

6 REFERENCES

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[3] EN 15662: Determination of Pesticide Residues Using GC-MS and/or LC-MS (/MS) following Acetonitrile Extraction/Partitioning and Clean-up by Dispersive SPE-QuEChERS method. In European Committee for Standardization, Technical Committee CEN/TC 275; "Food Analysis – Horizontal Methods"; Brussels, Belgium, 2008.

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7 APPENDICES

Appendix 1 List of Laboratories registered to participate in the EUPT-SRM5

Lab- Location		Institution Name	Analyzing on behalf of…	Lab type	Re-ported results
Country	City				
Austria	Innsbruck	AGES CC PSMR Innsbruck	Austria	NRL-SRM	Yes
Belgium	Zwijnaarde	Fytolab	Belgium	CL	Yes
Belgium	Bruxelles	Scientific Institute of Public Health	Belgium	NRL-SRM	Yes
Belgium	Gentbrugge	Federal Food Agency Belgium	Belgium	OFL	Yes
Belgium	Geel	LOVAP NV	Belgium	CL	Yes
Bulgaria	Sofia	Central Laboratory for Chemical Testing and Control	Bulgaria	NRL-SRM	Yes
Croatia	Zagreb	Faculty of food technology and biotechnology	Croatia	OFL	No
Cyprus	Nicosia	State General Laboratory	Cyprus	NRL-SRM	Yes
Czech Republic	Prague	Czech Agriculture and Food Inspection Authority	Czech Republic	NRL-SRM	Yes
Czech Republic	Prague	Institute of Chemical Technology Prague	Czech Republic	OFL	Yes
Denmark	Ringsted	Danish Veterinary and Food Administration	Denmark	OFL	Yes
Denmark	Soeborg	National Food Institute	Denmark	NRL-SRM	Yes
Egypt	Giza	Central Lab of Residue Analysis of Pesticides and Heavy metals in Foods	Egypt	OFL	Yes
Estonia	Tartu	Health Board	Estonia	NRL-SRM	Yes
Estonia	Saku	AGRICULTURAL RESEARCH CENTRE	Estonia	OFL	Yes
Finland	Espoo	Finnish Customs Laboratory	Finland	NRL-SRM	Yes
France	Montpellier	Laboratoire du SCL de Montpellier	France	OFL	Yes
France	Massy	SCL laboratoire d'Ile de France Massy	France	OFL	Yes
France	Ploufragan	LABORATOIRE de DEVELOPPEMENT et D' ANALYSE des COTES D' ARMOR (L.D.A 22)	France	OFL	Yes
France	Saint-Denis	SERVICE COMMUN DES LABORATOIRES	France	OFL	Yes
France	Illkirch	SCL Strasbourg	France	OFL	Yes
France	Garons	CERECO SUD	France	CL	Yes
Germany	Berlin	Federal Office of Consumer Protection and Food Safety (BVL)	Germany	NRL-SRM	Yes
Germany	Oldenburg	Niedersaechsisches Landesamt fuer Verbraucher schutz und Lebensmittelsicherheit	Germany	OFL	Yes
Germany	Speyer	Landesuntersuchungsamt	Germany	OFL	Yes
Germany	Bonn	Amt fuer Umwelt, Verbraucherschutz und Lokale Agenda der Stadt Bonn	Germany	OFL	Yes
Germany	Erlangen	Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit, Erlangen	Germany	OFL	Yes
Germany	Berlin	Landeslabor Berlin-Brandenburg	Germany	OFL	Yes
Germany	Muenster	Chemisches- und Veterinaeruntersuchungsamt Muensterland-Emscher-Lippe (CVUA-MEL)	Germany	OFL	Yes
Germany	Halle/Saale	Landesamt für Verbraucherschutz Sachsen-Anhalt	Germany	OFL	Yes
Germany	Hamburg	Institut fuer Hygiene und Umwelt	Germany	OFL	Yes
Germany	Neumünster	Landeslabor Schleswig-Holstein	Germany	OFL	Yes
Germany	Krefeld	CVUA RRW	Germany	OFL	Yes
Germany	Kiel	LUFA-ITL GmbH	Belgium	CL	Yes
Germany	Duesseldorf	Amt fuer Verbraucherschutz Duesseldorf	Germany	OFL	Yes
Greece	Kiphissia - ATHENS	Benaki Phytopathological Institute	Greece	NRL-SRM	Yes

Lab- Location		Institution Name	Analyzing on behalf of…	Lab type	Re-ported results
Country	City				
Greece	Athens	General Chemical State Laboratory	Greece	NRL-SRM	Yes
Greece	Patras	Regional Center of Plant Protection & Quality Control of Achaia	Greece	OFL	Yes
Greece	IRAKLION	REGIONAL CENTRE OF PLANT PROTECTION & QUALITY CONTROL OF IRAKLION	Greece	OFL	Yes
Hungary	Velence	Agricultural Office of County Fejer, PPSCD	Hungary	OFL	Yes
Hungary	Kaposvar	Agricultural Office of Somogy County	Hungary	OFL	Yes
Hungary	Miskolc	Agricultural Office of B.-A.-Z. County	Hungary	NRL-SRM	Yes
Ireland	Celbridge, Co. Kildare	Department of Agriculture, Food and Fisheries	Ireland	NRL-SRM	Yes
Italy	Verona	ARPA-VENETO	Italy	OFL	Yes
Italy	Ferrara	ARPA Regione Emilia-Romagna	Italy	OFL	No
Italy	Bozen	Agentur für Umwelt	Italy	OFL	Yes
Italy	Rome	National Institute of Health	Italy	NRL-SRM	Yes
Italy	Avola (SR)	Cefit srl	Malta	CL	Yes
Italy	Rome	ARPA LAZIO SEZIONE P.LE DI ROMA	Italy	OFL	Yes
Italy	Latina	ARPA LAZIO	Italy	OFL	No
Italy	Legnaro (Pa-dova)	Istituto Zooprofilattico Sperimentale delle Venezie	Italy	OFL	No
Latvia	Riga	Institute of Food Safety, Animal Health and Envi-ronment (BIOR)	Latvia	NRL-SRM	Yes
Lithuania	Vilnius	National food and veterinary risk assessment institute	Lithuania	NRL-SRM	Yes
Norway	Aas	Bioforsk	Norway	NRL-SRM	Yes
Poland	Rzeszow	Institute of Plant Protection	Poland	OFL	Yes
Poland	Skierniewice	Research Institute of Pomology & Floriculture	Poland	OFL	No
Poland	Poznan	Institute of Plant Protection	Poland	OFL	Yes
Poland	Trzebnica	Instytut Ochrony Roslin - PIBExperimental Station of Institute of Plant Protection	Poland	OFL	Yes
Poland	Sosnicowice	Institute of Plant Protection - National Research Institute Sosnicowice Branch	Poland	OFL	Yes
Poland	Bydgoszcz	Laboratory of Bydgoszcz Voivodeship Sanitary-Epidemiological Station	Poland	OFL	Yes
Poland	Wroclaw	Wojewodzka Stacja Sanitarno-Epidemiologiczna we Wroclawiu	Poland	OFL	Yes
Poland	Warsaw	Voivodship Sanitary-Epidemiological Station	Poland	OFL	Yes
Poland	Opole	Wojewódzka Stacja Sanitarno-Epidemiologiczna w Opolu	Poland	OFL	Yes
Poland	Torun	Main Inspectorate of Plant Health and Seed Inspection	Poland	OFL	Yes
Portugal	Oeiras	INRB-L-INIA	Portugal	NRL-SRM	Yes
Portugal	Funchal	Direccao de Servicos de Laboratorios Agro-Alimentares	Portugal	OFL	Yes
Portugal	Senhora da Hora	DRAPN	Portugal	OFL	Yes
Portugal	Faro	Direcção Regional de Agricultura e Pescas do Algarve	Portugal	OFL	Yes
Slovakia	Bratislava	State Veterinary and Food Institute	Slovakia	NRL-SRM	Yes
Slovenia	Maribor	Institute of Public Health Maribor	Slovenia	NRL-SRM	Yes
Slovenia	Ljubljana	Agricultural institute of Slovenia	Slovenia	OFL	Yes
Slovenia	Ljubljana	Institute of public health	Slovenia	OFL	Yes
Spain	Agüimes	Instituto Tecnológico de Canarias, S. A.	Spain	OFL	Yes
Spain	Zaragoza	GOBIERNO DE ARAGON	Spain	OFL	Yes

Lab- Location		Institution Name	Analyzing on behalf of…	Lab type	Reported results
Country	City				
Spain	Navarra	NASERSA	Spain	OFL	No
Spain	Madrid	MINISTERIO DE MEDIO AMBIENTE MEDIO RURAL Y MARINO	Spain	OFL	Yes
Spain	Burjassot	Laboratorio Agroalimentario de la Generalitat Valenciana	Spain	OFL	Yes
Spain	Huelva	Laboratorio de Sanidad Vegetal de Huelva	Spain	OFL	No
Spain	Burgos	Junta de Castilla y León	Spain	OFL	Yes
Spain	JAEN	LABORATORIO DE PRODUCCION Y SANIDAD VEGETAL DE JAEN	Spain	OFL	Yes
Sweden	Lidköping	Eurofins Food/Agro Sweden AB	Sweden	CL	Yes
Switzerland	Zürich	Kantonales Labor Zürich	Switzerland	OFL	Yes
Switzerland	Basel	Kantonales Laboratorium Basel-Stadt	Switzerland	OFL	No
Netherlands	Amsterdam	VWA - Food and Consumer Product Safety Authority	Netherlands	NRL-SRM	Yes
Netherlands	Graauw	Grond-, Gewas- en Milieulaboratorium "Zeeuws-Vlaanderen" b.v.	Belgium	CL	Yes
UK	York	The Food and Environment Research Agency	UK	NRL-SRM	Yes
UK	Teddington	Laboratory of the Government Chemist	UK	CL	Yes
UK	Wolverhampton	Eurofins Laboratories Ltd	UK	CL	No
UK	Edinburgh	SASA	UK	OFL	Yes

CL= Contract lab

Appendix 2 Data of homogeneity test

Bottle No.	Fluazifop [mg/kg]		Ethephon [mg/kg]	
	Portion 1	Portion 2	Portion 1	Portion 2
085	0.270	0.252	0.311	0.340
045	0.248	0.299	0.331	0.320
012	0.276	0.257	0.337	0.334
006	0.262	0.302	0.323	0.341
046	0.314	0.275	0.327	0.329
030	0.276	0.267	0.333	0.324
028	0.241	0.305	0.340	0.348
023	0.276	0.242	0.338	0.327
147	0.315	0.254	0.345	0.326
108	0.272	0.271	0.343	0.327

Bottle No.	Abamectin [mg/kg]		Fenbutatin oxide [mg/kg]	
	Portion 1	Portion 2	Portion 1	Portion 2
085	0.370	0.355	0.167	0.162
045	0.378	0.387	0.170	0.192
012	0.375	0.385	0.186	0.192
006	0.373	0.409	0.181	0.170
046	0.366	0.366	0.192	0.164
030	0.380	0.354	0.179	0.186
028	0.380	0.365	0.176	0.183
023	0.384	0.365	0.158	0.175
147	0.376	0.459	0.169	0.167
108	0.396	0.430	0.179	0.171

Bottle No.	Dithiocarbamates [mg/kg]	
	Portion 1	Portion 2
085	0.350	0.361
034	0.336	0.317
012	0.273	0.263
003	0.308	0.295
046	0.246	0.262
030	0.277	0.287
028	0.265	0.263
023	0.312	0.306
078	0.270	0.256
108	0.298	0.334

Appendix 3 Data of stability test

Bottle No.108	Fluazifop [mg/kg]			Ethephon [mg/kg]		
Subsample	20.09.2010	01.10.2010	19.10.2010	20.09.2010	01.10.2010	19.10.2010
1	0.272	0.288	0.261	0.351	0.336	0.351
2	0.326	0.332	0.241	0.352	0.364	0.319
3	0.310	0.293	0.261	0.334	0.358	0.326
4	0.295	0.281	0.281	0.342	0.352	0.320
5	0.271	0.271	0.269	0.333	0.342	0.341
Mean [mg/kg]	**0.295**	**0.293**	**0.263**	**0.342**	**0.350**	**0.331**
RSD* [%]	**8.12 %**	**7.96 %**	**5.56 %**	**2.63 %**	**3.26 %**	**4.24 %**
% Diviation (ref. 1. Anaylsis)	**—**	**-0.61 %**	**-10.92 %**	**—**	**2.34 %**	**-3.21 %**

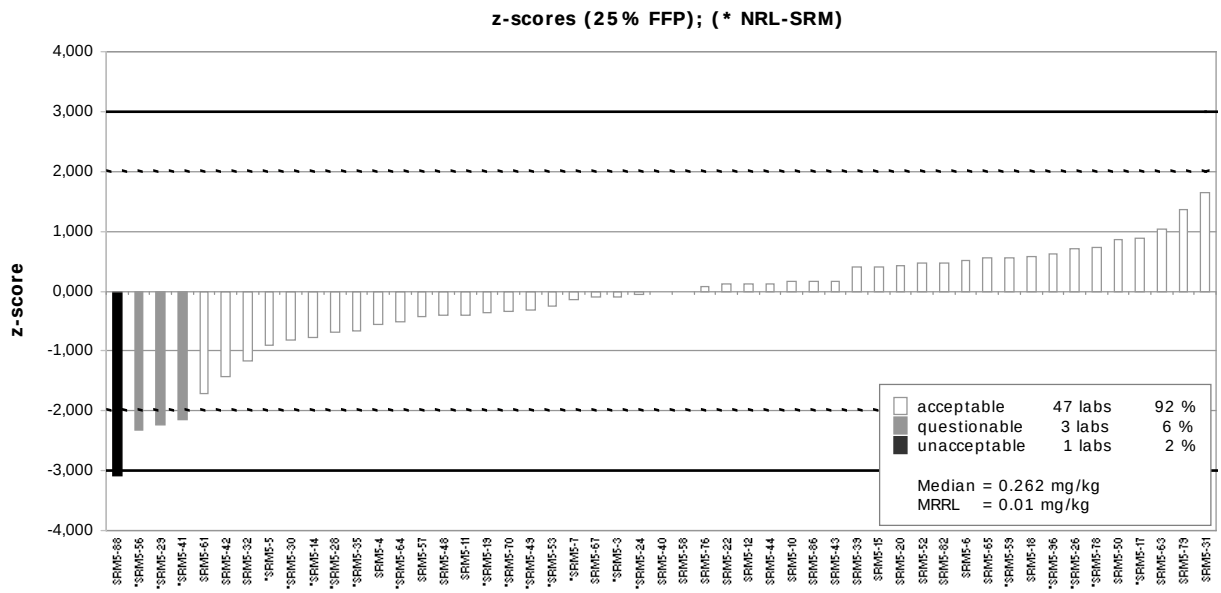
Bottle No.108	Abamectin [mg/kg]			Fenbutatin oxide [mg/kg]		
Subsample	20.09.2010	01.10.2010	19.10.2010	20.09.2010	01.10.2010	19.10.2010
1	0.390	0.367	0.374	0.303	0.272	0.320
2	0.432	0.376	0.361	0.327	0.285	0.329
3	0.382	0.382	0.378	0.277	0.304	0.303
4	0.403	0.413	0.375	0.276	0.321	0.297
5	0.411	0.399	0.388	0.295	0.282	0.316
Mean [mg/kg]	**0.403**	**0.387**	**0.375**	**0.295**	**0.293**	**0.313**
RSD* [%]	**4.84 %**	**4.81 %**	**2.54 %**	**7.14 %**	**6.65 %**	**4.09 %**
% Diviation (ref. 1. Anaylsis)	**—**	**-4.00 %**	**-6.97 %**	**—**	**-0.95 %**	**5.96 %**

Bottle No. 046	Dithiocarbamates [mg/kg]		
Subsample	20.09.2010	01.10.2010	19.10.2010
1	0.293	0.298	0.319
2	0.297	0.301	0.329
3	0.300	0.302	0.332
4	0.298	0.313	0.329
5	0.297	0.280	0.330
Mean [mg/kg]	**0.297**	**0.299**	**0.330**
RSD* [%]	**0.94 %**	**4.01 %**	**2.71 %**
% Diviation (ref. 1. Anaylsis)	**—**	**0.70 %**	**11.24 %**

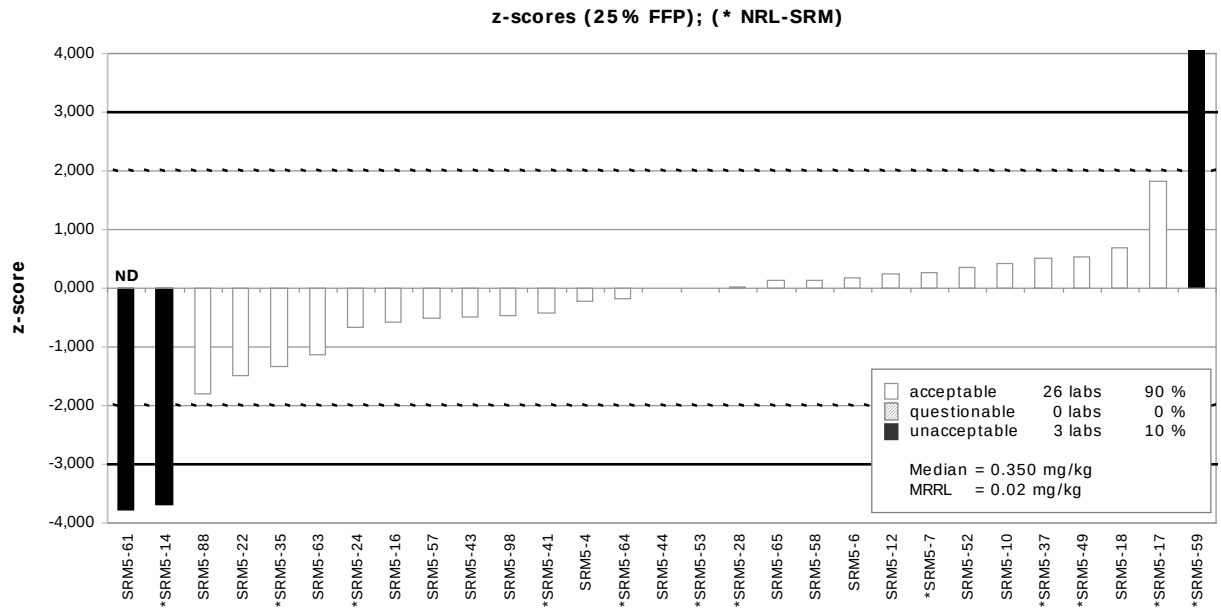
***** RSD = relative standard diviation

Appendix 4 Graphical presentation of z-scores for each pesticide

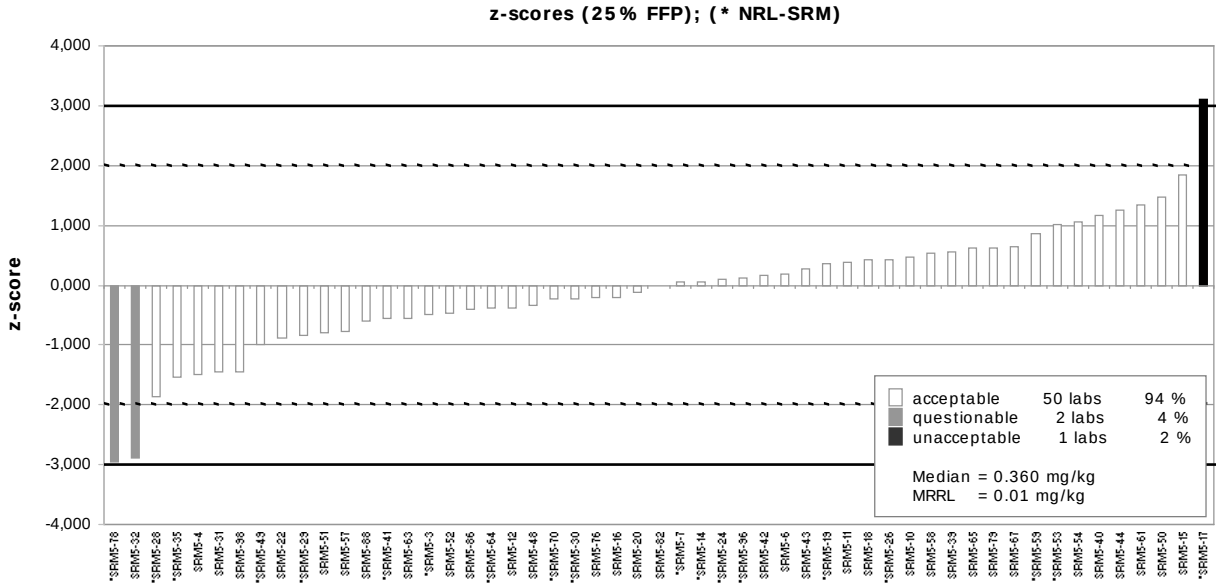
Fluazifop



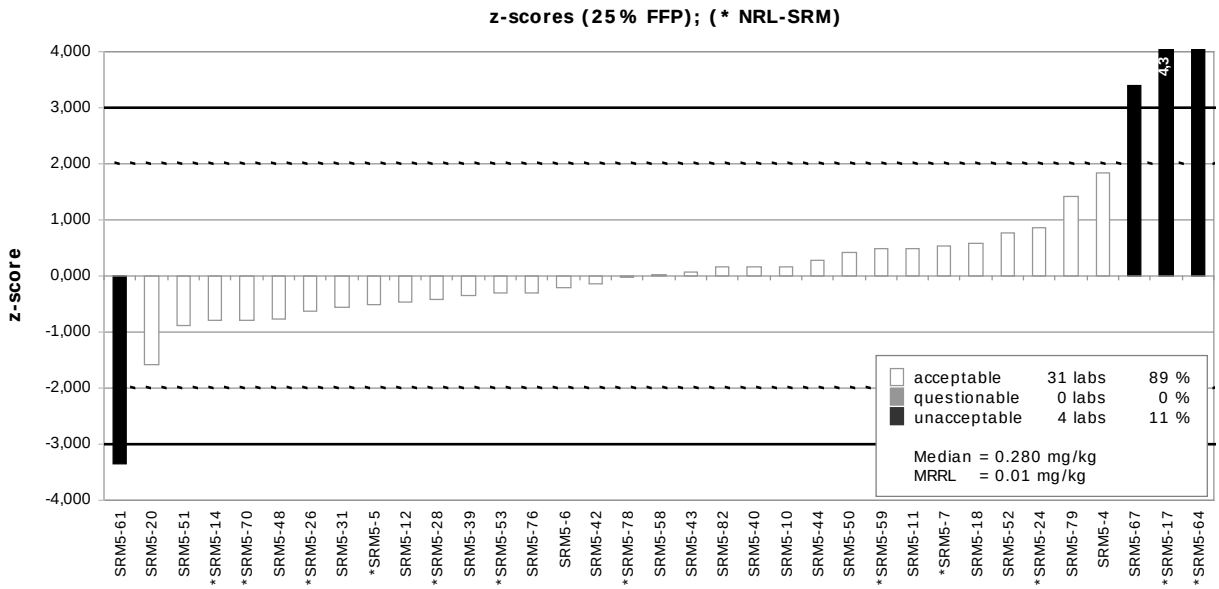
Ethephon



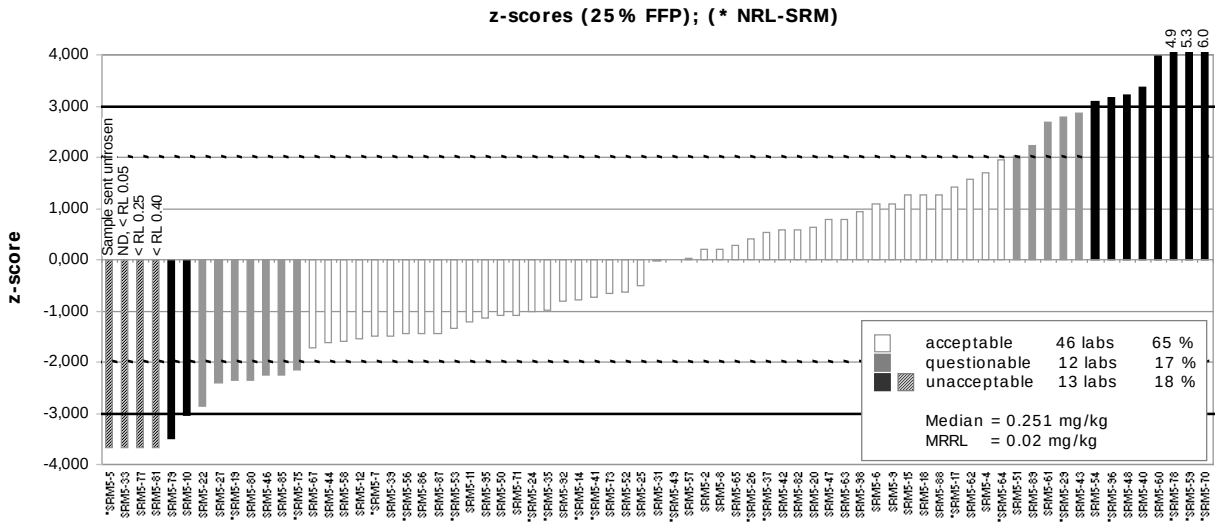
Abamectin



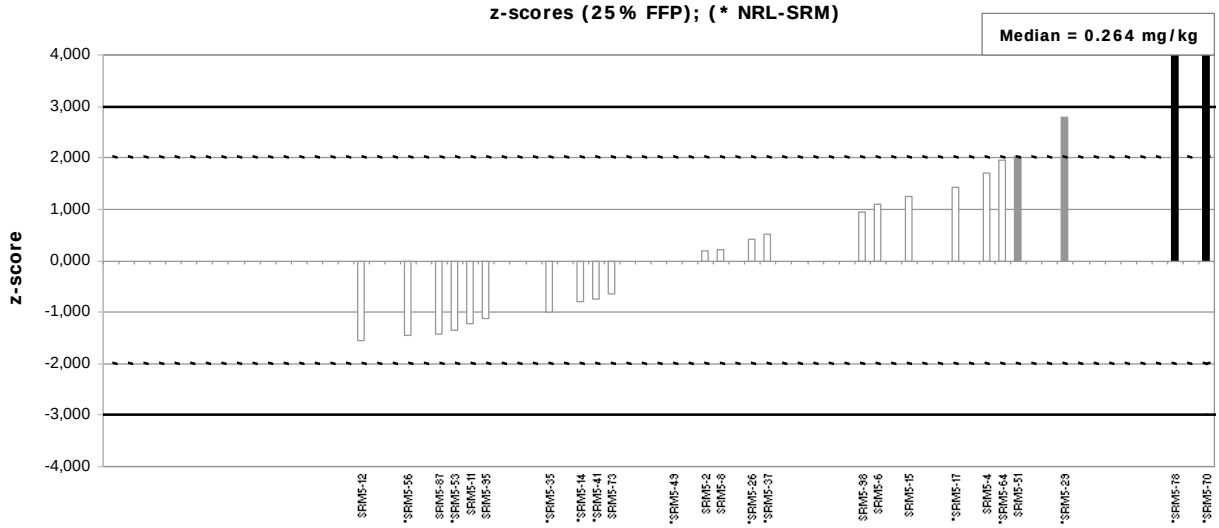
Fenbutatin Oxide



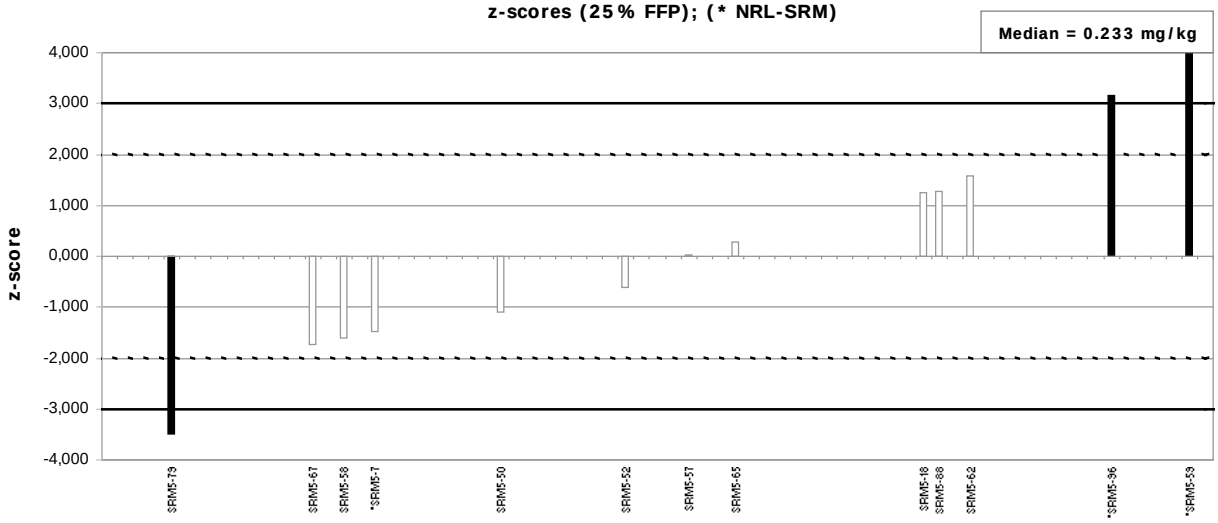
Dithiocarbamates



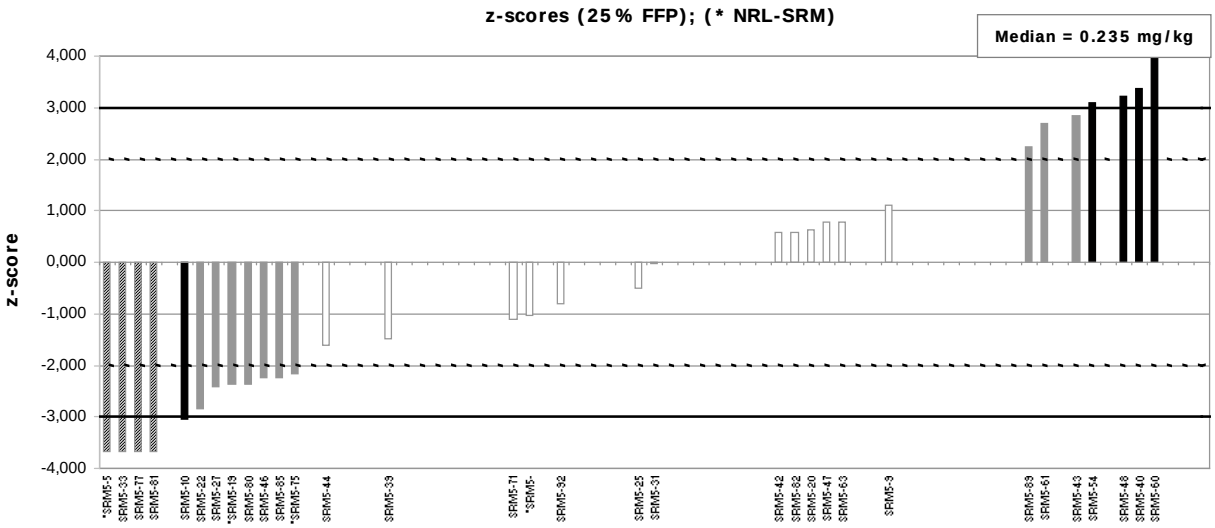
Liq-Liq-Part. to non-polar Solvent + GC Analysis



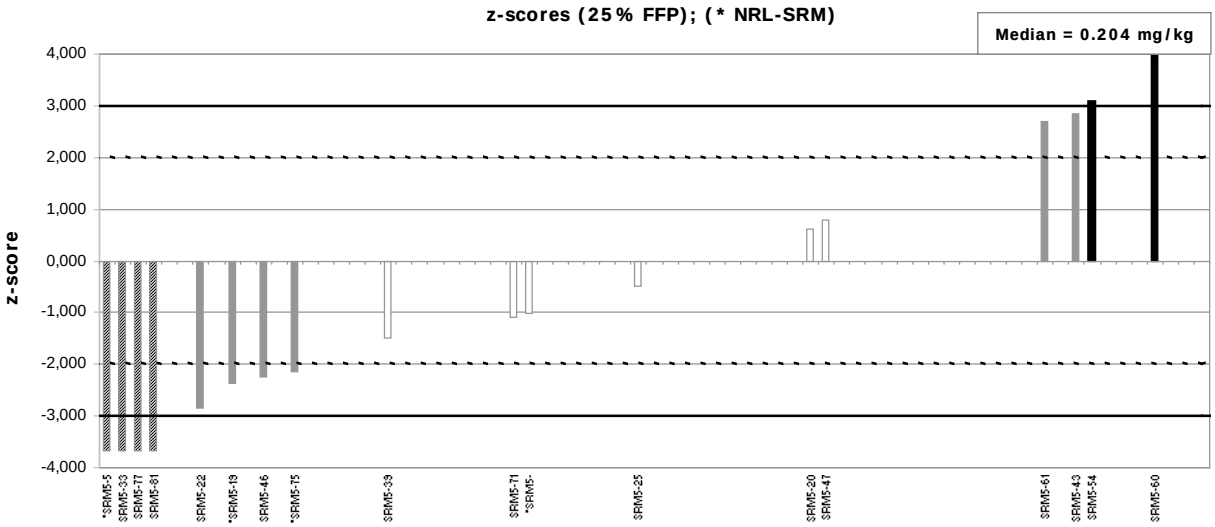
Headspace Sampling + GC-Analysis



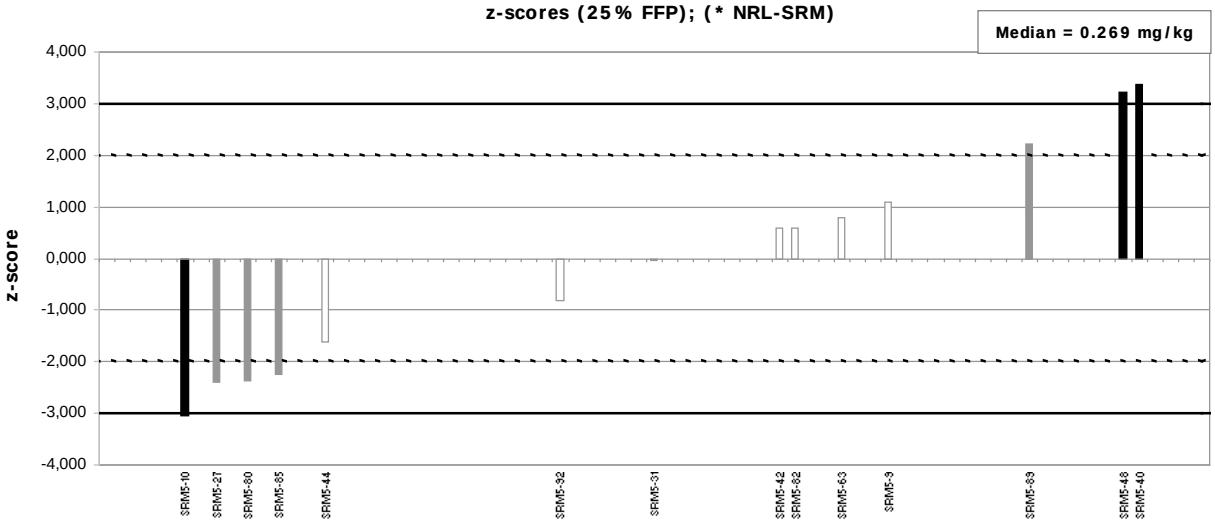
Spectrophotometric Approach (total)



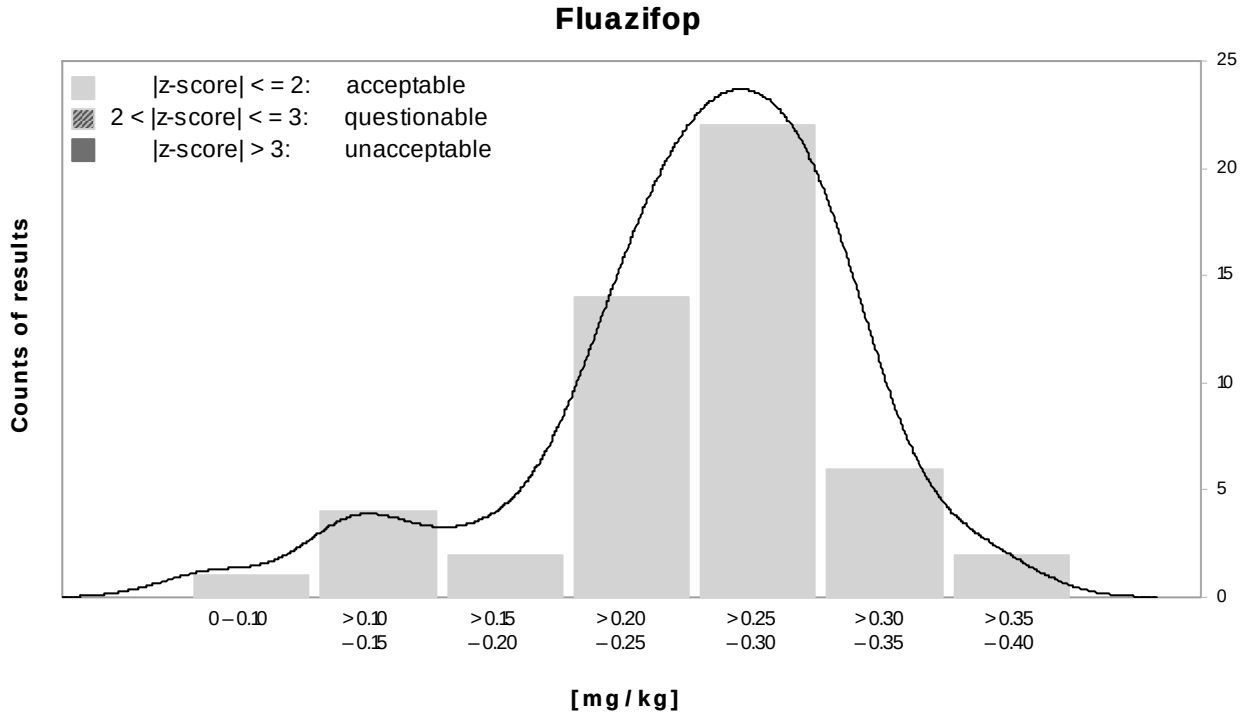
Spectrophotometric Approach | Cu(II) Acetate-Method

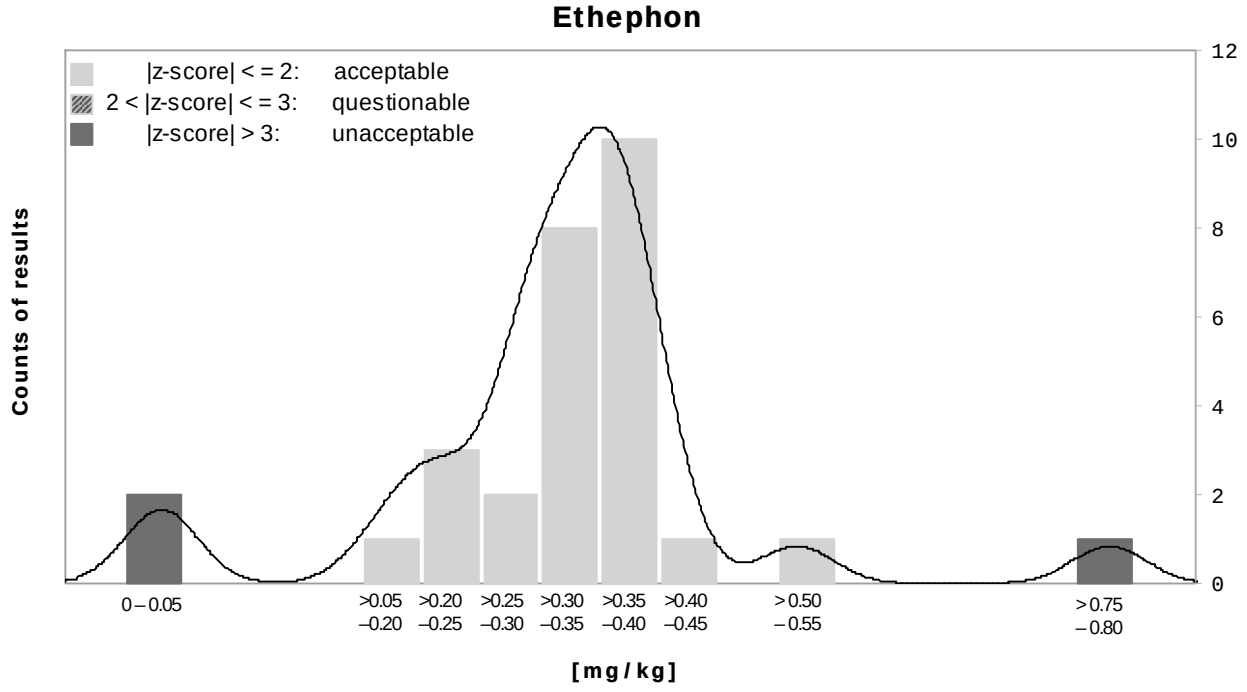


Spectrophotometric Approach | Xanthogenate-Method

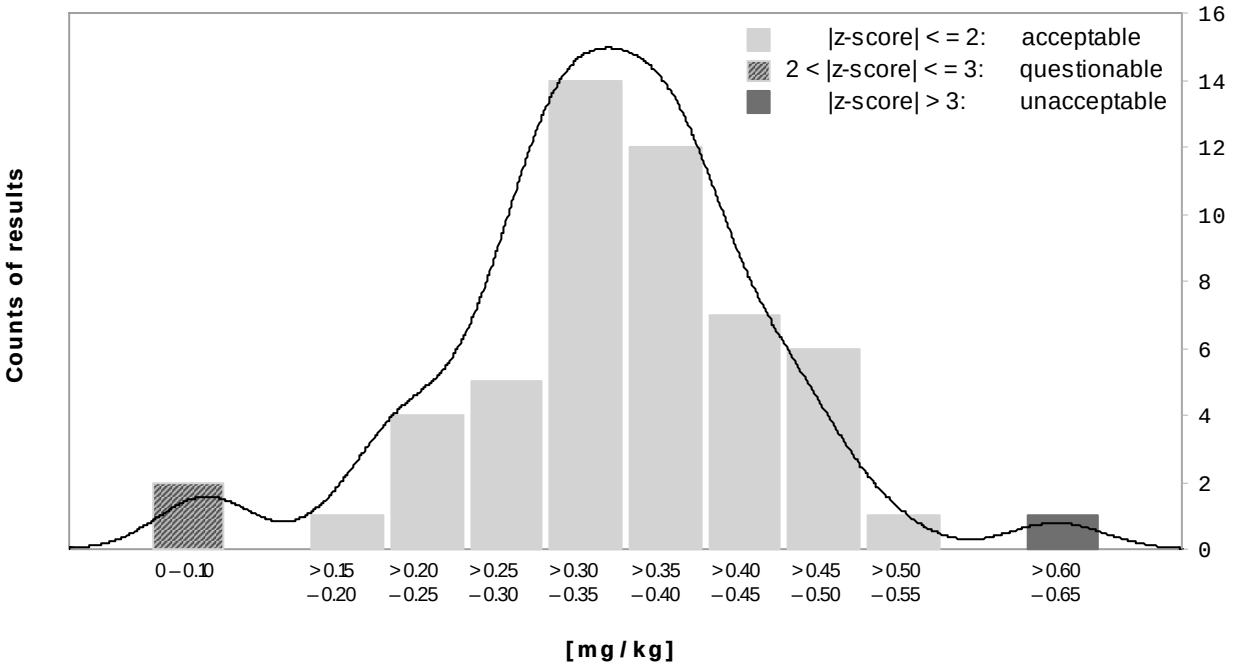


Appendix 5 Histograms showing the distribution of results for each pesticide

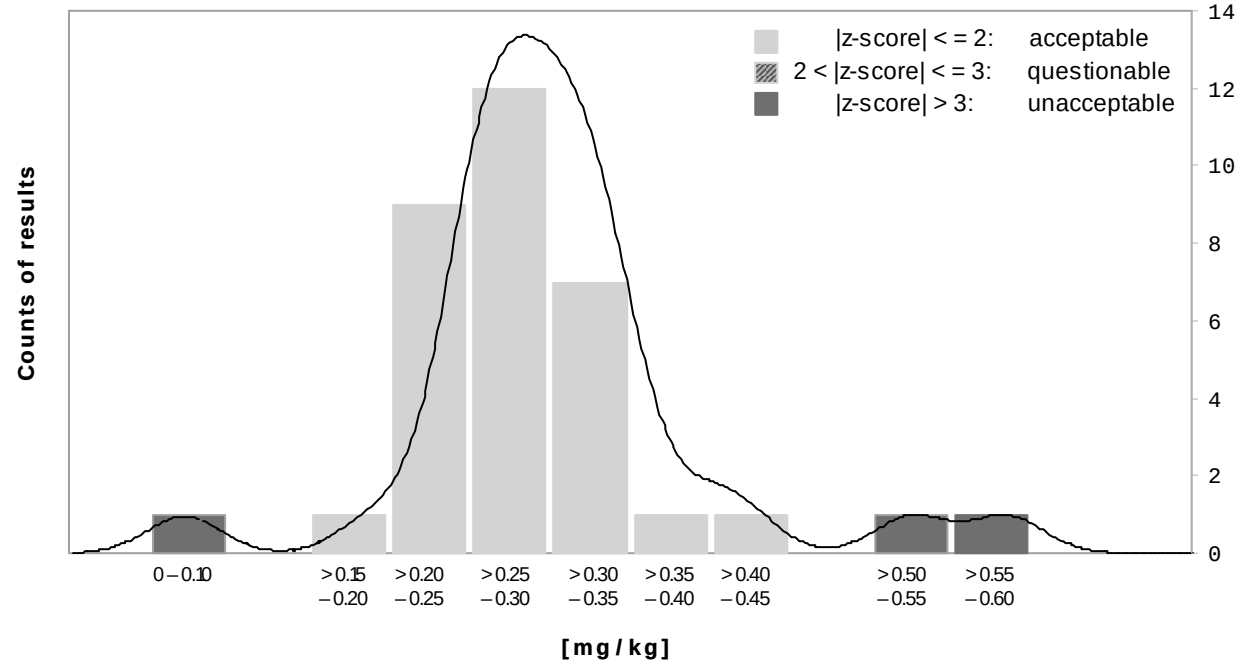


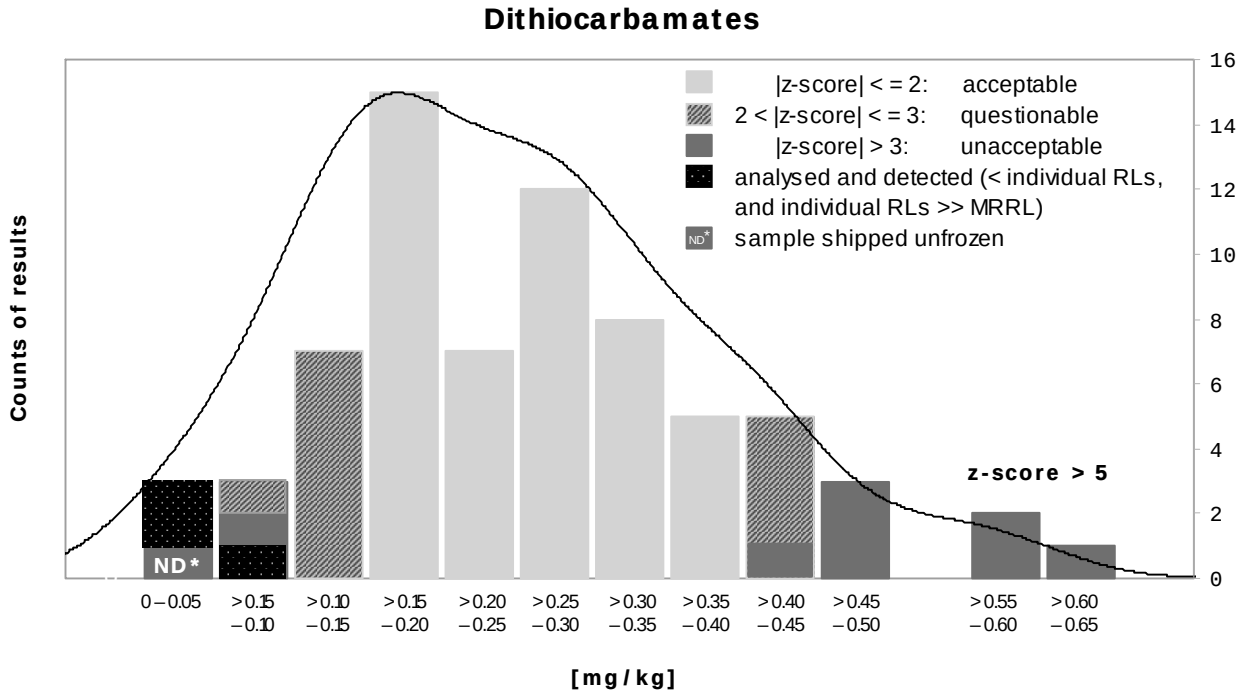


Abamectin



Fenbutatin Oxide




Dithiocarbamates
|z-score| < = 2: acceptable
2 < |z-score| < = 3: questionable
|z-score| > 3: unacceptable
analysed and detected (< individual RLs, and individual RLs >> MRRL)
sample shipped unfrozen
ND*
z-score > 5
Counts of results
[mg/kg]
0 – 0.05
> 0.05 – 0.10
> 0.10 – 0.15
> 0.15 – 0.20
> 0.20 – 0.25
> 0.25 – 0.30
> 0.30 – 0.35
> 0.35 – 0.40
> 0.40 – 0.45
> 0.45 – 0.50
> 0.55 – 0.60
> 0.60 – 0.65
0
2
4
6
8
10
12
14
16

Appendix 6 SRM-Methods used by the participating Laboratories

Abamectin

Lab-Code SRM5-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1)]	ISTD used [2)]	Result recovery corrected? [3)]	Recovery % (compound. level)	Recovery ob-tained from [4)]	Recovery repli-cates considered	Method details
78	x	Yes	> 2 y	0.095	-2.944	0.005	25	–	–	–	SPE-Column (Silica)	EA	Yes, with Trifluoroacetic anhy-dride	LC-FLD	None	PS-ML	None	No	82 (Avermectin B1a , Avermectin B1b)	SB-EUPT	2	Internal laboratory validated method
32		No	> 2 y	0.100	-2.889	0.01	10	No	No	Citrate Buffer	–	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No				EN 151662 (QuEChERS - Citrate buffered),
28	x	Yes	< 1 y	0.192	-1.867	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	TDCPP	No	108.3 (at 0.25 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered), not acidified before measurement
35	x	Yes	1y – 2y	0.222	-1.533	0.04	10	No	No	Citrate Buffer	LLP	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	TPP	No	112	–	–	EN 151662 (QuEChERS - Citrate buffered),
04		Yes	> 2 y	0.225	-1.500	0.05	10	No	No	–	Filtration	EA	No	LC-MS/MS	None	MM-SL	IL - Pirimi-carb D6	No	107	SB-EUPT	1	other
31		Yes	1y – 2y	0.230	-1.444	0.02	10	Yes	No	–	LLP (ChemE-lut 5 ml)	MeOH / DCM	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	62,1	SB-EUPT	2	Klein, Alder, J. AOAC 86/115/23
98		Yes	> 2 y	0.230	-1.444	0.01	10	–	No	Citrate Buffer	–	ACN	No	LC-MS/MS	–	–	None	No	102 (Abamectin)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
49	x	Yes	1y – 2y	0.270	-1.000	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	(Abamectin B1a)	–	–	EURL SRM method
22		Yes	> 2 y	0.280	-0.889	0.05	10	–	–	–	–	MeOH	–	LC-MS/MS	LC-MS/MS	PS-ML	TPP	No	86,5	SB-EUPT	1	–
29	x	Yes	< 1 y	0.285	-0.833	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No	74 (Abamectin)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered)
51		Yes	< 1 y	0.289	-0.789	0.01	10	No	No	sodium hydrogen carbon-ate added	None	EA	No	LC-MS/MS	LC-MS/MS (2nd MSMS transition)	MM-ML	IL - Methomyl D3, Car-bendazim D4 or Pendi-methalin D5	No	84 (Abamectin at 0.02mg/kg)	SB-Other	1	Ethylacetate type (e.g. Janson et al. J. Chromatogr. A 123
57		Yes	1y – 2y	0.291	-0.767	0.01	5	No	No	–	–	MeOH	No	LC-MS/MS	None	Std-Add	None	Yes-2	–	–	3	extraction with methanol and dilution
88		Yes	> 2 y	0.306	-0.600	0.01	–	No	–	–	–	EA	–	LC-MS/MS	LC-MS/MS	–	–	No				–
41	x	Yes	< 1 y	0.310	-0.556	0.01	50	no	no	Yes, with $NaHCO_3$ to pH 6-8	none	EA	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	95	SB-Other	3	ethyl acetate extraction (MRM)
63		–	None	0.310	-0.556	0.01	–	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	GC-MS/MS	MM-SL	TDCPP	No	96.8	SB-EUPT	–	EN 151662 (QuEChERS - Citrate buffered),
03	x	Yes	1y – 2y	0.315	-0.500	0.01	10	–	No	Citrate Buffer	–	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	IL - Car-baryl D7	No	117 (Abamectin)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
52		Yes	> 2 y	0.318	-0.467	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-DAD	None	PS-ML	None	No	83	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Abamectin

Lab-Code SRM5-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
86		No	None	0.323	-0.411	0.02	10	No	No	–	None	ACN	No	LC-MS/MS	LC-MS/MS	Std-Add	None	No	93,1 (Abamectin)	SB-EUPT	3	QuEChERS (original version) J. AOAC 86 (23)
12		Yes	> 2 y	0.325	-0.389	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	IL - Pirimi-carb D6	No	111	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
64	x	Yes	> 2 y	0.325	-0.389	0.01	10	–	No	Acetate Buffer	None	ACN	No	LC-MS/MS	GC-MS/MS	MM-ML	None	No	94	SB-Other	1	AOAC Official Method 27.1 (QuEChERS - Acetate buff-ered)
48		No	None	0.329	-0.344	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS (Zorbax C18)	MM-ML	None	No	71	SB-EUPT	4	EN 151662 (QuEChERS - Citrate buffered)
70	x	No	< 1 y	0.339	-0.233	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	–	PS-ML	2-(4-chloro-3,5-dimethyl-phenoxy)-acetic acid	No	79	SB-EUPT	3	EN 151662 (QuEChERS - Citrate buffered)
30	x	No	–	0.340	-0.222	–	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	70	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
76		Yes	> 2 y	0.341	-0.211	0.01	10	No	No	Citrate Buffer	without PSA	ACN	No	LC-MS/MS	–	MM-ML	none	No	93 (Abamectin B1a)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered),
16		Yes	< 1 y	0.342	-0.200	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	None	MM-ML	TPP	No	87,7 (at 0,05 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
20		No	None	0.350	-0.111	0.005	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	TPP	No	92	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered)
82		No	< 1 y	0.360	0.000	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	None	MM-SL	TPP	No	92.4	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
96	x	Yes	1y – 2y	0.370	0.111	0.01	10	No	No	Citrate Buffer	SPE-column (C18 eluent methanol)	ACN	Yes, with 1-methylimi-dazole and trifluoroace-tic anhy-dride	LC-FLD	None	MM-ML	Nemadectin	No				EN 151662 (QuEChERS - Citrate buffered), extraction with C18 column
42		Yes	< 1 y	0.375	0.167	0.025	10	No	No	Citrate Buffer	DSPE with PSA	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No				EN 151662 (QuEChERS - Citrate buffered)
06		Yes	> 2 y	0.376	0.178	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	82 (at 0.01 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered),
43		Yes	1y – 2y	0.384	0.267	0.02	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	105	SB-EUPT	1	–
19	x	Yes	1y – 2y	0.392	0.356	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	–	LC-MS/MS	MM-ML	TPP	No	91.2 (Avermectin B1a)	SB-EUPT	2	QuEChERS (original), EN 15662:29
11		Yes	> 2 y	0.395	0.389	0.005	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No	97.2	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
18		Yes	> 2 y	0.398	0.422	0.01	10	No	No	–	None	ACN	No	LC-MS/MS	–	MM-ML	TPP	No	83	SB-EUPT	1	QuEChERS (original version) J. AOAC 86 (23),
26	x	Yes	1y – 2y	0.399	0.433	0.02	10	No	No	No	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	104 (Abamectin)	SB-EUPT	2	QuEChERS (original version) J. AOAC 86 (23), without PSA cleaning
07	x	Yes	> 2 y	0.364	0.444	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	None	MM-ML	–	No	91 (via Matrix-matched Calibra-tion)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered), Extrakt 1 used (without PSA), diluted with water
10		Yes	> 2 y	0.403	0.478	0.01	10	Yes	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	None	MM-ML	IL - Linuron-D6	No	97 (Abamectin)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),

Abamectin

Lab-Code SRM5-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
58		Yes	1y – 2y	0.408	0.533	0.01	15	No	No	–	Filtration	Acetone / DCM-PE	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No	80	SB-EUPT	2	Mini-Luke-Type (acetone/DCM-PE),
14	x	No	> 2 y	0.365	0.556	0.05	10	No	No	–	None	Metha-nol/Wate r	No	LC-MS/MS	LC-MS/MS	MM-ML	Oxfenda-zole	No	78 (Abamectin)	SB-EUPT	3	interne method
39		Yes	1y – 2y	0.411	0.567	0.01	10	No	No	Citrate Buffer	DSPE (PSA+$MgSO_4$)	ACN	No	LC-MS/MS	None	PS-ML	TDCPP	No				EN 151662 (QuEChERS - Citrate buffered),
65		Yes	> 2 y	0.415	0.611	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	None	PS-ML	None	No	109	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
79		Yes	> 2 y	0.416	0.622	0.005	10	No	No	Citrate Buffer	DSPE (PSA+$MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	Std-Add	None	No	102	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered)
67		No	None	0.417	0.633	0.01	10	No	No	HCl	None	ACN	No	LC-MS/MS	LC-MS/MS	Std-Add	IL - Atrazin D5	Yes-2				QuEChERS (original version) J. AOAC 86 (23), without PSA; with HCl
59	x	Yes	> 2 y	0.437	0.856	0.01	–	–	No	Citrate Buffer	–	ACN	No	–	–	–	–	No	–	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
24	x	Yes	> 2 y	0.368	0.889	0.01	10	–	No	Citrate Buffer	DSPE (PSA+$MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	124	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
53	x	No	< 1 y	0.451	1.111	0.01	5	Yes	No	–	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	94 (Abamectin)	SB-EUPT	1	Modified QuEChERS
40		Yes	< 1 y	0.464	1.156	0.01	10	No	No	Citrate Buffer	DSPE (PSA+$MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	110 (Avermectin B1a und B1b)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
44		Yes	> 2 y	0.473	1.256	0.01	5	–	No	–	SPE-Column (Silica)	ACN	Yes, with Methylimi-dazol, Acetic acid anhydride	LC-FLD	–	PS-ML	None	Yes-4	70	SB-EUPT	2	ACN-Extraktion, SPE, derivatization, Cleanup
61		Yes	1y – 2y	0.480	1.333	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	PS-SL	TPP	No	76 (Avermectin B1a at 0.085 mg/kg)	SB-Other	3	EN 151662 (QuEChERS - Citrate buffered),
50		Yes	> 2 y	0.492	1.467	0.01	10	–	No	Citrate Buffer	–	ACN	No	LC-MS/MS	None	–	None	No	99	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
54		Yes	1y – 2y	0.455	1.556	0.02	10	No	No	Citrate Buffer	–	ACN	No	LC-MS/MS	LC-MS/MS (Ion Ratio, RRT)	MM-ML	None	–	94 (Avermectin)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered), Without PSA
15		Yes	1y – 2y	0.526	1.844	0.01	20	Yes	No	–	SPE-Column for enrichment	ACN / Water	No	LC-MS/MS	None	MM-ML	None	No	107	SB-EUPT	3	in house=extraction with AcN/water-SPE clenanin using C18 columns-elution with DCM-concentation and reconsti-tution in MeOH/amonformiat buffer pH4-injection in LC-MS/MS
17	x	No	< 1 y	0.640	3.111	0.01	10	No	No	Citrate Buffer	DSPE (PSA+$MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-SL	None	No	93,4 (Avermectin B1a)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Dithiocarbamates as CS_2

Lab-Code SRM5-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
05	x	Yes	> 2 y	< 0.4	-3.681	0.4	50	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	–	–	No	–	SB-Other	–	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis, G.U. N.155 8/6/1981 pg 3658
33		Yes	> 2 y	ND (FN)	-3.681	0.2	–	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	–	–	–				$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
77		Yes	> 2 y	< 0.25	-3.681	0.25	200	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	–	–	No	94 (Thiram)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis; EN 12396-1:1998
81		No	> 2 y	ND	-3.681	0.05	50	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	PS-ML	–	–				$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
79		Yes	> 2 y	0.032	-3.494	0.01	4	No	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	No	HS-GC-ECD	–	MM-ML	None	No	93 (Sodiumdie-thyldithiocarba-mate trihydrate)	SB-EUPT	1	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
10		Yes	> 2 y	0.060	-3.438	0.01	50	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	None	PS-ML	None	No				$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
22		Yes	> 2 y	0.072	-2.853	0.05	200	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	PS-ML	None	No	75	SB-EUPT	1	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
27		Yes	–	0.100	-2.464	0.05	–	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	–	PS-ML	–	No	86.8	SB-EUPT	4	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
19	x	Yes	> 2 y	0.103	-2.359	0.05	200	No	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	PS-ML	–	No	64.0 (Maneb)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
80		Yes	> 2 y	0.103	-2.359	0.01	200	No	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	None	PS-ML	None	No	98	SB-EUPT	1	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
46		Yes	> 2 y	0.110	-2.247	0.05	100	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	None	PS-ML	–	No	78	SB-EUPT	3	EN12396-1
85		Yes	> 2 y	0.110	-2.247	0.01	100	–	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	None	–	None	No	80	SB-EUPT	3	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis, PN-EN 12396-3:22
75	x	Yes	> 2 y	0.116	-2.151	0.1	100	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	None	PS-ML	None	No	92 (Thiram)	SB-EUPT	1	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis, EN 12396-1:1998
50		Yes	> 2 y	0.182	-1.996	0.02	2	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	No	HS-GC-?	None	–	None	Yes-2	119	SB-EUPT	1	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2

Dithiocarbamates as CS_2

Lab-Code SRMS-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
71		Yes	> 2 y	0.182	-1.996	0.17	–	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	–	–	No				$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
67		Yes	> 2 y	0.143	-1.721	0.01	–	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	No	HS-GC-ECD	None	MM-ML	None	No				$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2,
44		Yes	> 2 y	0.150	-1.696	0.01	200	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	UV-Spectrum	PS-ML	None	No	118	SB-Other	2	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
58		Yes	1y – 2y	0.151	-1.594	0.05	2	Yes	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	No	HS-GC-MSD	GC-MS	PS-SL	None	No	80	SB-EUPT	2	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2,
12		Yes	> 2 y	0.154	-1.546	0.005	25	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-MSD	CS2 deri-vatiza-tion/spectrop hotometric analysis	PS-ML	–	No	99,7	SB-EUPT	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
07	x	Yes	> 2 y	0.158	-1.483	0.02	25	–	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	No	HS-GC-MSD	None	MM-ML	–	No	81	SB-Other	3	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
39		No	> 2 y	0.158	-1.483	0.125	100	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	PS-ML	None	No				$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
56	x	Yes	> 2 y	0.160	-1.452	0.05	50	–	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-MSD	–	MM-ML	None	No	58	SB-EUPT	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
86		Yes	> 2 y	0.160	-1.452	0.01	50	–	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	No	HS-GC-MSD	GC-MS	PS-ML	None	No	73,2 (Maneb)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
87		–	–	0.161	-1.434	0.02	10	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	No	GC-MSD	–	–	–	No	100	SB-EUPT	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
53	x	Yes	> 2 y	0.167	-1.339	0.02	50	Yes	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-FPD	GC-MS	PS-ML	None	No	99 (Thiram)	SB-EUPT	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
11		Yes	> 2 y	0.174	-1.228	0.05	50	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-ECD	GC-MS	PS-ML	None	No	94.2	SB-EUPT	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2,
24	x	Yes	> 2 y	0.187	-1.199	0.1	100	–	Cleavage to CS_2	HCl		$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	GC-MS	PS-ML	None	No	105	SB-Other	1	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
95		Yes	> 2 y	0.180	-1.131	0.01	5	no	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-ECD	None	PS-ML	None	No				$SnCl_2$/HCL-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-Analysis of CS_2
35	x	Yes	> 2 y	0.189	-0.988	0.03	30	–	Cleavage to CS_2	HCl	LLP	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-MSD	GC-MS	PS-SL	–	No	50 (Propineb)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2,

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Dithiocarbamates as CS_2

Lab-Code SRMS-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
92		Yes	> 2 y	0.200	-0.813	0.05	100	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	–	PS-ML	–	No	72.6	SB-EUPT	2	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
14	x	Yes	> 2 y	0.201	-0.797	0.04	25	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooctane	No	GC-ECD	–	PS-ML	None	No	63 (Thiram)	SB-EUPT	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2,
41	x	Yes	> 2 y	0.205	-0.734	0.1	50	no	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl/Isooctane	No	GC-FPD	None	MM-ML	None, Thiophene for QC	No	85,5	SB-EUPT	2	isooctane extraction of CS_2 and subsequent GC FPD analysis
73		Yes	> 2 y	0.210	-0.653	0.02	4	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooctane	No	GC-FPD	None	PS-ML	None	No	90 (Thiram)	QC	>5	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2,
52		Yes	> 2 y	0.212	-0.622	0.02	25	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	No	HS-GC-FPD	None	MM-ML	None	No	80	SB-EUPT	1	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
25		Yes	> 2 y	0.220	-0.494	0.05	200	Yes	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	–	–	No	89	SB-Other	3	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
31		Yes	> 2 y	0.249	-0.319	0.02	100	No	Cleavage to CS_2	HCl	NaOH, $H2SO_4$	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	spectropho-tometric analysis	PS-ML	None	No	93,8 (Thiram)	SB-EUPT	1	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
49	x	Yes	> 2 y	0.251	0.000	0.05	50	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooctane	No	GC-FPD	None	PS-ML	Thiophene	No	(Thiram)	–	–	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2, EN 12396-2 (modif.)
02		Yes	> 2 y	0.263	0.191	0.02	50	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooctane	No	GC-MSD	GC-MS	PS-ML	None	No	98,8 (Thiram)	same batch using other matrix	3	Sn/Cl_2HCl-cleavage, GC-MS analysis of CS_2
08		Yes	> 2 y	0.264	0.272	0.05	–	–	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooctane	No	GC-FPD	GC-MS	PS-ML	–	–	67	SB-Other	1	$SnCl_2$/HCL-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-Analysis of CS_2
65		Yes	> 2 y	0.269	0.287	0.02	50	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	No	HS-GC-FPD	None	PS-ML	None	No	103	SB-EUPT	1	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
57		Yes	> 2 y	0.253	0.319	0.02	5	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	No	HS-GC-MSD	None	Std-Add	Thiophene	Yes-2	–	–	3	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
26	x	Yes	> 2 y	0.277	0.414	0.05	50	No	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl/Isooctane	No	GC-ECD	None	MM-ML	–	No	89 (Thiram)	SB-EUPT	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
37	x	Yes	> 2 y	0.284	0.526	0.02	25	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Toluene	No	GC-FPD	GC-MS	PS-ML	None	No	82 (Thiram at 0.02; 0.2 and 0.3 mg/Kg)	SB-EUPT	3	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
42		Yes	> 2 y	0.288	0.590	0.04	100	Yes	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	–	PS-ML	–	No				$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
82		Yes	> 2 y	0.288	0.590	0.05	50	–	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	–	PS-ML	None	No	95.6	SB-EUPT	2	PN EN 12396-3
20		Yes	> 2 y	0.290	0.622	0.5	50	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	–	–	No				NF EN 12396-1

Dithiocarbamates as CS_2

Lab-Code SRMS-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
47		Yes	> 2 y	0.300	0.789	0.3	200	–	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	CS2 spec-trum	–	None	No	84 (Thiram)	SB-EUPT	2	EN 12396-1 Spectrometric method
63		–	> 2 y	0.300	0.789	0.04	200	No	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	–	PS-ML	–	No	82.3	SB-EUPT	–	EN12396-3
98		Yes	> 2 y	0.310	0.942	0.01	50	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-MSD	–	–	None	No	95 (Ethylenebisdi-thiocarbamates)	SB-EUPT	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
15		Yes	> 2 y	0.330	1.259	0.05	25	No	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-MSD	None	PS-ML	None	No	80 (Thiram)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
18		Yes	> 2 y	0.330	1.259	0.02	2	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	No	HS-SPME-GC-MS (ITD)	None	Std-Add	None	Yes-2				$SnCl_2$/HCl-cleavage, headspace SPME, GC-analysis of CS_2,
88		Yes	> 2 y	0.331	1.275	0.01	–	No	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	No	HS-GC-MSD	–	–	–	No				–
17	x	Yes	< 1 y	0.340	1.418	0.1	50	No	Cleavage to CS_2	HCl	LLP	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-FPD	None	PS-ML	None	No	83,8 (Thiram)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
62		No	> 2 y	0.350	1.578	0.02	50	Yes	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	No	HS-GC-ECD	None	PS-ML	None	No	81.9	SB-EUPT	2	PN-EN 12396-2:22
04		Yes	> 2 y	0.358	1.752	0.025	50	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-ECD	None	MM-SL	None	No	88	SB-Other	1	other
64	x	Yes	> 2 y	0.373	1.944	0.02	25	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-FPD	GC-MS	MM-ML	None	No	88	SB-Other	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
06		Yes	> 2 y	0.320	1.996	0.02	2	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooc tane	No	GC-FPD	–	PS-ML	None	No	92 (at 0.02 and 0.05 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
09		Yes	> 2 y	0.320	1.996	0.05	50	Yes	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	None	PS-ML	–	No	101 (Sodium diethyldithiocar-bamate trihydrate)	QC	>5	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
89		Yes	–	0.391	2.232	0.05	30	Yes	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	–	PS-ML	–	No	99	QC	5	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
51		Yes	> 2 y	0.378	2.239	0.05	50	–	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	No	GC-MSD	GC-MS (repeat std, samp and spike)	MM-ML	None	No	105 (Ziram at 0.1mg/kg)	SB-Other	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
61		Yes	> 2 y	0.420	2.693	0.25	50	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	None	PS-ML	None	No	90 (Thiram)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Dithiocarbamates as CS_2

Lab-Code SRMS-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1)]	ISTD used [2)]	Result recovery corrected? [3)]	Recovery % (compound. level)	Recovery ob-tained from [4)]	Recovery repli-cates considered	Method details
29	x	Yes	> 2 y	0.426	2.789	0.01	50	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooctane	No	GC-MSD	GC-MS	PS-ML	None	No	67 (Thiram)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
43		Yes	> 2 y	0.430	2.853	0.4	50	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	–	None	No	70-130	QC	3	–
96	x	Yes	> 2 y	0.450	3.171	0.02	50	No	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	No	HS-GC-ECD	None	MM-ML	None	No				$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS2,
48		Yes	> 2 y	0.453	3.219	0.01	50	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	spectopho-tometric analysis	–	None	No	72 (Maneb)	QC	3	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
40		Yes	> 2 y	0.462	3.363	0.01	25	Yes	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, to potasium-xanthogenate	Spectropho-tometric	LC-MS/MS	PS-ML	None	No	88 (Thiram)	SB-EUPT	1	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis, ASU §64 LFGB L..-49/3
54		Yes	> 2 y	0.445	3.916	0.4	50	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	Lambda max	PS-ML	None	–	90 (CS2)	SB-EUPT	1	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis, EN 12396-1
60		Yes	> 2 y	0.500	3.968	0.1	100	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectropho-tometric	–	–	–	No	111 (Ziram 0.15 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
78	x	Yes	> 2 y	0.558	4.892	0.03	50	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl/Isooctane	No	GC-ECD	None	PS-ML	None	No	94 (Thiram)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
59	x	Yes	> 2 y	0.586	5.339	0.02	–	–	Cleavage to CS_2	HCl	–	$H_2O/SnCl_2$ /HCl	No	HS-GC-FPD	–	–	–	No	–	SB-EUPT	3	SnCl2/HCl-cleavage, headspace sampling, GC-analysis of CS2,
70	x	Yes	> 2 y	0.626	5.977	0.05	25	No	Cleavage to CS_2	HCl	None	$H_2O/SnCl_2$ /HCl/Isooctane	No	GC-MSD	–	PS-ML	None	No	78	SB-Other	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2

Ethephon

Lab-Code SRM5-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
61		No	None	ND (FN)	-3.771	0.05	–	–	–	–	–	–	–	–	–	–	–	–				–
14	x	No	None	0.027	-3.691	0.02	10	No	No	1% HCOOH	None	MeOH	No	LC-MS/MS	LC-MS/MS	MM-SL	IL - Target Compound	Yes-1				CRL, but need to concentrate, sensibility far away
88		Yes	> 2 y	0.192	-1.8571429	0.1	–	No	Cleavage to ethylene	NaOH	–	Water	–	HS-GC-FID	GC-MS	–	–	No				–
22		Yes	> 2 y	0.220	-1.486	0.01	5	–	–	H2SO4	–	EA	Yes, with diazo methane	GC-FPD	Two col-umns	MM-ML	None	No	82,7	SB-EUPT	1	–
35	x	No	< 1 y	0.234	-1.326	0.2	10	No	–	1% HCOOH	None	MeOH	–	LC-MS (ITD)	LC-Ion trap	MM-SL	IL - Glypho-sate	Yes-2				sample prep.-CRL method for polar pesticides (v. 2, MetOH extraction), ion-LC on AS 11-HC
63		Yes	> 2 y	0.250	-1.143	0.05	6	Yes	Cleavage to ethylene	NaOH	None	Water	No	HS-GC-FID	–	MM-ML	None	No	98.5	SB-EUPT	1	in situ,with NaOH formation of ethylen , GC headspace
24	x	No	None	0.291	-0.674	0.1	10	–	–	1% HCOOH	None	MeOH	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	83	SB-EUPT	1	CRL-SRM method for polar pesticides
16		Yes	1y – 2y	0.300	-0.571	0.02	10	No	Cleavage to ethylene	NaOH	None	Water	No	HS-GC-FID	None	MM-ML	None	No	107 (at 0,5 mg/kg)	QC	>5	§64 LFBG L.-47
57		No	None	0.305	-0.514	0.02	5	No	No	–	–	MeOH	No	LC-MS/MS	None	Std-Add	None	Yes-2	–	–	3	extraction with methanol and dilution
43		No	None	0.308	-0.480	0.01	10	No	No	1% HCOOH	None	MeOH	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	62	SB-EUPT	1	–
98		Yes	1y – 2y	0.310	-0.457	0.02	10	–	–	1% HCOOH	–	MeOH	–	LC-MS/MS	–	–	None	No	91 (Ethephon)	SB-EUPT	1	CRL-SRM
41	x	No	None	0.313	-0.423	0.05	10	Yes	no	1% HCOOH	None	MeOH	No	LC-MS/MS	LC-MS/MS	MM-ML	IL - Target Compound	Yes-1	106,6	SB-EUPT	1	EURL-SRM-method for polar pesticides
04		No	None	0.331	-0.217	0.02	10	No	No	–	Filtration	MeOH	No	LC-MS/MS	None	MM-SL	IL - Target Compound	Yes-1	102	SB-EUPT	1	other
64	x	No	< 1 y	0.334	-0.183	0.02	5	–	–	–	–	Water	No	LC-MS/MS	LC-MS/MS	MM-ML	IL - Target Compound	Yes-1	108	SB-Other	1	in house method
44		Yes	> 2 y	0.350	0.000	0.02	2	No	Cleavage to ethylene	NaOH	–	Water	–	HS-GC-FID	LC-MS/MS	Std-Add	None	Yes-2	–	SB-EUPT	5	basic hydrolysis to ethylene
53	x	No	> 2 y	0.350	0.000	0.02	10	Yes	Cleavage to ethylene	NaOH	None	Water	–	HS-GC-FID	hydrolysis without NaOH	MM-ML	–	No	90 (Ethephon)	SB-EUPT	1	Hydrolysis with NaOH, headspace
65		No	1y – 2y	0.361	0.126	0.01	10	Yes	No	No	None	MeOH	No	LC-MS/MS	None	PS-ML	None	No	101	SB-EUPT	1	MSZ EN 15055
58		Yes	1y – 2y	0.362	0.137	0.01	10	Yes	Cleavage to ethylene	NaOH 120 g/l	None	Water	No	HS-GC-FID	None	PS-ML	None	No	85	SB-EUPT	2	Indirect method by measurement of ethyleen with GC-FID
06		No	None	0.366	0.183	0.02	10	No	No	1% HCOOH	None	MeOH	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	100	SB-EUPT	3	Polar pesticides EURL-SRM (adapted)
28	x	Yes	1y – 2y	0.352	0.229	0.01	10	No	No	1% HCOOH	Filtration 0.45 µm	MeOH	No	LC-MS/MS	LC-MS/MS	Std-Add	IL - Target Compound	Yes-3				method polar pesticides: extraction with acidified methanol, centrifugation, filtration (.45 Âµm)

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Ethephon

Lab-Code SRM5-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1)]	ISTD used [2)]	Result recovery corrected? [3)]	Recovery % (compound. level)	Recovery obtained from [4)]	Recovery replicates considered	Method details
12		Yes	> 2 y	0.372	0.251	0.01	10	No	No	1% HCOOH	None	MeOH	No	LC-MS/MS	–	MM-ML	IL - Target Compound	Yes-1	97,5	SB-EUPT	1	EUCRL website: Polar Pesticides
07	x	Yes	< 1 y	0.374	0.274	0.05	10	No	No	1% HCOOH	None	MeOH	No	LC-MS/MS	None	Std-Add	IL - Target Compound	Yes-3		SB-EUPT	–	Extaction according to method https://fis-vl.bund.de/Members/irc/fis-vl/crl-pesticides/library?l=/crl-pesticides-srm/methods_provided_by_crl-srm/polarpesticides_crlsrm_919pdf/_EN_1._&a=d, but different chromatography
52		Yes	> 2 y	0.382	0.366	0.01	10	No	No	–	None	MeOH / Water	Yes, with BSTFA	GC-MS/MS	None	MM-ML	None	No	78	SB-EUPT	1	in house method
10		Yes	< 1 y	0.386	0.411	0.02	10	Yes	No	1% HCOOH	Filtration	MeOH	No	LC-MS/MS	None	MM-ML	IL - Target Compound	Yes-1	112 (Ethephon)	SB-EUPT	2	LC-MS/MS Analysis of Highly Polar Pesticides, CRL-SRM (CVUA Stuttgart), Version 2
37	x	No	< 1 y	0.394	0.529	0.02	10	No	No	1% HCOOH	None	MeOH	No	LC-MS/MS	–	MM-ML	None	No	98 (Ethephon at 0.02,0.30 mg/kg.)	SB-EUPT	1	EU RL SRM
49	x	No	< 1 y	0.397	0.537	0.02	10	No	No	1% HCOOH	None	MeOH	No	LC-MS/MS	LC-MS/MS	PS-ML	IL - Target Compound	Yes-1	112 (Ethephon)	SB-EUPT	1	EURL SRM method
18		No	< 1 y	0.410	0.686	0.02	10	No	No	1% HCOOH	None	MeOH	No	LC-MS/MS	–	MM-ML	None	No	113	SB-EUPT	1	other
17	x	No	None	0.510	1.829	0.02	5	No	No	1% HCOOH	None	MeOH	No	LC-MS/MS	LC-MS/MS	MM-SL	None	No	129 (Ethephon)	SB-EUPT	1	http://www.crl-pesticides.eu/library/docs/srm/meth_PolarPesticides_CrlSrm.pdf
59	x	No	< 1 y	0.749	4.560	0.02	10	–	–	1% HCOOH	–	ACN	–	LC-MS/MS	–	MM-SL	–	No	–	SB-EUPT	2	other

Fenbutatin Oxide

Lab-Code SRM5-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
61		No	None	0.045	-3.357	0.05	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	PS-SL	TPP	No	55 (at 0.1 mg/kg)	SB-Other	2	EN 151662 (QuEChERS - Citrate buffered),
20		No	None	0.170	-1.571	0.005	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	TPP	No	115	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered)
51		Yes	< 1 y	0.218	-0.886	0.01	25	No	No	sodium hydrogen carbonate added	None	ACN	No	LC-MS/MS	LC-MS/MS (2nd MSMS transition)	MM-ML	IL - Metho-myl D3, Carben-dazim D4 or Pendi-methalin D5	No	92 (Fenbutatin oxide at 0.02mg/kg)	SB-Other	1	acetonitrile extraction
14	x	No	None	0.224	-0.800	0.01	10	No	No	No	None	Metha-nol/Water	No	LC-MS/MS	LC-MS/MS	MM-ML	Oxfendazole	No	74 (Fenbutatin oxide)	SB-EUPT	3	interne method
70	x	No	< 1 y	0.225	-0.786	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	–	PS-ML	2-(4-chloro-3,5-dimethyl-phenoxy)-acetic acid	No	86	SB-EUPT	3	EN 151662 (QuEChERS - Citrate buffered)
48		No	None	0.227	-0.757	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS (Zorbax C18)	MM-ML	None	No	74	SB-EUPT	4	EN 151662 (QuEChERS - Citrate buffered)
26	x	Yes	< 1 y	0.236	-0.629	0.02	10	No	No	No	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	92 (Fenbutatin oxide)	SB-EUPT	2	QuEChERS (original version) J. AOAC 86 (23), without PSA cleaning
31		Yes	1y – 2y	0.241	-0.557	0.02	10	Yes	No	–	GPC	Acetone / EA-CH	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	84,5	–	1	S-19 (Â§64 LFGB L.-334), module E1, GPC
05	x	Yes	None	0.245	-0.500	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	None	MM-SL	TPP	No	92 (Fenbutatin oxide)	SB-EUPT	–	EN 151662 (QuEChERS - Citrate buffered)
12		No	1y – 2y	0.248	-0.457	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	IL - Pirimi-carb D6	No	96	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
28	x	Yes	< 1 y	0.250	-0.429	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	Std-Add	TDCPP	Yes-2				EN 151662 (QuEChERS - Citrate buffered), not acidified before measurement
39		No	< 1 y	0.255	-0.357	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	None	PS-ML	TDCPP	No				EN 151662 (QuEChERS - Citrate buffered),
53	x	No	< 1 y	0.259	-0.300	0.01	5	Yes	No	–	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	89 (Fenbutatin oxide)	SB-EUPT	1	Modified QuEChERS
76		Yes	> 2 y	0.259	-0.300	0.01	10	No	No	Citrate Buffer	without PSA	ACN	No	LC-MS/MS	–	MM-ML	none	No	130 (Fenbutatin oxide)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered),
78	x	No	< 1 y	0.278	-0.286	0.05	10	–	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS (ITD)	LC-Ion trap (MS/MS)	MM-ML	None	No	95 (Fenbutatin oxide)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered)
06		Yes	> 2 y	0.265	-0.214	0.05	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	99 (at 0.05 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered),
42		No	None	0.270	-0.143	0.1	10	No	No	Citrate Buffer	DSPE with PSA	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No				EN 151662 (QuEChERS - Citrate buffered)
82		No	< 1 y	0.291	0.157	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	None	MM-SL	TPP	No	99.1	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
10		Yes	> 2 y	0.292	0.171	0.01	10	Yes	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	None	MM-ML	IL - Linuron-D6	No	97 (Fenbutatin oxide)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Fenbutatin Oxide

Lab-Code SRMs-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1)]	ISTD used [2)]	Result recovery corrected? [3)]	Recovery % (compound. level)	Recovery ob-tained from [4)]	Recovery repli-cates considered	Method details
40		No	< 1 y	0.292	0.171	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	120 (Fenbutatin oxid)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
58		No	None	0.282	0.286	0.01	10	No	No	Citrate Buffer + 0.02% acetic acid ?	None	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No	88	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
44		Yes	> 2 y	0.300	0.286	0.01	10	Yes	No	–	–	MeOH / DCM	–	LC-MS/MS	LC-MS/MS	Std-Add	TPP	Yes-2	–	SB-EUPT	3	Klein, Alder, J. AOAC 86/115/23,
50		Yes	> 2 y	0.309	0.414	0.01	10	–	No	Citrate Buffer	–	ACN	No	–	–	–	–	No	102	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
11		No	1y – 2y	0.314	0.486	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS	LC-MS	MM-ML	None	No	98.8	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
59	x	No	< 1 y	0.314	0.486	0.01	–	–	No	Citrate Buffer	–	ACN	No	–	–	–	–	No	–	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
07	x	No	> 2 y	0.318	0.543	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	None	MM-ML	–	No	100	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered), Extrakt 1 used (without PSA), diluted with water
18		Yes	> 2 y	0.321	0.586	0.01	10	No	No	No	None	ACN	No	LC-MS/MS	–	MM-ML	TPP	No	87	SB-EUPT	1	QuEChERS (original version) J. AOAC 86 (23),
43		Yes	< 1 y	0.285	0.714	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	96	SB-EUPT	1	–
52		No	1y – 2y	0.334	0.771	0.02	10	No	No	–	None	Isooctane	Yes, with Methylmag-nesium chloride	GC-MS/MS	None	MM-ML	None	No	91	SB-EUPT	1	in house method
24	x	No	None	0.341	0.871	0.01	10	–	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	78	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
79		Yes	> 2 y	0.380	1.429	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	95	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered)
04		Yes	> 2 y	0.408	1.829	0.05	25	Yes	Yes	–	Florisil, sodium sulphate	Isooc-tane/n-hexane	Yes, with methylmag-nesiumchlo-ride	GC-FPD	GC-ITD	PS-SL	None	No	106	SB-EUPT	1	other
67		No	None	0.518	3.400	0.01	10	No	No	HCl	None	ACN	No	LC-MS/MS	LC-MS/MS	Std-Add	IL - Atrazin D5	Yes-2				QuEChERS (original version) J. AOAC 86 (23), without PSA; with HCl
17	x	No	< 1 y	0.580	4.286	0.01	10	No	No	Citrate Buffer	DSPE ($PSA+MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-SL	None	No	123 (Fenbutatin oxide)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
64	x	No	> 2 y	1.580	18.571	0.01	10	–	No	Acetate Buffer	None	ACN	No	LC-MS/MS	GC-MS/MS	MM-ML	None	No	90	SB-Other	1	AOAC Official Method 27.1 (QuEChERS - Acetate buffered)

Fluazifop

Lab-Code SRM5-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
88		Yes	> 2 y	0.060	-3.840	0.01	–	No	–	pH 6-6.4	–	EA	–	LC-MS/MS	LC-MS/MS	–	–	No				–
56	x	Yes	> 2 y	0.110	-2.326	0.01	15	–	–	pH5	DSPE (PSA+$MgSO_4$)	ACN	–	LC-MS/MS	–	MM-ML	None	No	52,6	SB-EUPT	1	AOAC Official Method 27.1 (QuEChERS - Acetate buffered)
29	x	Yes	< 1 y	0.116	-2.230	0.02	10	No	No	Citrate Buffer	DSPE (PSA+$MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No	52 (Fluazifop)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered)
41	x	Yes	< 1 y	0.122	-2.137	0.05	10	no	no	Yes, with NaHCO3 to pH 6-8	None	EA	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	77	SB-EUPT	3	mini ethyl acetate extraction
61		No	None	0.150	-1.799	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	PS-SL	TPP	No	60 (at 0.1 mg/kg)	SB-Other	2	EN 151662 (QuEChERS - Citrate buffered),
42		No	> 2 y	0.169	-1.420	0.1	10	No	No	Citrate Buffer	DSPE (PSA+$MgSO_4$)	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	68			EN 151662 (QuEChERS - Citrate buffered)
32		No	> 2 y	0.186	-1.164	0.01	10	No	No	Citrate Buffer	–	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No				EN 151662 (QuEChERS - Citrate buffered),
05	x	Yes	1y – 2y	0.203	-0.976	0.01	10	No	No	0.1 mL phosphoric	–	ACN	No	LC-MS/MS	None	MM-SL	None	No	80 (2,4-D; Haloxyfop; fluazifop; dichlor-prop")	SB-EUPT	–	J. Environmental Science Health 29, Vol B44, 6, 584-59
03	x	Yes	1y – 2y	0.256	-0.916	0.01	10	–	Yes	First acidic hydrolysis then Citrate Buffer?	–	ACN	–	LC-MS/MS	LC-MS/MS	MM-ML	IL - Carbaryl D7	No	102 (Fluazifop)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered), acid hydrolysis
30	x	Yes	–	0.209	-0.892	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	80	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
14	x	No	> 2 y	0.212	-0.763	0.01	10	No	No	–	None	Metha-nol/Water	No	LC-MS/MS	LC-MS/MS	MM-ML	Oxfendazole	No	83 (Fluazifop)	SB-EUPT	1	interne method
28	x	Yes	< 1 y	0.217	-0.687	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	114.2 (at 0.05 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered), no PSA-cleanup; not acidified before measurement
35	x	Yes	1y – 2y	0.218	-0.672	0.002	10	No	–	Citrate Buffer	LLP	ACN	–	LC-MS/MS	LC-MS/MS	MM-ML	Nicarbazin	No	80	–	–	EN 151662 (QuEChERS - Citrate buffered),
24	x	Yes	> 2 y	0.258	-0.617	0.01	10	–	–	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	96	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered), Quechers for acidic pesticides
04		Yes	1y – 2y	0.225	-0.565	0.01	75	No	No	–	Filtration	EA	No	LC-MS/MS	None	MM-SL	IL - Pirimi-carb D6	No	81	SB-EUPT	1	other
64	x	Yes	> 2 y	0.229	-0.538	0.01	10	–	–	Acetate Buffer	None	ACN	No	LC-MS/MS	GC-MS/MS	MM-ML	None	No	91	SB-Other	1	AOAC Official Method 27.1 (QuEChERS - Acetate buffered)
57		Yes	> 2 y	0.234	-0.427	0.01	5	No	No	–	–	MeOH	No	LC-MS/MS	None	Std-Add	None	Yes-2	–	–	3	extraction with methanol and dilution
11		Yes	> 2 y	0.235	-0.412	0.005	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No	92.5	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
48		Yes	< 1 y	0.235	-0.412	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS (Phenome-nex LUNA 3µm 100A C8(2))	MM-ML	None	No	109	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered)
49	x	No	< 1 y	0.242	-0.353	0.01	10	No	No	pH 2	None	ACN	Yes, with diazome-thane	GC-MSD	GC-MS	MM-ML	IL - 2,4-DP-D6	No	(fluazifop)	–	–	in-house

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Fluazifop

Lab-Code SRMs-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
19	x	Yes	1y – 2y	0.239	-0.351	0.01	10	No	Yes	First alkaline hydrolysis with NaOH, then neutralization with H2SO4 and then Citrate Buffer	Freeze-out	ACN	No	–	LC-MS/MS	PS-ML	Nicarbazin	No	102.2 (Fluazifop)	SB-EUPT	2	Modified QuEChERS method for acidic pesticides
70	x	Yes	1y – 2y	0.240	-0.336	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	–	PS-ML	2-(4-chloro-3,5-dimethyl-phenoxy)-acetic acid	No	95	SB-EUPT	3	EN 151662 (QuEChERS - Citrate buffered)
53	x	Yes	> 2 y	0.246	-0.244	0.01	5	Yes	No	–	None	ACN	–	LC-MS/MS	LC-MS/MS	MM-ML	None	No	86 (Fluazifop)	SB-EUPT	1	Modified QuEChERS
67		Yes	> 2 y	0.255	-0.169	0.01	10	No	No	HCl	None	ACN	No	LC-MS/MS	LC-MS/MS	Std-Add	IL - Atrazin D5	Yes-2				QuEChERS (original version) J. AOAC 86 (23), without PSA; with HCl
07	x	Yes	> 2 y	0.253	-0.137	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	None	MM-ML	–	No	104	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered), Extrakt 1 used (without PSA), diluted with water
40		Yes	< 1 y	0.262	0.000	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-SL	None	No	113 (Fluazifop)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered), without PSA-Clean-up
58		Yes	1y – 2y	0.262	0.000	0.01	15	No	No	–	Filtration	Acetone / DCM-PE	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No	107	SB-EUPT	2	Mini-Luke-Type (acetone/DCM-PE),
12		Yes	> 2 y	0.270	0.122	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	–	MM-ML	Nicarbazin	No	99,6	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
22		Yes	> 2 y	0.270	0.122	0.01	10	–	–	–	–	Acetone / DCM-PE	–	LC-MS/MS	LC-MS/MS	PS-ML	TPP	No	100,6	SB-EUPT	1	Mini-Luke-Type (acetone/DCM-PE)
44		Yes	> 2 y	0.270	0.122	0.01	10	Yes	No	–	–	MeOH / DCM	–	LC-MS/MS	LC-MS/MS	Std-Add	Nicarbazin	Yes-2	–	SB-EUPT	3	Klein, Alder, J. AOAC 86/115/23,
10		Yes	> 2 y	0.272	0.153	0.01	10	Yes	No	Citrate Buffer	None	ACN	No	LC-MS/MS	None	MM-ML	IL - MCPA-D6	No	100 (Fluazifop)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered),
86		No	None	0.272	0.153	0.01	10	No	No	–	None	ACN	No	LC-MS/MS	LC-MS/MS	Std-Add	None	No	113,1 (Fluazifop)	SB-EUPT	3	QuEChERS (original version) J. AOAC 86 (23)
43		Yes	< 1 y	0.273	0.168	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	89	SB-EUPT	1	–
15		No	< 1 y	0.288	0.397	0.01	10	Yes	No	pH 7	LLP	MeOH / DCM	No	LC-MS/MS	None	MM-ML	None	No	94	SB-EUPT	2	Klein, Alder, J. AOAC 86/115/23
39		Yes	1y – 2y	0.288	0.397	0.01	10	No	No	Citrate Buffer	None	ACN	–	LC-MS/MS	None	PS-ML	TDCPP	No				EN 151662 (QuEChERS - Citrate buffered),
20		No	< 1 y	0.290	0.427	0.005	10	No	No	Citrate Buffer	None	ACN	–	LC-MS/MS	LC-MS/MS	PS-ML	TPP	No	120	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered)
52		Yes	> 2 y	0.292	0.458	0.01	10	No	No	Citrate Buffer	None	ACN	Yes, with PFBBr	GC-MS/MS	None	MM-ML	None	No	89	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
82		No	< 1 y	0.293	0.473	0.01	10	No	Yes	First hydrolysis at pH12 then neutralize and then Citrate Buffer	None	ACN	No	LC-MS/MS	None	MM-SL	None	No	93.3	SB-EUPT	2	Analysis of acidic pesticides in wheat flour samples by using the Quechers method (method CRL SRM)
06		Yes	> 2 y	0.296	0.520	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	75 (at 0.01 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered),
59	x	Yes	> 2 y	0.298	0.550	0.01	–	–	–	Citrate Buffer	–	ACN	–	–	–	–	–	No	–	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered),
65		Yes	> 2 y	0.298	0.550	0.01	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	None	PS-ML	None	No	106	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
18		Yes	> 2 y	0.300	0.582	0.01	10	No	No	–	None	ACN	No	LC-MS/MS	–	MM-ML	TPP	No	86	SB-EUPT	1	QuEChERS (original version) J. AOAC 86 (23),
96	x	Yes	< 1 y	0.303	0.626	0.01	10	No	No	Citrate Buffer	Freeze-out	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	Yes-4	135	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered),
26	x	Yes	1y – 2y	0.308	0.723	0.01	10	No	No	–	–	ACN	–	LC-MS/MS	LC-MS/MS	MM-ML	None	No	93 (Fluazifop)	SB-EUPT	1	QuEChERS (original version) J. AOAC 86 (23), without PSA cleaning

Fluazifop

Lab-Code SRMs-	NRL	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1)]	ISTD used [2)]	Result recovery corrected? [3)]	Recovery % (compound. level)	Recovery ob-tained from [4)]	Recovery repli-cates considered	Method details
78	x	Yes	1y – 2y	0.310	0.733	0.02	10	No	Yes	First hydrolysis with 5 N NaOH and then neutralization with 5 N H2SO4 then Citrate buffer	DSPE (C18)	ACN	Yes, with Trimethylsul-fonium hydroxide	GC-MSD	GC-MS (SIM)	MM-ML	None	No	115 (2,4-D , Fluazifop, Haloxyfop, Dichlorpop)	SB-EUPT	2	Internal laboratory method-Analysis of Acidic pesticides by GC-MS using the QuEChERS method
76		Yes	1y – 2y	0.267	0.763	0.01	10	No	No	Citrate Buffer	DSPE without PSA	ACN	No	LC-MS/MS	–	MM-ML	Nicarbazin	No	99 (Fluazifop)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered),
50		Yes	> 2 y	0.319	0.872	0.01	10	–	–	Citrate Buffer	–	ACN	–	–	–	–	–	No	105	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered)
17	x	Yes	1y – 2y	0.320	0.885	0.01	10	No	No	Citrate Buffer	DSPE without PSA	ACN	No	LC-MS/MS	LC-MS/MS	MM-SL	None	No	95 (Fluazifop)	SB-EUPT	1	http://www.crl-pesti-cides.eu/library/docs/srm/meth_acidicpesticides_wheat_quechers_EurlSrm.pdf
79		Yes	> 2 y	0.351	1.359	0.005	10	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	100	SB-EUPT	2	EN 151662 (QuEChERS - Citrate buffered)
63		Yes	> 2 y	0.330	1.382	0.01	–	No	No	Citrate Buffer	None	ACN	No	LC-MS/MS	GC-MS/MS	MM-SL	TDCPP	No	103	SB-EUPT	1	EN 151662 (QuEChERS - Citrate buffered),
31		Yes	> 2 y	0.370	1.649	0.005	10	Yes	No	pH 4,5	LLP (Che-mElut pH_4.5)	MeOH / DCM	No	LC-MS/MS	LC-MS/MS	MM-ML	None	No	106	SB-EUPT	1	Klein, Alder, J. AOAC 86/115/23, ChemElut 4.5

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

False Positive Results

Lab-Code SRM5-	NRL	Pesticides	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
65		Amitrole	No	1y – 2y	0.0518 (FP)	–	0.02	10	Yes	No	No	None	Methanol	No	LC-MS/MS	None	PS-ML	None	No	109	SB-EUPT	2	MSZ EN 15055
52		Amitrole	No	< 1 y	0.068 (FP)	–	0.01	10	No	No	–	None	MeOH/HCl	Yes (BSTFA)	GC-MS/MS	None	MM-ML	None	No	85	SB-EUPT	1	in house method
88		Amitrole	Yes	> 2 y	0.26 (FP)	–	0.01	–	Yes	–	–	–	H_2O:MeOH= 25:75	–	LC-MS/MS	LC-MS/MS	–	–	No				–
32		2,4-D	No	> 2 y	0.0462 (FP)	–	0.01	10	No	No	–	DSPE	ACN	No	–	LC-MS/MS	PS-ML	None	No				EN 151662 (QuEChERS - Citrate buffered),
32		Chlormequat	No	> 2 y)	0.0285 (FP)	–	0.01	10	No	No	–	–	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No				EN 151662 (QuEChERS - Citrate buffered),
32		Mepiquat	No	> 2 y	0.1 (FP)	–	0.01	10	No	No	–	–	ACN	No	LC-MS/MS	LC-MS/MS	PS-ML	None	No				EN 151662 (QuEChERS - Citrate buffered),

False Negative Results

Lab-Code SRM5-	NRL	Pesticides	Within routine scope	Experience	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extrac-tion/Partitioning - solvents	Derivatisation	Determination	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery ob-tained from [4]	Recovery repli-cates considered	Method details
61		Ethephon	No	None	ND	-3.771 (FN)	0.05	–	–	–	–	–	–	–	–	–	–	–	–				–
5	x	Dithiocarbama-tes	Yes	> 2 y	< 0.4	-3.681 (<RL*)	0.4	50	–	Cleav-age to CS_2	HCl	–	$H_2O/SnCl_2$/HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectrophotomet-ric	–	–	–	No	–	SB-Other	–	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis, G.U. N.155 8/6/1981 pg 3658
33		Dithiocar-bamates	Yes	> 2 y	ND	-3.681 (FN*)	0.2	–	–	Cleav-age to CS_2	HCl	–	$H_2O/SnCl_2$/HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectrophotomet-ric	–	–	–	–				$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis
77		Dithiocar-bamates	Yes	> 2 y	< 0.25	-3.681 (<RL*)	0.25	200	–	Cleav-age to CS_2	HCl	–	$H_2O/SnCl_2$/HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectrophotomet-ric	–	–	–	No	94 (Thiram)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis; EN 12396-1:1998
81		Dithiocar-bamates	No	> 2 y	ND	-3.681 (FN)	0.05	50	–	Cleav-age to CS_2	HCl	–	$H_2O/SnCl_2$/HCl	Yes, with Cu (II)-acetate /diethanolamine in ethanol	Spectrophotomet-ric	–	PS-ML	–	–				$SnCl_2$/HCl-cleavage, CS_2-Derivatization/spectrophotometric analysis

FN*: test material sent without dry ice and arrived the lab unfrozen thus not regarded as False Negative

<RL* = analysed, detected and reported as < RL with the RL being >> MRRL, these results had to be judged as false

5) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
6) IL : isotropically labelled
7) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
8) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

SPECIFIC PROTOCOL

for EU Proficiency Test for Pesticide Residues in Food by Single Residue Methods: EUPT – SRM5 (2010)

(last updated: 04.10.2010)

Introduction

This Specific Protocol concerning the 5th European Proficiency Test on pesticide residues in food using single residue methods (EUPT– SRM5) is complementary to the **"General Protocol for EU Proficiency Tests for Pesticide Residues in Food and Feed"**, which covers all EUPTs. The EUPT-SRM5 is jointly organised by the EU Reference Laboratory for pesticide residue analysis by Single Residue Methods (EURL– SRM) and the EURL for pesticides in Fruit and Vegetables (EURL– FV). It is to be performed by all National Reference Laboratories for Single Residue Methods (NRL-SRMs) as well as by all official EU laboratories (OfLs) responsible for official pesticide residue controls on fruits and vegetables, as far as their scope overlaps with that of the EUPT-SRM5.

Objectives

The aim of this proficiency test is to obtain information about the quality, accuracy and comparability of pesticide residue data generated by official laboratories within the frame of official controls conducted by EU member states. Participating laboratories will be provided with an assessment of both their own analytical performance and the reliability of their data – compared to the other participating laboratories.

Confidentiality

A unique laboratory code will be given to each participating laboratory at registration. The laboratory codes will be kept confidential and will not be revealed to other participants. Nevertheless, the organizers reserve the right to forward, upon request, PT results of certain countries to their corresponding NRLs which assure the maintainance of confidentiality and will use the results solely within the frame of their responsibilities as NRLs. Participants that object to this accord should inform the PT-organizers in due time.

NRLs aiming to evaluate the performance of official labs in their own countries, are also free to ask the official labs for their reported results, but not before **25 October, 2010**.

Communication between participating laboratories during the test on matters concerning this PT exercise is not permitted.

Test Material

The test material of this proficiency test is **apple sauce (purée).**

Participants will receive two containers:

1. approximately 400 g of test material containing spiked pesticides and
2. approximately 400 g of non-spiked material, as blank.

Registration and Participation Fees

Signing up for EUPT-SRM5 is to be applied via the **"EUPT-Registration Website" (http://thor.dfvf.dk/eupt-signup).** The website is accessible from **15 May until 30 June 2010**.

Upon singing up laboratories will receive a confirmation e-mail with their login data (username and password) as well a specific lab code for the EUPT– SRM5. The login data are valid for all other EUPTs in the future. Laboratories that have already participated in C3/SRM4, C4 or AO-05 should firstly login before signing up for the EUPT-SRM5.

Together with the NRLs and the COM the organizers will firstly check which of the laboratories signing up are eligible to participate. Rejected laboratories will be informed and deleted from the EUPT– SRM5 database.

A general **fee of 150 € (for sigle shipment)** will be charged to each participating laboratory, including NRLs, to cover the costs, handling and shipment of test material.

Double amount of material can be requested via e-mail (Address: **EUPT-SRM@cvuas.bwl.de**). The additional material will be sent in a separate package containing 2 containers with 400 g spiked test mateiral in one container and 400 g blank material in the other container or both two containers with á 400 g spiked material as specified in request e-mail.
The fee for the laboratories requiring double amount of material will be 300 €.

All laboratories that have been accepted to participate will be sent an invoice to the "invoice address" stated in the registration form.

Payment is expected to be made prior to the scheduled shipment date. No test material will be sent to labs from which no payment has been received by the shipment date. Details of payment will be given in the invoices.

Shipment of Test Material

Test material will be shipped frozen and packed in thermo-boxes together with a freezer block. **The test materials are planned to be shipped on 13 September, 2010**. The organisers will aim to ensure that all participating laboratories will receive their shipments on the same day. Prior to shipment a reminder will be sent to the participating laboratories by e-mail.

Laboratories planning to be on holiday in the week of shipment, should contact the organizer so that alternative arrangements can be made.

Calendar

Activity	Who ?	Dates
Opening of the **EUPT-SRM5 Website** with further information including links to **"Announcement/Invitation-Letter"**, **"Calendar"**, **"Target Pesticide List"**, **"General Protocol"**,	EURL-SRM	Feb 2010
Invitation to laboratories to participate	EURL-SRM	11 May 2010
Release of Specific Protocol	EURL-SRM	15 May 2010
Access to **"EUPT-Registration Website"**	EURL-SRM (in collaboration with EURL-CF)	**15 May 2010**
Deadline for registration	Invited Labs	**30 June 2010**
Preparation of Test Material	EURL-FV (on behalf of EURL-SRM)	July 2010 (pre-tests)
		Sept 2010 (final preparation)
Homogeneity tests	EURL-SRM	Sept 2010
Stability tests	EURL-SRM	Sept-Oct 2010
▪ **Distribution of Test materials** ▪ Information to the laboratories regarding shipment	EURL-FV (on behalf of EURL-SRM)	**13 Sept 2010**
Activation of **"EUPT-SRM5 Result Submission Website"**	EURL-SRM	**by 14 Sept 2010**
Deadline for Receipt and Acceptance of Test Materials: Online Submission of Form 0 (sub-page 0)	Participating Labs	**within 48 hr of receipt**
Deadline for Result Submission Pesticide scope, Results, Method Information Submission of Form 1 – 3 (sub-pages 1 – 3)	Participating Labs	**by 15 Oct 2010**
EUPT Evaluation Meeting	EURL-FV, EURL-SRM, Commission, EUPT-Scientific Committee	Oct/Nov 2010
Preliminary Report (only compilation of results)	EURL-SRM	08 Nov 2010
Final Report	EURL-SRM	Dec 2010

Contact information

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Quality Assurance Group

Antonio Valverde	University of Almería, Spain
Arne Andersson	NFA, Uppsala, Sweden

Annex 1

Preliminary Target Pesticide List

for the EUPT – SRM5 (2010)

Pesticides marked with an asterisk "*" will be considered in the overall performance-ranking of the labs. This concerns both the inclusion of those compounds in the scope of the labs as well as the results (z-scores) achieved by the labs for the compounds present in the sample.

Pesticides	Residue Definitions (valid within this EUPT)	MRRL (mg/kg)	Considered in overall performance-ranking	Included in EU CCP 2010?
ACIDIC PESTICIDES				
***2,4-D**	2,4-D (free acid only)	0.01	Yes	Yes
***Fluazifop**	Fluazifop (free acid only)	0.01	Yes	Yes
***Haloxyfop**	Haloxyfop (free acid only)	0.01	Yes	Yes
Dichlorprop (2,4-DP)	Dichlorprop (free acid only)	0.01	No	No
HIGHLY POLAR PESTICIDES				
***Chlormequat**	Chlormequat (free cation)	0.01	Yes	Yes
***Ethephon**	Ethephon	0.02	Yes	Yes
***Mepiquat**	Mepiquat (free cation)	0.01	Yes	Yes
Amitrole	Amitrole	0.02	No	Yes
OTHER CCP RELATED PESTICIDES				
***Dithiocarbamates**	Dithiocarbamates expressed as CS_2 (including maneb, mancozeb, metiram, propineb, thiram and ziram)	0.02	Yes	Yes
***Abamectin**	Avermectin B1a only	0.01	Yes	Yes
***Fenbutatin oxide**	Fenbutatin oxide	0.01	Yes	Yes

Notes:

- *For analytical and practical reasons the residue definitions applying in this EUPT do not always correspond to those in the legislation*
- *This document may be subject to minor changes, please thus check periodically, and especially after the start of the test to make sure you are using the latest version available*
- *CCP: Coordinated Community Control Programme*

For any questions about the EUPT– SRM5 please mail to **EUPT-SRM@cvuas.bwl.de**.

Document revision history:

04.06.2010: Fees for second shipment of PT-material were introduced

04.06.2010: Fosetyl Aluminium was deleted from the Target Pesticide List

General protocol
for EU proficiency Tests for Pesticide Residues in Food and Feed

Introduction

This protocol contains general procedures valid for all European Union proficiency tests (EUPTs) organised on behalf of the European Commission, Health & Consumer Protection Directorate-General (DG-SANCO) by the four Community Reference Laboratories (CRLs) for pesticide residues in food and feed. These EUPTs are directed at all National Reference Laboratories (NRLs) and Official Laboratories (OfLs) in the EU Member States. Laboratories outside this CRL/NRL/OfL-Network[1] may be permitted to participate on a case-by-case basis after consultation with DG SANCO.

The following four CRLs for pesticides were appointed by DG-SANCO based on regulation 882/2004/EC[2]:

- CRL for Fruits and Vegetables (CRL-FV),
- CRL for Cereals and Feedingstuff (CRL-CF),
- CRL for Food of Animal Origin and Commodities with high Fat Content (CRL-AO) and
- CRL for Single Residue Methods (CRL-SRM)

NRLs are appointed by the National Food or Feed Authorities based on the provisions of Regulation 882/2004/EC, whereas OfLs are laboratories that are actively involved in providing residue data for the national control programme and/or the co-ordinated multiannual Community control programme.

According to Regulation 396/2005/EC[3] all laboratories analysing samples for the official controls on pesticide residues shall participate in the Community proficiency test(s)

[1] For more information about the CRL/NRL/OfL-Network please refer to the CRL-Web-portal under: http://www.crl-pesticides.eu

[2] Regulation (EC) No 882/2004 of the European Parliament and of the Council on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules. Published at OJ of the EU L191 of 28.05.2004

Community Reference Laboratories for Pesticide **Residues**

organised by the Commission. The aim of these EUPTs is to obtain information regarding the quality, accuracy and comparability of the pesticide residue data in food and feed sent to the European Commission within the framework of the national control programmes and the co-ordinated multiannual community control programme. Participating laboratories will be provided with an assessment of their analytical performance and the reliability of their data - compared to the other participating laboratories.

EUPT-organisation

EUPTs are organised by individual CRLs or by more than one CRL in cooperation with one another.

For each EUPT an Organising Team is appointed by the CRL(s) that is responsible for the EUPT. This team is then responsible for all administrative and technical matters concerning the organisation of the PT, e.g. PT-announcement, production of the test material, undertaking the homogeneity and stability tests, packing and shipment of test material, and the handling and first assessment of participant's results.

A common Scientific Committee entailing the following two subgroups:

a) An Advisory Group (AG) and

b) An independent Quality Control Group (QCG)

consisting of expert scientists with long experience in pesticide residue analysis that have been appointed by the CRLs and approved by the DG-SANCO.

The role of the AG is to help the organisers in making decisions concerning the design of the EUPT: selection of pesticides to be included in the Target Pesticide List (see below), the establishment of the minimum required reporting levels (MRRLs), the evaluation and statistical treatment of the results and the drafting of the protocol anf final report. The QCG has the additional function of supervising the quality of the EUPT and to assisting the CRLs with confidential aspects such as the choice of the pesticides, and levels to be present in the test material.

The EUPT-Organising Team, AG and QCG together form the **EUPT-Panel**.

[3] Regulation (EC) No 396/2005, published at OJ of the EU L70 of 16.03.2005, as last amended by Regulation 839/2008 published at OJ of the EU L234 of 30.08.2008.

Confidentiality:

In each EUPT the laboratories are given a unique code only known to themselves, the Organisers, and DG-SANCO. In the final EUPT-Report the list of participating laboratories will not be linked to their laboratory codes. It should be noted that the organisers, at the request of the Commission may present the results to the Standing Committee on the Food Chain and Animal Health on a country-to-country basis. It is therefore possible that a link between codes and National Reference Laboratories could be made, especially for those Member States where only one laboratory has participated. The owner of all EUPT data is DG SANCO.

Communication

The official language used in all EUPTs is English.

Communication between participating laboratories during the test on matters concerning this PT exercise is not permitted.

Announcement

The announcement of the individual EUPT will be issued at least 3 months before the test material is distributed to the laboratories. The announcement will be published on the CRL portal and distributed via mail to the NRL/OfL mailing list available to the CRLs. The announcement will contain an invitation letter, details on how to register and where to locate additional related documents, and some preliminary information on the specific protocol such as the tentative calendar, the name of the commodity expected to be used, and the tentative Target Pesticide List.

Specific Protocol

For each PT a Specific Protocol will be published at least 2 weeks before the test material is distributed to the laboratories. This protocol will contain all information the included in the invitation in its final version, information on payment for delivery service and/or participation. Furthermore, it will also include instructions on how to handle the test material upon receipt, on how to submit results, and other relevant information.

General procedures for reporting results

Laboratories are responsible for reporting their results to the Organiser within the stipulated deadlines. Each laboratory must only report one result for each of the pesticides present in the test material, using the analytical procedure(s) that they would routinely use for each compound for monitoring purposes. More than one method may be used to cover all the compounds to be sought. The results (residue levels of the pesticides detected) must be, expressed in mg/kg.

Correction of results for recovery

According to the Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed, (Document SANCO in force each year) residues data should not normally be adjusted for recovery, when the mean recovery is within the range of 70-120%. If residues data are adjusted for recovery, then this must be clearly stated. Therefore laboratories are required to report whether their results were adjusted for recovery and if this was the case, the recovery factor used. No recovery factors are required where recovery adjustments resulted from using the 'standard addition(s)' approach, or from the use of isotopically labelled internal standards (with spiking of the test material at the beginning of the extraction procedures). In this case, the laboratories should report the technique used for calculation of the results instead of the recovery factor.

Evaluation of the Results

The procedures used for the treatment and assessment of results are described below.

- ***False Positives***

These are the results that show the apparent presence of pesticides that were listed in the Target Pesticide List, but which were (i) not used in the sample treatment, (ii) and not detected by the organiser, even after a repeat analysis. However, if a number of participants do detect the same additional pesticide, or if the concentration is above the MRRL, then a decision as to whether, or not, this should be considered to be a false

positive result will be made on a case-by-case basis. Any results reported that are lower than the MRRL will not be considered as false positives, even though these results should not have been reported.

– ***False Negatives***

These are results for pesticides reported by the laboratories as "analysed" but that no numerical values were given, although they were used by the Organiser to treat the test material and were detected by the majority of participants at or above the MRRL.

– ***Estimation of the true concentration (μ)***

The "true" concentration will be typically estimated using the median of all the results. Therefore a **median value** for every compound present will be calculated and used as the assigned value. In special justifiable cases, the EUPT Panel may decide to use only part of the population of results to establish the median (e.g. using only results with z-scores ≤ 5.0).

– ***Establishing the standard deviation of the assigned value (target standard deviation)***

The target standard deviation (δ) of the median will be calculated using a Fit-For-Purpose Relative Standard Deviation (FFP-RSD) approach, as follows:

$$\delta = b_i * \mu_i \quad \text{with } b_i \text{ i = FFP-RSD (= 0.25)}$$

The percentage FFP-RSD is typically set at 25% based on experience from previous EUPTs. The EUPT-Panel reserves the right to also employ other approaches on a case-by-case basis considering analytical difficulties, and experience gained from previous proficiency tests.

– ***z-scores***

This parameter is calculated using the following formula:

$$z_i = (x_i - \mu_i) / \delta_i$$

Where x_i is the value reported by the laboratory, μ_i the assigned value, and δ_i the standard deviation at that level for each pesticide (i).

Any z-scores of > 5 will be reported as "+5" particularly where summed z-scores of many pesticides are calculated (see SWZ below).

z-scores will be interpreted in the following way:

$|z| \leq 2$ Acceptable

$2 < |z| \leq 3$ Questionable

$|z| > 3$ Unacceptable

For results that are considered to be false negatives, z-scores will be calculated using the MRRL or RL (the laboratory's Reporting Limit), if the RL < MRRL.

The EUPT-Panel will consider whether, or not, these values should appear in the z-score histograms.

However, a z-score will not be calculated for any false positive result.

– ***Category A and B classification***

The EUPT-Panel will decide whether to classify the laboratories in two groups, A and B. Laboratories that detected a sufficiently high percentage of the pesticides present in the test material (e.g. at least 90%), reported no false positives, and sought all the pesticides on the Target Pesticide List marked with an asterisk that were present in the test material, will have demonstrated 'sufficient scope' and will therefore be classified in Category A.

- ***Combined z-scores***

For evaluation of the overall performance of the laboratories within Category A, a ranking according to the sum of weighted z-scores (SWZ) will be calculated.

The sum of weighted z-scores formula uses the z-scores with a fixed maximum value of 5 for individual z-scores, using the following formula:

$$\text{'Sum of weighted z-scores' } (Z) = \frac{\sum_{i=0}^{i\leq 2}|z|\cdot 1 + \sum_{i>2}^{i\leq 3}|z|\cdot 3 + \sum_{i>3}^{\infty}|z|\cdot 5}{n}$$

n = number of reported results

So for each laboratory:

- The first summation is the sum of all their /z-scores/ between zero to two, multiplied by 1.
- The second summation is the sum of all their /z-scores/ greater than two but less than or equal to, three, multiplied by 3.
- The third summation is the sum of all their z-scores greater than three, multiplied by 5.

This SWZ has the following classification similar to the z-score:

$Z \leq 2$ Good

$2 < Z \leq 3$ Satisfactory

$Z > 3$ Unsatisfactory

The sum of weighted z-scores is considered to be of lesser importance than the individual z-scores. Therefore the organiser, in agreement with the EUPT-Panel, retains the right not to use them if they are considered to be unhelpful.

Publication of results

The preliminary results from the EUPTs will be published within 2 months from the deadline for result submission.

The final report will be published shortly after the organiser and the EUPT-Panel have discussed the results. Taking into account that the EUPT-Panel normally only meets once a year, the final report may be published up to 8 months after the deadline for results submission.

Disclaimer

The EUPT-Panel retains the right to change any parts of this EUPT - General Protocol based on new scientific or technical information. Any changes will be communicated in due course.

Cover picture: Gojaz Alkimson, www.istockphoto.com; ID=10839174

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