EU PROFICIENCY TEST
EUPT-SRM11, 2016

Residues of Pesticides Requiring Single Residue Methods

Test Item: Spinach Homogenate

Final Report

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FOREWORD

Regulation 882/2004/EC [1] defines the general tasks and duties of the EU Reference Laboratories (EURLs) for Food, Feed and Animal Health[1] including the organisation of comparative tests (proficiency tests = PTs). These PTs 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 framework of the EU coordinated control programs as well as national monitoring programs. By participating in PTs laboratories can assess and at the same time demonstrate their analytical performance. The attention to details paid by laboratories during PT-analysis, together with the need to identify errors and to take corrective actions in cases of underperformance, typically lead to improvements in the quality of analytical results.

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 for pesticide residues within the framework of official controls shall participate in the European Union Comparative Proficiency Tests (EUPTs) for pesticide residues. Each Official Laboratory (OfL) must participate in EUPTs concerning the commodities included in its area of competence.

Since 2006 the EURL for pesticide residues requiring the use of Single Residue Methods, EURL-SRM, has annually conducted one scheduled Proficiency Test. Two of these eleven EUPT-SRMs, the EUPT-SRM7 (2012) based on milled dry lentils and the EUPT-SRM9 (2014) based on cow's milk, were organized by the EURL-SRM unilaterally. The EUPT-SRM9 was the only one within EUPT-SRMs so far, in which a commodity of animal origin was used. Five other EUPT-SRMs were conducted in collaboration with the EURL for pesticide residues in Fruits and Vegetables (EURL-FV) with apple juice (EUPT-SRM1, 2006), carrot homogenate (EUPT-SRM3, 2008), apple purée (EUPT-SRM5, 2010), potato homogenate (EUPT-SRM8, 2013) and the present EUPT-SRM11 with spinach homogenate as test items. The remaining four EUPT-SRMs were conducted in collaboration with the EURL for pesticide residues in Cereals and Feeding Stuff (EURL-CF) with wheat flour (EUPT-C1/SRM2, 2007), oat flour (EUPT-C3/SRM4, 2009), rice flour (EUPT-C5/SRM6, 2011) and EUPT-C9/SRM10 with maize flour as test items.

Participation in the respective EUPTs is mandatory for all NRLs for pesticides requiring Single Residue Methods (NRL-SRMs) and for all OfLs analysing pesticide residues within the framework of national or EU control programs in commodities represented by the respective EUPT test item. Laboratories in EU Member States analysing pesticide residues within the frame of import controls according to Reg. 669/2009/EC are also considered as performing official controls in the sense of Reg. 882/2005/EC and 396/2005/EC and are thus also obliged to take part in EUPTs. OfLs from EFTA countries (Iceland, Norway and Switzerland) contributing data to the EU-coordinated community control programs, EU laboratories analysing official organic samples within the frame of Reg. 889/2008/EC, as well as OfLs from EU-acceding or -candidate countries (FYROM, Montenegro, Serbia and Turkey) are also invited to take part. A limited number of laboratories from third countries are allowed to take part in this exercise, too. However, only results submitted by labs from EU and EFTA countries are included in the calculation of the assigned values.

Based on information about the commodity scope and labs' NRL-status a tentative list of EU-labs considered as being obliged to participate in the EUPTs is published at the beginning of each year. The pesticide scope is not taken into account in these lists. NRLs and OfLs listed as being obliged to participate in an EUPT exercise in a given year but deciding not to take part, are always asked to state the reason(s) for their non-participation. The same applies to laboratories originally registering to participate in a certain EUPT but finally not submitting results.

[1] Formerly known as Community Reference Laboratories (CRLs)

DG-SANTE has full access to all data of EUPTs including the lab-code/lab-name key. The same applies to all NRLs as far as laboratories belonging to their own country networks are concerned. Results for this EUPT or a series of EUPTs, evaluated on a country by country basis, may be further presented to the European Commission Standing Committee on Plants, Animals, Food and Feed (PAFF) -Section Pesticides Residues, or during the EURL-Workshops.

CONTENT

EUROPEAN COMMISSION –
EU-PROFICIENCY TEST ON RESIDUES OF PESTICIDES
REQUIRING SINGLE RESIDUE METHODS
TEST ITEM: SPINACH HOMOGENATE
EUPT-SRM11, 2016

INTRODUCTION

On 11 January, 2015 all relevant National Reference Laboratories (NRLs) of the 27 EU-Member States (MS), as well as all relevant EU-Official Laboratories (OfLs) whose contact details were available to the organisers (EURL-SRM) were invited to participate in the 10th European Commission's Proficiency Test Requiring Single Residue Methods (EUPT-SRM11). The EUPT-SRM11-Website contained links to the Announcement/ Invitation Letter, the Calendar, as well as to the Target Pesticides List (**Appendix 11**). The Target Pesticides List contained 27 compounds potentially being present in the test item. 11 of them were compulsory compounds and were thus considered in the Category A/B classification (based on scope). The compounds of the Target Pesticides List were selected based on a number of criteria and following consultation with the EUPT-Scientific Committee. For each compound a residue definition valid for the PT and the minimum required reporting level (MRRL) were stipulated. Links to the latest version of the "General Protocol" (**Appendix 9**) containing information common to all EUPTs, and to the "Specific Protocol" (**Appendix 10**) valid for the current PT, were also provided. The laboratories were able to register on-line from 8 February to 11 March, 2016.

Based on their commodity scope (fruit and vegetable) and their NRL-status (NRL-SRMs) a tentative list of the laboratories considered as being obliged to participate in the EUPT-SRM11 was published on the EURL-Website as well as on the CIRCA BC-platform. To ensure that all relevant official laboratories were informed about this EUPT, the NRLs were asked to forward the invitation to all relevant official laboratories within their countries. It was made clear that the list of obliged laboratories prepared by the EURLs was only tentative, and the real obligation to participate was based on Reg. 396/2005/EC and Reg. 882/2004/EC. Obliged labs that did not intend to participate were asked to provide an explanation.

In total 124 laboratories from EU and EFTA countries agreed to participate in the test with 4 of them failing to submit results. One laboratory from EU-candidate countries and one laboratory from third countries have also registered for the present EUPT, and both of them have submitted results.

The production of the blank material as well as the test item, containing both incurred (field-sprayed) and non-incurred (post-harvest sprayed) compounds, was subcontracted to the EURL-FV in Almería/Spain. More details are given in **Chapter 1 "Test Materials"**.

1. TEST ITEM AND BLANK MATERIAL

1.1 Selection of PT-Commodity and of Compounds for the Target Pesticides List

In agreement with the EUPT- Scientific Committee spinach homogenate was chosen as commodity for the EUPT-SRM11.

The compounds to be included in the Target Pesticides List (**Appendix 11**) were selected by the organiser and the EUPT-Scientific Committee (Advisory Group and Quality Control Group) taking the following points into account: 1) the present and upcoming scope of the EU-coordinated control program; 2) a pesticide priority, ranking the pesticides according to their risk potential; 3) the relevance of pesticides to the specific commodity; 4) the overall scope and capability of the OfLs as assessed in previous PTs or surveys; 5) the need of data to be able to evaluate the analytical proficiency of labs that offer analytical services via the SRM-PinBoard Service of the EURL-SRM.

The minimum required reporting levels (MRRLs) were set at 0.01 mg/kg for 2,4-D, cyromazine, dodine, fluazifop, haloxyfop, TFNA, TFNG, tolyfluanid, DDAC-C10, dithianon, MCPA, MCPB, pymetrozine, quizalofop and triclopyr; at 0.02 mg/kg for ethephon, BAC-C10, BAC-C12, BAC-C14, BAC-C16, BAC-C18, chlorate, fosetyl, and perchlorate; at 0.03 mg/kg for dithiocarbamates and glyphosate, and at 0.05 mg/kg for phosphonic acid.

The production of the test item and the blank material was subcontracted to the EURL-FV. Part of the analytes were applied during cultivation of the spinach and part of them post harvest. The spinach was cultivated in one of the experimental greenhouse belonging to the University of Almería. During cultivation it prooved necessary to treat the plants with pymetrozine to avoid insect infestation. Furthermore, the plants were irrigated with water containing high levels of chlorate and perchlorate. Therefore, these three analytes were contained both in the blank material as well as in test item. This was communicated to the participants with the advice not to use the blank material for matrix-mateched calibration purposes.

1.2 Preparation and Bottling of the Blank Material

As mentioned above the blank material contained pymetrozine, chlorate and perchlorate. As the blank material was harvested ca. 3 weeks earlier than the treated one, the levels of these three compounds in the blank material differed considerably from those in the test item.

Approximately 3 weeks after gemination, approximate 2 kg of the spinach was homogenated, sent to the EURL-SRM and checked there for the absence of the pesticides included in the Target Pesticides List. The necessary amount for blank material (approximately 53 kg) were harvested and frozen homogenized by the EURL-FV using liquid nitrogen. Ca. 350 g of blank spinach homogenate was weighed out into leak-proof screw-capped polyethylene plastic bottles, sealed, and stored in a freezer at about –20 °C until the distribution to participants or transport to EURL-SRM. A randomly chosen bottle of blank material was later analyzed by the EURL-SRM for the pesticides to verify that there was no cross-contamination during test item preparation.

The remaining spinach was grown further to be used for the production of the test item (see below).

1.3 Preparation and Bottling of the Test Item

After the spinach for the blank material was harvested, the remaining crops were treated with cyromazine, propineb, dodine, flonicamid, dithianon, and phosphonic acid. **Table 1-1** shows the compounds applied

Table 1-1: Analytes present in the test material

	Applied in the Field		Spiked post Harvest	
	Analytes	**Treatment Form**	**Analytes**	**Treatment Form**
Compusory Compounds	Cyromazine	Formulation	Tolylfluanid	Standard solution
	Propineb (as dithiocarbamates)	Formulation		
	Dodine	Formulation		
	TFNA (metabolite of flonicamid)	Formulation of flonicamid		
	TFNG (metabolite of flonicamid)	Formulation of flonicamid		
Optional Compounds	Pymetrozine	Formulation	BAC-C14	Standard solution
	Dithianon	Formulation	Triclopyr	Standard solution
	Phosphonic acid	Standard solution	Quizalofop	Standard solution
	Chlorate	Contained in irrigation water		
	Perchlorate	Contained in irrigation water		

both in the field and post-harvest. One week later, approximate 2 kg of the treated spinach was homogenized and sent to the EURL-SRM to check the concentration of the target analytes. Approximately 70 kg treated spinach were harvested for the test material and additionally spiked with BAC C14, triclopyr, tolylfluanid, quizalofop post harvest. The concentration of the analytes in the treated corp was analysed again and it was decided that no post-harvest spiking was necessary.

The following steps of homogenisation, portioning and storage were conducted in exactly the same way as for the blank material described above.

1.4 Packaging and Delivery of PT Materials to Participants

The EURL-FV was also subcontracted for the packaging and distribution of the PT materials from Almería to the participating laboratories. In general, one test item (ca. 350 g) and one blank material (ca. 350 g) were packaged in thermo-insulated polystyrene boxes covered with approx. 2 kg dry ice. The packages for laboratories in coutries, where according to IATA Dangerous Goods Regulations shipments with dry ice were not allowed, were shipped with cooling elements instead of dry ice. .

For logistical reasons, it was decided to ship the parcels to laboratories in Spain and Portugal using a local transportation company and to other destinations using DHL express. The parcels to Spain and Portugal were shipped on Monday 4 April, 2016 and most parcels to other countries on Tuesday 5 April, 2016. Some shipments to laboratories in remote locations or in countries, where according to IATA Dangerous Goods Regulations shipments with dry ice were not allowed, were shipped on a different day. All participating laboratories were informed on 24 March, 2016 on the date of shipment.

In the evening of 5 April, 2016 there was a birds strike on a plane at the Airport of Alicante, which delayed the shipment of ca. 2/3 of the parcels by almost a day. The participants were informed on 6 April about the delayed delivery, and asked to report the state of the PT-materials at arrival and their acceptance via the online submission tool. Due to a workers' strike, the airport Athens was closed on 7 April, 2016, so that parcels to the laboratories in Greece and Cyprus were additionally delayed by a further day. These materials were more than 3 days on the way and arrived the laboratories in a defrosted state, although approximate 2 kg dry ice was packed in each box. In four cases it was decided to arrange a second shipment on the following week. All second shipments arrived the recipeints in good condition and within the DHL regulary shipment duration.

Due to the unexpected problems with the shipment and because some of the laboratories received their materials a week later, the organisers decided to shift the submission deadline from 10 May to 20 May, 2016.

Among the 124 packages sent to the participants in the EU and EFTA countries that were accepted and finally used by the laboratories for the current PT, 48 (37 %) reached the participating labs within 24 hours, 66 (53 %) within 48 hours and 10 (8 %) within 72 hours. The two deliveries to laboratories in countries outside the EU and EFTA zones were accomplished within 48 hours in 1 case and, due to delays at the customs, within 6 days in the other case. In the latter case, the parcel was kept in a freezer while waiting for customs clearance, so that the material was still frozen at arrival. Details on the shipments and the condition of the test items upon arrival are shown in **Appendix 2**.

Overall, the EUPT-materials arrived at the laboratories in acceptable condition despite the unexpected problems with delivery.

1.5 Analytical Methods

The analytical methods used by the organisers to check the homogeneity and storage-stability of the target analytes contained in the test item as well as the absence of target analytes in the blank material are summarized in **Table 1-2**. For more details on the methods used, please refer to the EURL-SRM website: http://www.eurl-pesticides.eu (EURL-SRM-website → Services → Methods).

1.6 Homogeneity Test

After filling the test item in bottles, 15 of them were randomly chosen and sent, together with two bottles of blank material, to the EURL-SRM for the homogeneity and stability tests. This shipment was done without additional cooling by dry ice All material was still deeply frozen at arrival. The analyses for the homogeneity test were performed on two analytical portions taken from 10 bottles. Before withdrawing the analytical portions, the entire content of each bottle was quickly remixed with a high speed mixer with addition of dry ice, analytical portions for both homogeneity test and the stability test were made therefrom. The portions for the second and third storage stability test were immediately frozen at –20 °C till the date of performing storage stability test. Both the order of sample preparation and the order of extract injection into the analytical instruments were random. Except for pymetrozine, chlorate and perchlorate that were contained in the blank material, matrix-matched calibrations, using extract prepared from blank material, were applied for quantification. For pymetrozine, chlorate and perchlorate a commercial spinach from organic farming was used for preparing matrix-matched calibrations. Analytical portions of 50 g for dithiocarbamates and 10 g for all other compounds were used.

The statistical evaluation of the homogeneity test data was performed according to the International Harmonized Protocols published by IUPAC, ISO and AOAC [4, 6]. An overview of the statistical evaluations of the homogeneity test is shown in **Table 1-3**. The individual residue data of the homogeneity test is given in **Appendix 3**.

The acceptance criterion for the test item to be sufficiently homogeneous for the Proficiency Test was that s_{sam}^2 is smaller than c with s_{sam} being the between-bottle sampling standard deviation and $c = F_1 \times \sigma_{all}^2 + F_2 \times s_{an}^2$, F_1 and F_2 being constants with values of 1.88 and 1.01, respectively, and applying when duplicate samples are taken from 10 bottles. $\sigma_{all}^2 = 0.3 \times$ FFP-RSD (25 %) $\times$ the analytical sampling mean of the analyte, and s_{an} is the estimate of the analytical standard deviation.

Table 1-2: Analytical methods used by the organisers to check for the homogeneity and storage-/transport-stability of the pesticides present in the test item and to demonstrate the absence of other pesticides in the blank material.

Compound	Extraction	IS	Determinative analysis		Notes
BAC-C14	**Modified QuEChERS-method** [3] involving: weighing of 10 g spinach homogenate into a sealable vessel, addition of IS / ILISs, extraction with ACN + 1 % formic acid (15 min), addition of partitioning salts (4 g $MgSO_4$, 1 g NaCl), 1 min shaking, centrifugation (twice with interval of 30 min), and direct determination by LC-MS/MS in the ESI (neg.) and ESI (pos) mode.	**Chlorpyrifos D_{10} / BAC-C14 D_7**	**LC-MS/MS**	**ESI (pos)**	
Dithianon		**BNPU / Dithianon D_4**	**LC-MS/MS**	**ESI (neg)**	
Dodine		**Chlorpyrifos D_{10}**	**LC-MS/MS**	**ESI (pos)**	
Quizalofop		**BNPU / Quizalofop D_3**	**LC-MS/MS**	**ESI (neg)**	
TFNA		**BNPU / TFNA D_3**	**LC-MS/MS**	**ESI (neg)**	
TFNG		**BNPU / TFNG D_3**	**LC-MS/MS**	**ESI (neg)**	
Tolylfluanid		**Chlorpyrifos D_{10} / Tolylfluanid D_{10}**	**LC-MS/MS**	**ESI (pos)**	
Triclopyr		**BNPU**	**LC-MS/MS**	**ESI (neg)**	
*2,4-D**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
*BAC-C10**		*Chlorpyrifos D_{10}*	*LC-MS/MS*	*ESI (pos)*	
*BAC-C12**		*Chlorpyrifos D_{10}*	*LC-MS/MS*	*ESI (pos)*	
*BAC-C16**		*Chlorpyrifos D_{10}*	*LC-MS/MS*	*ESI (pos)*	
*BAC-C18**		*Chlorpyrifos D_{10}*	*LC-MS/MS*	*ESI (pos)*	
*DDAC-C10**		*Chlorpyrifos D_{10} / DDAC-$C_{10}D_6$*	*LC-MS/MS*	*ESI (pos)*	
*Fluazifop**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
*Haloxyfop**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
*MCPA**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
*MCPB**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
Cyromazine	**Modified QuEChERS-method** involving: weighing of 10 g spinach homogenate into a sealable vessel, addition of ILISs or ISs, extraction with ACN (15 min), addition of partitioning salts (4 g $MgSO_4$, 1 g NaCl, 0.5 g Na-Acetate), 1 min shaking, centrifugation (twice with interval of 30 min), and direct determination by LC-MS/MS in the ESI (pos) mode.	**Cyromazine D_4**	**LC-MS/MS**	**ESI (pos)**	
Pymetrozine		**Chlorpyrifos D_{10}**	**LC-MS/MS**	**ESI (pos)**	
Chlorate	**QuPPe-PO method** [5] involving: weighing of 10 g spinach homogenate into a sealable vessel, addition of ILISs, addition of methanol containing 1 % formic acid, shaking, centrifugation, filtration and direct determination by LC-MS/MS in the ESI (neg.) or ESI (pos.) mode.	**Chlorate $^{18}O_3$**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.4**
Perchlorate		**Perchlorate $^{18}O_4$**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.4**
Phosphonic acid		**Phosphonic acid $^{18}O_3$**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.4**
*Ethephon**		*Ethephon D_4*	*LC-MS/MS*	*ESI (neg)*	*QuPPe M1.3*
*Glyphosate**		*Glyphosate ^{13}C, ^{15}N*	*LC-MS/MS*	*ESI (neg)*	*QuPPe M1.3*
*Fosetyl**		*Fosetyl D_5*	*LC-MS/MS*	*ESI (neg)*	*QuPPe M1.3*
CS_2	**Dithiocarbamate method** involving: weighing of 50 g spinach homogenate into a sealable vessel, addition of chloroform (as IS) and 25 ml iso-octane and 150 ml $SnCl_2$/HCl, followed by cleavage to CS_2 in a shaking water bath for 2 h at 80° C, followed by GC-ECD analysis.	**Chloroform**	**GC-ECD**	–	

* : To check for absence in Blank Material

Table 1-3: Statistical evaluation of homogeneity test data (n = 20 analyses), details please see **Appendix 3**.

COMPULSORY COMPOUNDS								
	Cyromazine	Dithiocarbamates	Dodine	TFNA	TFNG	Tolylfluanid		
Analytical portion size [g]	10	50	10	10	10	10		
Mean [mg/kg]	1.561	1.424	1.294	0.831	0.486	0.942		
s_{sam}^2	0.00×10^{0}	1.42×10^{-2}	8.24×10^{-4}	0.00×10^{0}	0.00×10^{0}	0.00×10^{0}		
c	1.06×10^{-4}	2.25×10^{-4}	1.55×10^{-2}	3.20×10^{-4}	4.43×10^{-3}	4.43×10^{-3}		
Passed/Failed	passed	passed	passed	passed	passed	passed		
OPTIONAL COMPOUNDS								
	BAC-C14	Chlorate	Dithianon	Phosphonic acid	Perchlorate	Pymetrozine	Quizalofop	Triclopyr
Analytical portion size [g]	10	10	10	10	10	10	10	10
Mean [mg/kg]	0.331	2.316	3.786	9.490	0.263	0.506	0.171	0.202
s_{sam}^2	1.05×10^{-3}	0.00×10^{0}	9.84×10^{-2}	1.31×10^{-1}	4.36×10^{-5}	0.00×10^{0}	2.94×10^{-4}	2.62×10^{-4}
c	2.67×10^{-3}	6.23×10^{-2}	3.21×10^{-1}	1.05×10^{0}	7.60×10^{-4}	3.69×10^{-3}	5.92×10^{-4}	5.68×10^{-4}
Passed/Failed	passed	passed	passed	passed	passed	passed	passed	passed

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

As all target compounds passed the homogeneity test, the test item was considered to be sufficiently homogenous and suitable for the EUPT-SRM11. In the Specific Protocol and in a short instruction distributed to the participants prior to the shipment, laboratories were, furthermore, strongly recommended thoroughly mixing the received test items before taking any analytical portions in order to ensure good homogeneity.

1.7 Storage Stability Test

Except one laboratory with delays caused by customs clearance, all other laboratories received their test items within 72 hours in frozen or very cool condition. Since the package at the customs was kept in freezer, the material was in frozen state at arrival after 6 days. In the Specific Protocol laboratories were recommended storing the samples in the freezer until analysis. Possible losses during the transport to the participants were studied separately in the transport stability test (see below). For the storage stability test, two analytical portions from three randomly chosen test item bottles were withdrawn on three dates, with the first and last one enclosing the period of the test, and analysed as described in **Section 1.5 (p. 4)**:

Table 1-4: Results of storage stability test (storage at -18 °C). Please see the text or **Appendix 4** for the dates of analysis for each analytes.

COMPULSORY COMPOUNDS								
	Cyromazine	Dithiocarbamates	Dodine	TFNA	TFNG	Tolylfluanid		
Storage at –18 °C (mean values in mg/kg)								
Analysis 1 6 – 8.04.2016/25.04.2016	1.695	1.377	1.190	0.812	0.490	1.080		
Analysis 2 12.05.2016/13.06.2016	1.721	1.322	1.177	0.810	0.487	1.043		
Analysis 3 25.05.2016/22.06.2016	1.731	1.294	1.175	0.785	0.458	1.092		
Deviation [mg/kg] ([%]) Analysis 3 vs. Analysis 1	0.035 (2.1 %)	0.083 (-6.0 %)	0.015 (-1.3 %)	0.027 (-3.3 %)	0.032 (-6.4 %)	0.012 (1.1 %)		
$0.3 \times \sigma_{pt}$ [mg/kg]	0.113	0.097	0.093	0.057	0.034	0.045		
Passed/Failed	passed	passed	passed	passed	passed	passed		

OPTIONAL COMPOUNDS								
	BAC-C14	Chlorate	Dithianon	Phosphonic acid	Perchlorate	Pymetrozine	Quizalofop	Triclopyr
Storage at –18 °C (mean values in mg/kg)								
Analysis 1 6 – 8.04.2016/25.04.2016	0.371	2.342	3.460	10.131	0.247	0.478	0.195	0.223
Analysis 2 12.05.2016	0.346	2.501	3.548	9.661	0.230	0.472	0.182	0.213
Analysis 3 25.05.2016/22.06.2016	0.346	2.481	3.087	10.288	0.246	0.459	0.189	0.208
Deviation [mg/kg] ([%]) Analysis 3 vs. Analysis 1	0.025 (-6.7 %)	0.139 (5.9 %)	0.373 (-10.8 %)	0.158 (1.6 %)	0.001 (-0.4 %)	0.020 (-4.1 %)	0.006 (-3.1 %)	0.015 (-6.6 %)
$0.3 \times \sigma_{pt}$ [mg/kg]	0.021	0.152	0.131	0.737	0.020	0.032	0.013	0.013
Passed/Failed	(passed)	passed	**failed**	passed	passed	passed	passed	(passed)

Stability test 1 (extraction directly after shipment, except for ***cyromazine*** and ***pymetrozine****):
05 April 2016 (***chlorate, perchlorate*** and ***phosphonic acid***)
06 April 2016 (all other analytes)
08 April 2016 (***dithiocarbamates***)
25 April 2016 (***cyromazine*** and ***pymetrozine****)

Stability test 2 (extraction five weeks after shipment):
12 May 2016 (all other analytes)
13 May 2016 (***dithiocarbamates***)

Stability test 3 (extraction three weeks after deadline for results submission):
25 May 2016 (all other analytes)
22 June 2016 (***cyromazine*** and ***pymetrozine****)

* The analysis of ***cyromazine*** and ***pymetrozine*** had to be postponed due to technical problems. In order to cover the whole test period, the third stability test for these two analytes was thus conducted later.

A target compound is considered to be adequately stable if $|y_i - y| \leq 0.3 \times \sigma_{pt}$, where y_i is the mean value of the last period of the stability test, y is the mean value of the first period of the stability test and σ_{pt} the standard deviation used for proficiency assessment, typically 25 % of the assigned value. Except dithianon none of the other 13 target compounds present in the test item showed any significant degradation under the recommended storage condition at –18 °C within a storage period of one week longer than the duration of the exercise. It is thus assumed that if the recommended storage conditions were followed, the influence of sample storage on the results of these 13 analytes was negligible.

Considering that a) significant losses on dithianon were observed both in the storage stability test and in the transport stability test (see **Section 1.8**), and b) the wide distribution of results submitted by the participants and the high uncertainty of its assigned value driven therefrom (see **Section 4.3, p. 32**), the Scientific Committee decided to exclude dithianon from the evaluation.

The results of all analyses conducted within the framework of the stability test are shown in **Table 1-4** (p. 5) and **Appendix 4**.

1.8 Transport Stability Test

To complement the storage stability test, the stability under conditions of shipment was also studied. For this purpose, prior to shipment from Almería, the content of four randomly chosen test items were poured in a larger container, remixed thoughly under slightly thawed condition and refilled in the bottles. During this procedure, degradation of thermo-labile analytes like dithianon and tolylfluanid may take place, however, the four bottles could be regarded as equal in their content. Four parcels, each with one of the remixed and refilled test item and one bottle blank material, were packed in the same way as the real packages to the participants and sent by DHL Express to the EURL-SRM for the transport stability test. The four parcels arrived the EURL-SRM within 24 hours, and there was dry ice left in the boxes. Upon arrival, one of the parcel was immediately put in the freezer at –18 °C. This parcel was later used for another purpose. The other three parcels were left in the laboratory at ambient temperature for additional 1, 2 and 5 days and then put in the freezer at –18 °C till analysis on 8 July, 2016. The intention was to simulate the transport of 2,3 and 6 days. It was assumed that the average transport temperature was in vast majority of the cases lower than 21°C (the average temperature of the laboratory), and that this experiment simulated relatively critical transport/storage conditions. Each sample was analyzed in quintuplicate.

Table 1-5: Transport stability test. Delivery units, deep frozen, packed with dry ice in thermo-insulated polystyrene boxes and left in the laboratory at room temperature

COMPULSORY COMPOUNDS								
	Cyromazine	Dithiocarbamates	Dodine	TFNA	TFNG	Tolylfluanid		
Day-2 [mg/kg]	1.836	0.986	1.268	0.806	0.484	0.502		
Day-3 [mg/kg]	1.739	0.953	1.260	0.790	0.472	0.459		
Day-6 [mg/kg]	1.788	0.873	1.220	0.879	0.476	0.041		
Deviation [%] Day-3 vs. Day-2	-5.3 %	-3.4 %	-0.6 %	-2.0 %	-2.4 %	-8.6 %		
Deviation [%] Day-6 vs. Day-2	-2.6 %	-11.4 %	-3.8 %	9.0 %	-1.6 %	-91.9 %		
OPTIONAL COMPOUNDS								
	BAC-C14	Chlorate	Dithianon	Phosphonic acid	Perchlorate	Pymetrozine	Quizalofop	Triclopyr
Day-2 [mg/kg]	0.277	2.465	2.792	11.303	0.223	0.501	0.176	0.191
Day-3 [mg/kg]	0.275	2.341	2.244	10.793	0.218	0.465	0.179	0.192
Day-6 [mg/kg]	0.289	2.017	0.034	9.762	0.209	0.426	0.170	0.249
Deviation [%] Day-3 vs. Day-2	-0.4 %	-5.0 %	-19.6 %	-4.5 %	-2.0 %	-7.2 %	1.5 %	0.7 %
Deviation [%] Day-6 vs. Day-2	4.6 %	-18.2 %	-98.8 %	-13.6 %	-6.2 %	-15 %	-3.6 %	30.3 %

Following 2 days of transport simulation, there was still a small amount of dry ice left in the parcels and the test materials within the parcel still entirely frozen. It is thus assumed that all target compounds remained sufficiently stable up to 2 days. The results from the test material opened on Day-2 were therefore used as a reference point for this test. More than 90 % of the participating labs in the EU and EFTA countries received the PT-materials within two days. Comparing Day-2 and Day-3, where the material started defrosting, most of the analytes still remained acceptably stable with exception of ***dithianon*** which experienced a 20 % concentration drop. Overall it was considered that any differences in the degradation rates of these analytes during the transport to the participating laboratories, were considered negligible up to two days for all compounds but ***dithianon*** and up to three days for all other compounds.

At longer shipping simulation times without additional cooling, the concentration of ***dithianon*** and ***tolylfluanid*** dropped drastically with only 1.2 % of ***dithianon*** and 8.1 % of ***tolylfluanid*** remaining intact on Day-6 (= 4 days after Day-2, which was used as reference). Moderate concentration drops were also observed for ***dithiocarbamates***, ***chlorate***, ***phosphonic acid*** and ***pymetrozine***, but these may be partly due to analytical errors caused by the alteration of the matrix during storage. In any case these extreme times concern only a very small number of laboratories outside EU or EFTA receiving the samples extremely late and not affecting the assigned value. The results of the transport stability test are shown in **Table 1-5**.

Considering that dithianon failed the stability test, showing unacceptable degradation even in the frozen material, and considering its rapid degradation when leaving the sample to defrost as well as the extremely large distribution of the participants results (see **Section 4.3, p. 32**), the Scientific Committee decided to completely abstain from evaluating dithianon in this PT.

Tolylfluanid passed the stability test but also showed a very rapid degradation in the thawed material which influenced the results of many laboratories and introduced a strong bias in the robust mean (see **Section 4.3**). Even though the uncertainty of the robust mean was marginally acceptable, it was decided that this compound should be only evaluated for information only as the robust mean was considered biased due to the large number of laboratories not properly protecting this compound prior or during analysis.

1.9 Organisational Aspects

1.9.1 Preparation and Distribution of a Tentative List of Obliged Laboratories

A tentative list of laboratories (NRLs and OfLs) obliged to participate in the current EUPT was compiled based on available information on NRL-status and commodity scope as recorded in the EURL-DataPool. The available data on the information on the pesticide scope of the laboratories was not considered when drafting this list due to concerns that it was not up-to-date and/or not applicable to the present commodity (spinach). The draft list was distributed to the OfLs and the NRLs so that all laboratories could check their own data including status and contact information, and they have to report any errors. The errors were corrected periodically, and a new version was released. The NRLs were reminded of their responsibility for taking care of their network and were prompted to carefully check the status, commodity scope and contact data of the OfLs within their network. They were also asked to amend and complement the list, if necessary, and to ensure that all obliged OfLs within their network were informed of this EUPT. It was made clear to all NRLs and OfLs that the list of obliged laboratories was tentative, the real obligation for participation is derived in accordance with Art. 28 of Reg. 396/2005/EC (for OfLs) and from Art. 33 of Reg. 882/2004/EC (for NRL-SRMs). Following DG-SANTE instructions, obliged labs that were not intending to participate in the EUPT-SRM11 were instructed to provide explanations for their non-participation.

1.9.2 Announcement / Invitation and EUPT-SRM11-Website

Within the EURL-Web-Portal an EUPT-SRM11-Website was constructed with links to all documents relevant to this EUPT (i.e., Announcement/Invitation Letter, Calendar, Target Pesticides List, Specific Protocol and General EUPT Protocol). These documents were uploaded to the EURL-Web-Portal, the CIRCA BC and the CIRCA/FIS-VL platform.

The Announcement/Invitation Letter for the EUPT-SRM11 was published on the EUPT-SRM11-Website in January 2016 and sent to all NRL-SRMs, all OfLs analysing pesticide residues in food and feeding stuff within the framework of official controls, all laboratories performing import controls according to Reg. 669/2009/EC and exsisting in the laboratorie database, and EU laboratories analysing official organic samples within the frame of Reg. 889/2008/EC. The latter labs were considered eligible but not obliged to participate. It was indicated to the OfLs that their obligation to participate in EUPTs arises from Reg. 396/2005/EC, irrespective of the content of the tentative list of obliged laboratories. NRLs and OfLs from EFTA and EU-candidate countries were also invited if their contact data was available. A number of laboratories from third countries were also invited to take part in this exercise. The acceptance of their registration was, however, decided case by case, and the laboratories were informed individually of the acceptance or rejection of their registration.

1.9.3 Registration and Confidentiality

An EUPT-SRM11 registration website was constructed in collaboration with the EURL-CF. All laboratories listed in the tentative list as being obliged to participate in the current EUPT, regardless of whether they were intending to participate in this exercise or not, were requested to either register or to state their reasons for non-participation using the same website.

Upon registration, the labs received an electronic confirmation about their participation or non-participation in the current PT. On the day of sample shipment, participating labs were provided via e-mail with a unique laboratory code as well as with unique, automatically generated login data to access the online Result-Submission-Website. This ensured confidentiality throughout the entire duration of the PT.

For further information on confidentiality please refer to the General EUPT Protocol (**Appendix 9**).

1.9.4 Distribution of the Test Items and the Blank Material

One bottle of test item (approx. 350 g) and one bottle of blank material (approx. 350 g) were shipped on 4 or 5 April, 2016 to each participant in thermo-insulated polystyrene boxes with dry ice. The packages for laboratories in coutries where according to IATA Dangerous Goods Regulations shipments with dry ice were not allowed contained instead of dry ice cooling elements.

Three days prior to the shipment, a short instruction sheet on handling the sample, important information on the presence of ***pymetrozine***, ***chlorate*** and ***perchlorate*** in the blank material as well as internal standards suitable for their analysis was sent to the participant by e-mail.

Due to the unexpected problems with the shipment described in **Sec. 1.4**, laboratories were asked to check the integrity and condition of the PT-materials upon receipt in any case and to report to the organisers via the website or e-mail any observations or complaints and whether the PT-materials are accepted. Detailed instructions on how to treat the test item and blank material upon receipt were provided to the participating laboratories in the Specific Protocol (**Appendix 10**) that was dispatched three weeks prior to the shipment date.

1.9.5 Submission of Results and Additional Information

An online submission tool allowed participants to submit their results via the Internet. Using their individual login data, all participants had access to the Result-Submission-Website from a week after the sample shipment until the result submission deadline (20 May, 2016). Participants were asked not only to report their analytical results but also to state whether the compounds on the Target Pesticides List were part of their routine scope and to indicate their experience with the analysis of these compounds. In addition, laboratories had to provide details about the methods applied and to state their own reporting limits (RLs) for each target compound they had analysed.

Three weeks prior to the deadline of results submission, a reminder was sent to the participants together with mathelogical information on analysis of dithianon, pymetrozine and BNPU/Nicarbazine.

1.9.6 Actions Following Results Submission and Distribution of Preliminary Report

Where information on analytical methods or results was inconsistent, laboratories were contacted. Laboratories that originally registered to participate in the current PT but finally did not submitted any results were asked to state the reason. On 2 Jue, 2016, the preliminary report on the EUPT-SRM11 with the preliminary assigned values was released and sent to the participants. Laboratories having submitted false positive or negative results were also contacted and asked to provide information on the methods used for analysing those compounds. Laboratories were also asked to investigate the reasons for results with | z-score | > 2 and to report them. Since ***pymetrozine***, ***chlorate*** and ***perchlorate*** were present in the blank material, laboratories were further asked to provide details on the calibration approach followed for these three analytes, e.g., to name the types of blank commodities used to prepare matrix-based calibration standards. Since propineb was applied as dithiocarbamate in the test material, and results from several experiments indicated that the release of CS_2 from propineb requires more harsh conditions than from thiram, usually used in recovery checks, and in order to evaluate the PT-results correctly, detailed information on performing analysis of dithiocarbamates were also requested from the participants at a later stage.

2. EVALUATION RULES

2.1 False Positives and Negatives

2.1.1 False Positives (FPs)

Any reported result with a concentration at or above the Minimum Required Reporting Level (MRRL) of an analyte in the Target Pesticides List which was (a) not detected by the organiser, even following repetitive analysis, and/or (b) not detected by the overwhelming majority (e.g. > 95 %) of the participants that tested for this compound, is treated as a false positive result. Results of an analyte absent in the test item but with a value lower than the MRRL are excluded by the organiser and not considered as false positives. No z-scores are calculated for false positive results.

2.1.2 False Negatives (FNs)

These are results of target analytes reported as "analysed" but without reporting numerical values, although they were used by the organiser to prepare the test item and were detected, at or above the MRRL, by the organiser and the overwhelming majority of the participating laboratories. In accordance with the General Protocol z-scores for false negatives are calculated using the MRRL as the result, or using the lab's reporting-limits (RLs), whichever is lower. Any RLs that are higher than the MRRL are not taken into account. Following the General Protocol, results reported as "< RL" without providing a numerical value are also judged as false negatives if the RL exceeds the MRRL.

2.2 Establishment of the Assigned Values (x_{pt}) and Calculation of the Respective Uncertainties ($u(x_{pt})$)

In accordance with EUPT-General Protocol (**Appendix 8**) the assigned values x_{pt} of each pesticide in the PT is established using the mean value of robust statistics using Algorithms A (x^*) [6] of all reported results from EU and EFTA countries. Results associated with obvious mistakes and gross errors may be excluded from the population for the establishment of the assigned values. The add-in "RobStat" provided by Royal Society of Chemistry was used to calculate the assigned values with the convergence criterion = 10^{-6}.

The uncertainty of the assigned values of each analyte is calculated according to ISO 13528:2015 [6] using the following equation:

$$u(x_{pt}) = 1.25 \times [(s^*)/\sqrt{p}\,]$$

Where $u(x_{pt})$ is the uncertainty of the assigned value in mg/kg, s^* is the robust standard deviation estimate in mg/kg and p is the number of datapoints considered (= the number of results used to calculate the assigned value).

The tolerance for the uncertainty of the assigned value of each pesticide is calculated as $0.3 \times FFP\text{-}\sigma_{pt}$, where $FFP\text{-}\sigma_{pt}$ is the target standard deviation of the assigned value derived using a fixed standard deviation of 25 % (see **Section 2.3**). If $u(x_{pt}) < 0.3 \times FFP\text{-}\sigma_{pt}$, is met, then the uncertainty of the assigned value is considered to be negligible and not needed to be considered in the interpretation of the proficiency test results.

2.3 Fixed Target Standard Deviation using FFP-Approach ($FFP\text{-}\sigma_{pt}$)

Based on experience from previous EU Proficiency Tests on fruit and vegetables and cereals, the EUPT-Scientific Committee agreed to apply a fixed fit-for-purpose relative standard deviation (FFP-RSD) of 25 % for calculating the z-scores. The fixed target standard deviation using the fit-for-purpose approach ($FFP\text{-}\sigma_{pt}$), for each individual target analyte is calculated by multiplying the assigned value by the FFP-RSD of 25 %. In addition, the robust relative standard deviation of the assigned value (CV^*) is calculated for informative purposes.

2.4 z-Scores

For each combination of laboratory and target analyte a z-score is calculated according to the following equation:

$$z_i = (x_i - x_{pt}) \,/\, FFP\text{-}\sigma_{pt}$$

Where

- x_i is the result for the target analyte (i) as reported by the participant
  (For results considred as false negatives, x_i is set as equal to the respective minimum required reporting level (MRRL) or the laboratory reporting level (RL), if RL < MRRL.)
- x_{pt} is the assigned value for the target analyte (i)
- $FFP\text{-}\sigma_{pt}$ is the standard deviation for proficiency assessment using the fit-for-purpose approach (see above).

  Any z-scores > 5 are set at 5 in calculations of combined z-scores (see **2.5.2**).

The z-scores are classified as follows:

$\lvert z\rvert \leq 2$	acceptable
$2 < \lvert z\rvert < 3$	questionable
$\lvert z\rvert \geq 3$	unacceptable

For results considered to be false negatives, z-scores are calculated using the MRRL or the RL, if RL < MRRL. No z-scores are allocated to false positive results.

2.5 Laboratory Classification

2.5.1 Category A and B classification

Based on the scope of target analytes covered by the laboratories in this exercise, laboratories are subdivided into Categories (A and B) in accordance with the rules in the General Protocol (**Appendix 9**). To be classified into Category A a laboratory should

a) have analysed at least 90 % of the compulsory pesticides on the Target Pesticides List,
b) have correctly reported concentration values for at least 90 % of the compulsory pesticides present in the test item,
c) not have reported any false positive results.

2.5.2 Combined z-Scores

For informative purposes and to allow comparison of the overall performance of the laboratories the Average of the Absolute z-Scores (AAZ) is calculated for laboratories with 5 or more z-scores. **Combined z-scores are, however, considered to be of lesser importance than the individual z-scores**.

Average of the Absolute z-Scores (AAZ)

The AAZ is calculated using the following formula:

$$AAZ = \frac{\sum_{i=1}^{n} |z_i|}{n}$$

where "n" is the number of each laboratory's z-scores that are considered in this formula. This includes z-scores assigned for false negative results.
For the calculation, any z-score > 5 is set at 5.

3. PARTICIPATION

126 laboratories from 31 countries (28 EU-Member States, 1 EFTA-country, 1 EU-candidate country and 1 third country) registered for participation in the EUPT-SRM11. Out of those laboratories 122 submitted at least one result; those were 119 laboratories from EU-Member States, 1 laboratory each from an EFTA-country, an EU-candidate country and a third country. An overview of the participating laboratories and countries is given in **Table 3-1**.

A list of all individual laboratories that registered for this EUPT is presented in **Appendix 1**. Croatia and Romania were the only EU-countries not represented by an NRL-SRM. Croatia had not yet designated an NRL-SRM, whereas the Romanian NRL-SRM indicated that the commodity as well as the target pesticides were out of its analytical scope. Malta was represented by its proxy-NRL-SRM based in the United Kingdom.

All 3 laboratories from non-EU countries submitted results. The results submitted by the laboratories based in third and EU-candidate countries were not taken into account when calculating the assigned values.

Based on the commodities analysed routinelly in the laboratories, a tentative list of labs obliged to participate in the current PT was distributed to the labs of the network prior to the registration period for this EUPT. The list included all NRL-SRMs, regardless of their commodity scope, and all EU-OfLs analysing for pesticide residues in food and vegetables.

All laboratories tentatively considered as obliged to participate had to either participate or to provide an explanation for their non-participation. After excluding those laboratoreis originally considered as obliged to participate but having submitting sufficient explanation for their non-obligation, there were finally 124 laboratories obliged to participate in the current PT, among them 21 (17 %) did not participate. Among the 103 laboratories having registered for participation, three were finally not able to report any result and were asked to provide explanations. One of those not participating laboratories reported problems with the analytical instruments and the other one personnel shortage as a reason for not being able to report any results.

Table 3-2 gives an overview of the participation and non-participation of EU-labs obliged to take part in the EUPT-SRM11.

Table 3-1: Number of laboratories listed as being obliged to participate in the EUPT-SRM11, labs that registered to participate, and labs that finally submitted results (grouped by contracting country)

EU: NRLs and OfLs										
Contracting Country [1)]	Labs originally considered as obliged (*based on scope)	Labs providing sufficient expl. for non-participation		Finally considered as obliged	Registered for Participation		Submitted Results		Obliged labs non particip. w/o giving expl.	Notes
		Prior to PT	During the PT		All	NRL-SRMs	All	NRL-SRMs		
AT	3	0	0	3	3	1	3	1	0	
BE	8	1	0	7	7	1	6	1	0	
BE/NL/FR	1	0	0	1	1	0	1	0	0	
BG	3	0	0	3	1	1	1	1	2	
HR	5	1	0	4	2 + [1]	0	2 + [1]	0	1	HR has not yet established an NRLSRM.
CY	1	0	0	1	1	1	1	1	0	
CZ	4	0	0	4	3	1	3	1	1	
DK	2	0	0	2	2	1	2	1	0	
EE	2	0	0	2	2	1	2	1	0	
FI	2	0	0	2	2	2	2	2	0	FI has appointed two NRL-SRMs with different responsibilities.
FR	8	0	0	8	8	1	8	1	0	
DE	20	1	0	19	15 + [5]	1	15 + [5]	1	3	
DE/MT	1	0	0	1	1	0	1			
GR	4	0	0	4	4 + [1]	2	4 + [1]	2	0	GR has appointed two NRL-SRMs.
HU	4	0	0	4	4	1	4	1	0	
IE	1	0	0	1	1	1	1	1	0	
IT	14	[1]	0	14	11 + [2]	1	10 + [1]	1	4	
LV	1	0	0	1	1	1	1	1	0	
LT	1	0	0	1	1 + [1]	1	1 + [1]	1	0	
LU	1	0	0	1	1	1	1	1	0	
MT	0*	0*	0	0*	0*	0*	0*	0*	0*	*MT-NRL-SRM represented by proxy by the UK-NRL-SRM; MT subcontracted routine analysis to an OfLs in DE and ES
NL	1	0	0	1	1	1	1	1	0	
PL	6	0	0	6	2 + [6]	1	2 + [6]	1	4	Various labs in PL are involved in preharvest controls
PT	2	0	0	2	2 + [1]	1	2 + [1]	1	0	
RO	1	0	0	1	1 + [1]	1	1 + [1]	1	0	
SK	3	0	0	3	3	1	1	1	2	
SI	2	0	0	2	2	1	3	1	0	
ES	20	0	0	20	15 + [1]	2	15 + [1]	2	5	ES has appointed two NRL-SRMs
ES/MT	1	0	0	1	1	2	1	2	0	
SE	1	0	0	1	1	1	2	1	0	
UK/MT	3	1	0	2	2	1	1	1	1	UK-NRL-SRM represents also MT
UK	2	0	0	2	2 + [1]	0	2 + [1]		0	
EU-total	**127**	**4+[1]**	**0**	**124**	**103 + [20]**	**29**	**100 + [19]**	**29**	**22**	

Table 3-1 (cont.): Number of laboratories listed as being obliged to participate in the EUPT-SRM11, labs that registered to participate, and labs that finally submitted results (grouped by contracting country)

EFTA										
Contracting Country [1)]	Labs originally considered as obliged (*based on scope)	Labs providing sufficient expl. for non-participation		Finally considered as obliged	Registered for Participation		Submitted Results		Obliged labs non particip. w/o giving expl.	Notes
		Prior to PT	During the PT		All	NRL-SRMs	All	NRL-SRMs		
NO					[1]	1	[1]	1		
EU+EFTA Total					103 + [21]	30	100 + [20]	30		
Third Countries / EU candidate country										
SR					1	–	1	–		
EG					1	–	1	–		
Third Countries / EU candidate country Total					2		2			
Overall Sum				124	126	30	122	30		

4. RESULTS

4.1 Overview of Results

An overview of the percentage of laboratories having targeted the analytes on the Target Pesticides List is shown in **Table 4-1**. The table also shows the percentage among the OfLs from EU and EFTA countries that have registered to the PT as well as the percentage among the laboratories that were finally considered to be obliged to participate in this PT that have finally targeted the analytes.

Table 4-2 (p. 22) gives an overview of all results submitted by each laboratory. The individual numerical results reported by the laboratories are shown in **Table 4-7 (p. 39)** and **Table 4-18 (p. 71)**.

Table 4-1: Percentage of EU and EFTA laboratories that have analysed for the compounds in the Target Pesticides List

Compounds		Present in test item	Labs analysed for the compound			
			Participating EU [1]- and EFTA-Labs		Obliged Labs	
			No. [2]	% (based on *n* = 120 [3])	No. [2]	% (based on *n* = 124 [4])
Compulsory Compounds	**2,4-D**	no	93	78 %	81	65 %
	Cyromazine	**yes**	88	73 %	78	63 %
	Dithiocarbamates	**yes**	95	79 %	79	64 %
	Dodine	**yes**	83	69 %	73	59 %
	Ethephon	no	72	60 %	64	52 %
	Fluazifop	no	86	72 %	75	60 %
	Glyphosate	no	71	59 %	61	49 %
	Haloxyfop	no	90	75 %	79	64 %
	TFNA	**yes**	63	53 %	55	44 %
	TFNG	**yes**	63	53 %	55	44 %
	Tolylfluanid	**yes**	87	73 %	77	62 %
Optional Compounds	**BAC-C10**	no	56	47 %	50	40 %
	BAC-C12	no	59	49 %	52	42 %
	BAC-C14	**yes**	58	48 %	51	41 %
	BAC-C16	no	57	48 %	51	41 %
	BAC-C18	no	32	27 %	27	22 %
	Chlorate	**yes**	46	38 %	39	31 %
	DDAC-C10	no	56	47 %	49	40 %
	Dithianon	**yes**	39	33 %	31	25 %
	Fosetyl	no	47	39 %	40	32 %
	Phosphonic acid	**yes**	40	33 %	33	27 %
	MCPA	no	85	71 %	74	60 %
	MCPB	no	61	51 %	53	43 %
	Perchlorate	**yes**	45	38 %	38	31 %
	Pymetrozine	**yes**	62	52 %	54	44 %
	Quizalofop	**yes**	58	48 %	48	39 %
	Triclopyr	**yes**	63	53 %	53	43 %

1) Including official laboratories participating on voluntary basis
2) Laboratories representing more than one country were counted only once.
3) 120 is the number of participating OfLs from EU and EFTA countries (including OfLs participating on voluntary basis) having registered for the present PT and having submitted at least one result.
4) 124 is the number of OfLs (including NRLs) from EU countries, which were finally considered as obliged to participate in the EUPT-SRM11 (taking into account any explanations for non-participation).

Table 4-2: Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

Compulsory Compounds														
Compulsory Compound listed in Target List			2,4-D	Cyromazine	Dithiocarbamates	Dodine	Ethephon	Fluazifop	Glyphosate	Haloxyfop	TFNA	TFNG	Tolylfluanid	Analysed / correctly found among COMPULSORY compounds within the EUPT-Target Pesticides List (max. 11 / 6)
within MACP [1]			Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	
present in Test Item			No	**Yes**	**Yes**	**Yes**	No	No	No	No	**Yes**	**Yes**	**Yes**	
evaluated in this PT			No	**Yes**	**Yes**	**Yes**	No	No	No	No	**Yes**	**Yes**	No	
Lab-Code SRM11-	NRL-SRM	Cat. [2]												
1		B	ND		V	V							V	4 / 3
2	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
3		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
4		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
5		B	ND	V	V	V	ND		ND	ND	V	V		9 / 5
6		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
7	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
8		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
9	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
11		B	ND	V	V	V		ND		ND	V	V	V	9 / 6
12	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
13	x	A	ND	V		V	ND	ND	ND	ND	V	V	V	10 / 5
14		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
15		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
16	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
17		B	ND	V	V									3 / 2
18		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
19	x	B	ND		V			ND		ND			**FN**	5 / 1
20		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
21		B	ND	V	V	V		ND	ND	ND				7 / 3
22		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
23	x	B	ND	V	V	V		ND		ND	V		V	8 / 5
24		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
25		B	ND	V	V	V		ND		ND				6 / 3
26	x	B		V	V								V	3 / 3
27		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have analysed at least 9 out of the 11 compulsory compounds on the Target Pesticides List, correctly detected 5 or more out of the 6 compulsory compounds present in the test item and have not reported any false positive result, see section **Section 4.4.4, p. 52**)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **Empty cells**: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "=< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

	Optional Compounds																	Total	
Optional Compound listed in Target List		BAC-C10	BAC-C12	BAC-C14	BAC-C16	BAC-C18	Chlorate	DDAC-C10	Dithianon	Fosetyl	Phosphonic acid	MCPA	MCPB	Perchlorate	Pymetrozine	Quizalofop	Triclopyr	Analysed / correctly found among OPTIONAL compounds within the EUPT-Target Pesticides List (max. 16/ 8)	analysed / correctly found among all compounds within the EUPT-Target Pesticides List (max. 27 / 14)
within MACP [1]		WD	WD	WD	WD	WD	WD	WD	Reg.	WD	WD	WD	WD	–	Reg.	WD	WD		
present in Test Item		No	No	**Yes**	No	No	**Yes**	No	**Yes**	No	**Yes**	No	No	**Yes**	**Yes**	**Yes**	**Yes**		
evaluated in this PT		No	No	**Yes**	No	No	**Yes**	No	No	No	**Yes**	No	No	**Yes**	**Yes**	**Yes**	**Yes**		
Lab-Code SRM11-	NRL-SRM																		
1		ND	ND	V	ND	ND		ND				ND						7 / 1	11 / 4
2	x	ND	ND	V	ND	ND		ND	V			ND	ND			V	V	11 / 4	22 / 10
3		ND	ND	V	ND		V	ND		ND	V	ND	ND	V		V	V	13 / 6	24 / 12
4		ND	ND	V	ND		V	ND	V	ND	V	ND		V	V	**FN**	V	14 / 7	25 / 13
5		ND	ND	V	ND		V	ND		ND	**FN**	ND		V	V			11 / 4	20 / 9
6		ND	ND	V	ND		V	ND	V	ND	V	ND	ND	V	V	V	V	15 / 8	26 / 14
7	x	ND	ND	V	ND	ND	V	ND	**FN**	ND	V	ND	ND	V	V	V	V	16 / 7	27 / 13
8		ND	ND	V	ND	ND	V	ND	V			ND	ND	V	V	V	V	14 / 7	25 / 13
9	x	ND	ND	V	ND		V	ND				ND	ND	V		V	V	11 / 5	22 / 11
11		ND	ND	V	ND			ND	V			ND	ND		V	V	V	11 / 5	20 / 11
12	x	ND	ND	V	ND		V	ND	V	ND	V	ND	ND	V	V	V	V	15 / 8	26 / 14
13	x	ND	ND		ND	ND		ND		ND		ND	ND					8 / 0	18 / 5
14									V			ND	ND		V	**FN**	**FN**	6 / 2	17 / 8
15		ND	ND	V	ND	ND	V	ND		ND	V	ND	ND	V	V	V	V	15 / 7	26 / 13
16	x											ND	ND		V	V		4 / 2	15 / 8
17												ND			V			2 / 1	5 / 3
18		ND	ND	V	ND	ND	**FN**	ND		ND	V	ND	ND	**FN**	V	V	V	15 / 5	26 / 11
19	x																	0 / 0	5 / 1
20							V			ND	V	ND	ND	V	V	V		8 / 5	19 / 11
21		ND	ND	V	ND			ND				ND	ND				V	8 / 2	15 / 5
22									V	ND		ND	ND			V	V	6 / 3	17 / 9
23	x	ND	ND	V	ND			ND	V			ND				V	V	9 / 4	17 / 9
24		ND	ND	V	ND	ND	V	ND	V	ND	V	ND	ND	V	V	V	V	16 / 8	27 / 14
25															V			1 / 1	7 / 4
26	x		ND	V	ND		V	ND						V				6 / 3	9 / 6
27							V			ND	V	ND		V				5 / 3	16 / 9

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have analysed at least 9 out of the 11 compulsory compounds on the Target Pesticides List, correctly detected 5 or more out of the 6 compulsory compounds present in the test item and have not reported any false positive result, see **Section 4.4.4, p. 52**)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **Empty cells**: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

			Compulsory Compounds											
Compulsory Compound listed in Target List			2,4-D	Cyromazine	Dithiocarbamates	Dodine	Ethephon	Fluazifop	Glyphosate	Haloxyfop	TFNA	TFNG	Tolylfluanid	Analysed / correctly found among COMPULSORY compounds within the EUPT-Target Pesticides List (max. 11 / 6)
within MACP [1]			Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	
present in Test Item			No	**Yes**	**Yes**	**Yes**	No	No	No	No	**Yes**	**Yes**	**Yes**	
evaluated in this PT			No	**Yes**	**Yes**	**Yes**	No	No	No	No	**Yes**	**Yes**	No	
Lab-Code SRM11-	NRL-SRM	Cat. [2]												
28		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
29		A	ND	V	V	V	ND	ND	(FP)	ND	V	V	V	11 / 6
30	x	B	ND		V			ND		ND			V	5 / 2
31		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
32		A	ND	V	V	V	ND	ND		ND	V	V	V	10 / 6
33	x	B	ND	V	V		ND	ND	ND	ND		V	V	9 / 4
34		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
35	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	**FN**	11 / 5
36		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
37		B	ND	V		V		ND		ND			V	6 / 3
38		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
39	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
40		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
41		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
42		B	ND	V	V	V	ND	ND	ND	ND			V	9 / 4
43		B		**FN**			ND			ND				3 / 0
45		B	ND						ND					2 / 0
46		B			V									1 / 1
47		B			V									1 / 1
48		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
49		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
50	x	B	ND	V		V		ND		ND	V	V	V	8 / 5
51		B			V									1 / 1
52	x	B	ND		V			ND		ND			V	5 / 2
53		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have analysed at least 9 out of the 11 compulsory compounds on the Target Pesticides List, correctly detected 5 or more out of the 6 compulsory compounds present in the test item and have not reported any false positive result, see section **Section 4.4.4, p. 52**)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **Empty cells**: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

[#] Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "=< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

		Optional Compounds																Total
Optional Compound listed in Target List		BAC-C10	BAC-C12	BAC-C14	BAC-C16	BAC-C18	Chlorate	DDAC-C10	Dithianon	Fosetyl	Phosphonic acid	MCPA	MCPB	Perchlorate	Pymetrozine	Quizalofop	Triclopyr	Analysed / correctly found among OPTIONAL compounds within the EUPT-Target Pesticides List (max. 16/ 8)	analysed / correctly found among all compounds within the EUPT-Target Pesticides List (max. 27 / 14)
within MACP [1]		WD	WD	WD	WD	WD	WD	WD	Reg.	WD	WD	WD	WD	–	Reg.	WD	WD		
present in Test Item		No	No	**Yes**	No	No	**Yes**	No	**Yes**	No	**Yes**	No	No	**Yes**	**Yes**	**Yes**	**Yes**		
evaluated in this PT		No	No	**Yes**	No	No	**Yes**	No	No	No	**Yes**	No	No	**Yes**	**Yes**	**Yes**	**Yes**		
Lab-Code SRM11-	NRL-SRM																		
28		ND	ND	V	ND	ND	V	ND	V	ND	V	ND	ND	V	V	V	V	16 / 8	27 / 14
29		ND	ND	V	ND	ND	V	ND	V	ND	V	ND	ND	V	V	V	V	16 / 8	27 / 14
30	x																	0 / 0	5 / 2
31							V		V		V	ND		V	V		V	7 / 6	18 / 12
32		ND	ND	V	ND	ND	V	ND	V	ND	V	ND	ND	V	V	**FN**	V	16 / 7	26 / 13
33	x											ND			V			2 / 1	11 / 5
34		ND	ND	V	ND	ND	V	ND		ND		ND	ND				V	11 / 3	22 / 9
35	x											ND						1 / 0	12 / 5
36		ND	ND	V	ND		V	ND		ND	V	ND	ND	V	V	V	V	14 / 7	25 / 13
37		ND	ND	V	ND	ND						ND	ND				V	8 / 2	14 / 5
38		ND	ND	V	ND	ND	V	ND	V	ND	V	ND	ND	V	V	V	V	16 / 8	27 / 14
39	x	ND	ND	V	ND	ND		ND		ND		ND	ND		V		V	11 / 3	22 / 9
40		ND	ND	V	ND	ND		ND		ND	V	ND	ND		V	V	V	13 / 5	24 / 11
41												ND	ND				V	3 / 1	14 / 7
42		ND	ND	V	ND		V	ND	V	ND	V	ND		V	V	V		13 / 7	22 / 11
43							V			ND	**FN**						V	4 / 2	7 / 2
45										ND		ND		V				3 / 1	5 / 1
46																		0 / 0	1 / 1
47																		0 / 0	1 / 1
48							V		V	ND	V	ND	ND	V	V	V	V	10 / 7	21 / 13
49		ND	ND	V	ND	ND	**FN**	ND		ND	V	ND	ND	**FN**	**FN**		V	14 / 3	25 / 9
50	x	ND	ND	V	ND			ND				ND	ND		V		V	9 / 3	17 / 8
51																		0 / 0	1 / 1
52	x											ND						1 / 0	6 / 2
53		ND	(FP)	V	(FP)	ND		(FP)	V			ND	ND		V	V	V	12 / 5	23 / 11

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have analysed at least 9 out of the 11 compulsory compounds on the Target Pesticides List, correctly detected 5 or more out of the 6 compulsory compounds present in the test item and have not reported any false positive result, see **Section 4.4.4, p. 52**)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **Empty cells**: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

Compulsory Compounds														
Compulsory Compound listed in Target List			2,4-D	Cyromazine	Dithiocarbamates	Dodine	Ethephon	Fluazifop	Glyphosate	Haloxyfop	TFNA	TFNG	Tolylfluanid	Analysed / correctly found among COMPULSORY compounds within the EUPT-Target Pesticides List (max. 11 / 6)
within MACP [1]			Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	
present in Test Item			No	**Yes**	**Yes**	**Yes**	No	No	No	No	**Yes**	**Yes**	**Yes**	
evaluated in this PT			No	**Yes**	**Yes**	**Yes**	No	No	No	No	**Yes**	**Yes**	No	
Lab-Code SRM11-	NRL-SRM	Cat. [2]												
54		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
55		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
56		A	ND	V	V	V	ND	ND	ND	ND	V	V		10 / 5
57		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
58		B	ND	V	V	V	ND	ND		ND	V		V	9 / 5
59		B			V									1 / 1
60		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
61		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
62	x	B	ND	V				ND		ND			V	5 / 2
63		B	ND	V		V	ND	ND	ND	ND			V	8 / 3
64		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
65		B			V									1 / 1
66	x	B	ND	V				ND		ND			V	5 / 2
67		A	ND		V	V	ND	ND	ND	ND	V	V	V	10 / 5
68	x	A	ND	V		V	ND	ND	ND	ND	V	V	V	10 / 5
69		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
70		B	ND			V				ND			**FN**	4 / 1
71		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
72		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
73		B	ND	V					ND	ND			V	5 / 2
74		B	ND	V				ND					V	4 / 2
75		B	ND	V	V	V	ND	ND	ND	ND			V	9 / 4
76	x	B	ND	V	V	V	ND	ND	ND	ND			V	9 / 4
77		B			**FN**									1 / 0
78	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
79	x	A	ND	V	V	V	ND	ND	ND	ND		V	V	10 / 5

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have analysed at least 9 out of the 11 compulsory compounds on the Target Pesticides List, correctly detected 5 or more out of the 6 compulsory compounds present in the test item and have not reported any false positive result, see section **Section 4.4.4, p. 52**)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **Empty cells**: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

[#] Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "=< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

	Optional Compounds																	Total	
	Optional Compound listed in Target List		BAC-C10	BAC-C12	BAC-C14	BAC-C16	BAC-C18	Chlorate	DDAC-C10	Dithianon	Fosetyl	Phosphonic acid	MCPA	MCPB	Perchlorate	Pymetrozine	Quizalofop	Triclopyr	Analysed / correctly found among OPTIONAL compounds within the EUPT-Target Pesticides List (max. 16/ 8)	analysed / correctly found among all compounds within the EUPT-Target Pesticides List (max. 27 / 14)
	within MACP [1]		WD	WD	WD	WD	WD	WD	WD	Reg.	WD	WD	WD	WD	–	Reg.	WD	WD		
	present in Test Item		No	No	**Yes**	No	No	**Yes**	No	**Yes**	No	**Yes**	No	No	**Yes**	**Yes**	**Yes**	**Yes**		
	evaluated in this PT		No	No	**Yes**	No	No	**Yes**	No	No	No	**Yes**	No	No	**Yes**	**Yes**	**Yes**	**Yes**		
	Lab-Code SRM11-	NRL-SRM																		
	54		ND	ND	V	ND	ND	V	ND	V	ND	V	ND	ND	V	V	V	V	16 / 8	27 / 14
	55		ND	ND	V	ND		V	ND		ND	V	ND	ND	V	V		V	13 / 6	24 / 12
	56										ND		ND			V		V	4 / 2	14 / 7
	57		ND	ND	V	ND	ND	V	ND	V	ND	V	ND	ND	V	V	V	V	16 / 8	27 / 14
	58		ND	ND	V	ND	ND		ND	V			ND	ND		V	V	V	12 / 5	21 / 10
	59																		0 / 0	1 / 1
	60												ND	ND		V	V	V	5 / 3	16 / 9
	61		ND	ND	V	ND	ND	V	ND	V	ND	V	ND		V	V	V	V	15 / 8	26 / 14
	62	x											ND			V			2 / 1	7 / 3
	63		ND	ND	V	ND	ND	V	ND				ND	ND	V	V	V		12 / 5	20 / 8
	64			ND	V			V	ND	V	ND	V	ND	ND	V	V	V	V	13 / 8	24 / 14
	65																		0 / 0	1 / 1
	66	x	ND	ND	V	ND			ND				ND						6 / 1	11 / 3
	67			ND	V				ND	V	ND	V	ND				V	V	9 / 5	19 / 10
	68	x						V			(FP)	V	ND	ND			V	V	7 / 4	17 / 9
	69							V			ND	V	ND	ND	V	V	V	V	9 / 6	20 / 12
	70												ND						1 / 0	5 / 1
	71		ND	ND	V	ND			ND		ND		ND	ND			V	V	10 / 3	21 / 9
	72									V			ND	ND		V	V	V	6 / 4	17 / 10
	73												ND				V		2 / 1	7 / 3
	74												ND			V			2 / 1	6 / 3
	75		ND	ND	V	ND			ND	V	ND	V	ND	ND			V	V	12 / 5	21 / 9
	76	x	ND	ND	V	ND			ND				ND	ND		V	V	V	10 / 4	19 / 8
	77																		0 / 0	1 / 0
	78	x	ND	ND	V	ND		V	ND		ND	V	ND	ND	V	V	V	V	14 / 7	25 / 13
	79	x						V		V	ND	V	ND	ND	V	V	V	V	10 / 7	20 / 12

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have analysed at least 9 out of the 11 compulsory compounds on the Target Pesticides List, correctly detected 5 or more out of the 6 compulsory compounds present in the test item and have not reported any false positive result, see **Section 4.4.4, p. 52**)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **Empty cells**: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

Compulsory Compounds														
Compulsory Compound listed in Target List			2,4-D	Cyromazine	Dithiocarbamates	Dodine	Ethephon	Fluazifop	Glyphosate	Haloxyfop	TFNA	TFNG	Tolylfluanid	Analysed / correctly found among COMPULSORY compounds within the EUPT-Target Pesticides List (max. 11 / 6)
within MACP [1]			Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	Reg.	
present in Test Item			No	**Yes**	**Yes**	**Yes**	No	No	No	No	**Yes**	**Yes**	**Yes**	
evaluated in this PT			No	**Yes**	**Yes**	**Yes**	No	No	No	No	**Yes**	**Yes**	No	
Lab-Code SRM11-	NRL-SRM	Cat. [2]												
80	x	B	ND	V			ND		ND					4 / 1
81		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
82		B	ND	V			ND	ND		ND			V	6 / 2
83		B	ND	**FN**	V	V	ND	ND	ND	ND			V	9 / 3
84		B			V	V		ND		ND				4 / 2
86	x	B		V	V	V							V	4 / 4
87		B			V				ND					2 / 1
88		B#	ND	V	V	V	**FP**	ND	(FP)	ND	V	V	V	11 / 6
89		B			V									1 / 1
90		B				V								1 / 1
91		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
92		B			V									1 / 1
93	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
94		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
95		B			V									1 / 1
96	x	B	ND	V	V	V		ND		ND			**FN**	7 / 3
97		B	ND	V	V								V	4 / 3
98		B	ND	V		V		ND		ND			V	6 / 3
100		B			V									1 / 1
101		B			V									1 / 1
102	x	B	ND		V		**FP**		ND					4 / 1
103		B			V									1 / 1
104		B							ND					1 / 0
105		B		V		V	ND			ND				4 / 2
106		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have analysed at least 9 out of the 11 compulsory compounds on the Target Pesticides List, correctly detected 5 or more out of the 6 compulsory compounds present in the test item and have not reported any false positive result, see section **Section 4.4.4, p. 52**)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **Empty cells**: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "=< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

	Optional Compounds																	Total	
Optional Compound listed in Target List		BAC-C10	BAC-C12	BAC-C14	BAC-C16	BAC-C18	Chlorate	DDAC-C10	Dithianon	Fosetyl	Phosphonic acid	MCPA	MCPB	Perchlorate	Pymetrozine	Quizalofop	Triclopyr	Analysed / correctly found among OPTIONAL compounds within the EUPT-Target Pesticides List (max. 16/ 8)	analysed / correctly found among all compounds within the EUPT-Target Pesticides List (max. 27 / 14)
within MACP [1]		WD	WD	WD	WD	WD	WD	WD	Reg.	WD	WD	WD	WD	–	Reg.	WD	WD		
present in Test Item		No	No	**Yes**	No	No	**Yes**	No	**Yes**	No	**Yes**	No	No	**Yes**	**Yes**	**Yes**	**Yes**		
evaluated in this PT		No	No	**Yes**	No	No	**Yes**	No	No	No	**Yes**	No	No	**Yes**	**Yes**	**Yes**	**Yes**		
Lab-Code SRM11-	NRL-SRM																		
80	x																	0 / 0	4 / 1
81									V			ND	ND		V	**FN**		5 / 2	16 / 8
82														V				1 / 1	7 / 3
83		ND	ND	V	ND	ND	V	ND				ND	ND	V	V		V	12 / 5	21 / 8
84																		0 / 0	4 / 2
86	x																	0 / 0	4 / 4
87																		0 / 0	2 / 1
88		ND	ND	V	ND	ND	V	ND	**FN**	ND	V	ND	ND	V	V	V	V	16 / 7	27 / 13
89																		0 / 0	1 / 1
90		ND	ND	V	ND			ND										5 / 1	6 / 2
91		ND	ND	V	ND	ND	V	ND		ND	V	ND	ND	V	V	**FN**	V	15 / 6	26 / 12
92																		0 / 0	1 / 1
93	x	ND	ND	V	ND		V	ND	V	ND		ND		V	V	V		12 / 6	23 / 12
94		ND	ND	V	ND							ND	ND			V	V	8 / 3	19 / 9
95																		0 / 0	1 / 1
96	x	ND	ND	V	ND				V			ND	ND		**FN**		V	9 / 3	16 / 6
97												ND			V			2 / 1	6 / 4
98									V			ND	ND		V	**FN**	V	6 / 3	12 / 6
100																		0 / 0	1 / 1
101																		0 / 0	1 / 1
102	x																	0 / 0	4 / 1
103																		0 / 0	1 / 1
104																		0 / 0	1 / 0
105																		0 / 0	4 / 2
106		ND	ND	V	ND	ND	V	ND	V	ND	V	ND	ND	V		V	V	15 / 7	26 / 13

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have analysed at least 9 out of the 11 compulsory compounds on the Target Pesticides List, correctly detected 5 or more out of the 6 compulsory compounds present in the test item and have not reported any false positive result, see **Section 4.4.4, p. 52**)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **Empty cells**: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

[#] Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

Compulsory Compounds														
Compulsory Compound listed in Target List			**2,4-D**	**Cyromazine**	**Dithiocarbamates**	**Dodine**	**Ethephon**	**Fluazifop**	**Glyphosate**	**Haloxyfop**	**TFNA**	**TFNG**	**Tolylfluanid**	**Analysed / correctly found among COMPULSORY compounds within the EUPT-Target Pesticides List (max. 11 / 6)**
within MACP [1)]			**Reg.**	**Reg.**	**Reg.**	**Reg.**	**Reg.**	**Reg.**	**Reg.**	**Reg.**	**Reg.**	**Reg.**	**Reg.**	
present in Test Item			No	**Yes**	**Yes**	**Yes**	No	No	No	No	**Yes**	**Yes**	**Yes**	
evaluated in this PT			No	**Yes**	**Yes**	**Yes**	No	No	No	No	**Yes**	**Yes**	No	
Lab-Code SRM11-	**NRL-SRM**	**Cat. [2)]**												
107		B	ND	V		V		ND		ND				5 / 2
108		B			V									1 / 1
109		B	ND					ND	ND	ND				4 / 0
110		B				V							V	2 / 2
111		A	ND	V		V	ND	ND	ND	ND	V	V	V	10 / 5
112		B			V									1 / 1
114		B	ND	V	V	V		ND		ND	**FN**	V	V	9 / 5
115	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
116		B			V			ND		ND			V	4 / 2
117		A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
118		B	ND	V		V	ND	ND		ND	V	V	V	9 / 5
119	x	A	ND	V	V	V	ND	ND	ND	ND	V	V	V	11 / 6
120		B	ND	V				ND		ND			V	5 / 2
121		B			V									1 / 1
122		B			V									1 / 1
123		B			V	V	ND							3 / 2
127	x	A	ND	V		V	ND	**ND**	ND	ND	V	V	V	10 / 5
128		A	ND	V	V	V	ND	**ND**	ND	ND	V	V	V	11 / 6
3rd-44		B	ND	V	V		ND		ND	ND			V	7 / 3
3rd-126		B	ND		V	V					V	V	V	6 / 5

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have analysed at least 9 out of the 11 compulsory compounds on the Target Pesticides List, correctly detected 5 or more out of the 6 compulsory compounds present in the test item and have not reported any false positive result, see section **Section 4.4.4, p. 52**)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **Empty cells**: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

[#] Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "=< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

	Optional Compounds																	Total	
	Optional Compound listed in Target List		BAC-C10	BAC-C12	BAC-C14	BAC-C16	BAC-C18	Chlorate	DDAC-C10	Dithianon	Fosetyl	Phosphonic acid	MCPA	MCPB	Perchlorate	Pymetrozine	Quizalofop	Triclopyr	Analysed / correctly found among OPTIONAL compounds within the EUPT-Target Pesticides List (max. 16/ 8)	analysed / correctly found among all compounds within the EUPT-Target Pesticides List (max. 27 / 14)
	within MACP [1]		WD	WD	WD	WD	WD	WD	WD	Reg.	WD	WD	WD	WD	–	Reg.	WD	WD		
	present in Test Item		No	No	**Yes**	No	No	**Yes**	No	**Yes**	No	**Yes**	No	No	**Yes**	**Yes**	**Yes**	**Yes**		
	evaluated in this PT		No	No	**Yes**	No	No	**Yes**	No	No	No	**Yes**	No	No	**Yes**	**Yes**	**Yes**	**Yes**		
	Lab-Code SRM11-	NRL-SRM																		
	107							**FN**		**FN**					V	V			4 / 2	9 / 4
	108																		0 / 0	1 / 1
	109												ND	ND			V	V	4 / 2	8 / 2
	110		ND	ND	V	ND			ND							V			6 / 2	8 / 4
	111							V			ND	V	ND	ND	V		V	V	8 / 5	18 / 10
	112																		0 / 0	1 / 1
	114		ND	ND	V	ND	ND	V	ND	V			ND	ND	V	V	V	V	14 / 7	23 / 12
	115	x	ND	ND	V	ND	ND	V	ND		ND	V	ND		V	V	V	V	14 / 7	25 / 13
	116															V			1 / 1	5 / 3
	117		ND	ND	V	ND	ND	V	ND	V	ND	V	ND	ND	V	V	V	V	16 / 8	27 / 14
	118												ND	ND				**FN**	3 / 0	12 / 5
	119	x	ND	ND	V	ND	ND		ND				ND	ND		V	V		10 / 3	21 / 9
	120																		0 / 0	5 / 2
	121																		0 / 0	1 / 1
	122																		0 / 0	1 / 1
	123		ND	ND	V	ND			ND	V									6 / 2	9 / 4
	127	x											ND			V	V		3 / 2	13 / 7
	128		ND	ND	V	ND	ND	V	ND	V	ND	V	ND	ND	V	V	V	V	16 / 8	27 / 14
	3rd-44		ND	ND	V	ND			ND	V									6 / 2	13 / 5
	3rd-126		ND	ND	V	ND			ND									V	6 / 2	12 / 7

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have analysed at least 9 out of the 11 compulsory compounds on the Target Pesticides List, correctly detected 5 or more out of the 6 compulsory compounds present in the test item and have not reported any false positive result, see **Section 4.4.4, p. 52**)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **Empty cells**: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

[#] Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

4.2 Analysis of Blank Material

As informed in an e-mail proior to the shipment of the test material, ***chlorate*** and ***perchlorate*** wer contained in the irrigation water, and ***pymetrozine*** had to be applied in the field to inhibit insect infestation. Therefore, these three optional compounds were contained in the blank material. Numerical results exceeding the respective MRRLs of ***chlorate*** (0.02 mg/kg), ***perchlorate*** (0.02 mg/kg), and ***pymetrozine*** (0.01 mg/kg) were reported by 32, 32 and 40 laboratories, respectively. These values were in the range between 0.338 and 4.2 mg/kg for ***chlorate***, between 0.076 and 0.608 mg/kg for ***perchlorate*** and between 0.07 and 1.58 mg/kg for ***pymetrozine*** and thus exceeding the MRRLs in all cases. Additional 2 laboratories reported "found the analytes, but not quantified" for each of these three compounds. Details are shown in **Table 4-3.** The robust mean and CV^* values for these three compounds were as follows: ***chlorate*** (2.03 mg/kg/44.6 %), ***perchlorate*** (0.260 mg/kg/35.9 %) and ***pymetrozine*** (0.432 mg/kg/42.3 %).

Detection of other analytes on the target pesticides list in the blank material was reported in very few cases (**Table 4-3)**. The presence of ***dithiocarbamates*** was reported three times below the MRRL of 0.03 mg/kg and three times above the MRRL. ***Glyphosate*** (MRRL = 0.03 mg/kg) in the blank material was detected by 6 laboratories, five of them with a concentration lower than the MRRL and the other one not quantified. ***Phosphonic acid*** (MRRL = 0.05 mg/kg) was detected by SRM11-115 at 0.092 mg/kg. Since the organisers and all other laboratories having analysed for these compounds did not detect them in the blank material, these findings were regarded as analytical errors.

4.3 Assigned Values and Target Standard Deviations

The assigned value (x_{pt}) of each analyte present in the test item was established as the mean of robust statistics (x^*) of all numerical results submitted by laboratories from EU and EFTA countries calculated using Algorithm A [6, **Appendix 8**]. Results from third country laboratories were not taken into account. Based on these assigned values, z-scores were calculated for all submitted results using the FFP-approach (please see **Section 4.4.3, p. 38)**, and a preliminary report was released on 2 June, 2016. The uncertainties ($u(x_{pt})$) of the assigned values were calculated as described under **Section 2.2 (p. 13)**.

The statistical uncertainty of the robust mean of ***dithianon*** clearly exceeded the tolerance, with the relative standard deviation based on robust statistics (CV^*) being as high as 94.3 % (**Table 4-4, p. 34**). The extremly wide distribution of the ***dithianon*** results was mainly attributed to the extensive degradation of this oxidation- and base-sensitive compound when the material was left to thaw as well as to its degradation during analysis if not extracted under acidic conditions (see **Table 4-13, p. 66**). The significant losses of ***dithianon*** observed in the storage and transport stability tests support this conclusion (**Section 1.7** and **1.8**, **p. 6 – 7**). The Scientific Committee therefore decided not to calculate an assigned value and z-scores for ***dithianon***.

In the case of ***tolylfluanid*** the very wide distribution of the results was also reflected by a high CV^* value of 57.4 %. This was mainly attributed to the degradation of this base-sensitive compound especially when the test item was left by participants to defrost prior to analysis or when the pH was not kept low during analysis. As many participants experienced severe losses of ***tolylfluanid***, this had a severe influence on the robust mean value of the entire population of results. In fact, the overall robust mean for ***tolylfluanid*** was very distant from the concentration detected by the laboratories avoiding the defrosting of the sample and taking care of keeping the pH low during the analysis (see **Table 4-13, p. 66**). In addition, the robust mean was also very distant from the concentration determined by the organizer in the homogeneity test (see **Appendix 3, p. A-6**), during which acidified QuEChERS combined with LC-MS/MS and correction vias ILIS was used. Due to the broad distribution of results the robust mean was marginally outside the tolerance

Table 4-3: Concentration of analytes in the blank material determined by the participating laboratories

Compound (MRRL)	reported by	Reporting Limit [mg/kg]	Conc. in Blank Material [mg/kg]
Dithiocarbamates (0.03 mg/kg)	SRM11-71	0.001	0.0021
	SRM11-24	0.005	0.006
	SRM11-100	0.02	0.010
	SRM11-34	0.02	0.033
	SRM11-112	0.05	0.090
	SRM11-101	0.15	0.180
Glyphosate (0.03 mg/kg)	SRM11-61	0.05	0.0099
	SRM11-38	0.01	0.012
	SRM11-3	0.01	0.013
	SRM11-24	0.01	0.014
	SRM11-29	0.01	< 0.03
	SRM11-63	0.03	not quantified
Chlorate (0.02 mg/kg) Robust Mean$_{(blank)}$: 2.40 mg/kg $CV^*_{(blank)} = 52$ %	SRM11-26	0.15	0.338
	SRM11-31	0.02	0.443
	SRM11-64	0.01	0.540
	SRM11-27	0.01	0.650
	SRM11-55	0.01	0.830
	SRM11-54	0.01	0.978
	SRM11-15	0.02	1.30
	SRM11-48	0.01	1.543
	SRM11-7	0.01	1.77
	SRM11-42	0.05	1.96
	SRM11-91	0.02	2.00
	SRM11-57	0.01	2.25
	SRM11-36	0.02	2.26
	SRM11-4	0.01	2.52
	SRM11-88	0.01	2.529
	SRM11-106	0.005	2.60
	SRM11-117	0.01	2.60
	SRM11-69	0.01	2.75
	SRM11-24	0.01	2.89
	SRM11-128	0.01	3.04
	SRM11-20	0.02	3.05
	SRM11-83	0.02	3.13
	SRM11-12	0.02	3.17
	SRM11-8	0.01	3.18
	SRM11-93	0.05	3.31
	SRM11-38	0.01	3.40
	SRM11-61	0.01	3.45
	SRM11-115	0.01	3.60
	SRM11-79	0.02	3.61
	SRM11-29	0.01	4.20
	SRM11-68	0.1	4.20
	SRM11-78	0.02	found
	SRM11-63	0.01	not quantified
Phosphonic acid (0.05 mg/kg)	SRM11-115	0.05	0.092
Perchlorate (0.02 mg/kg) Robust Mean$_{(blank)}$: 0.269 mg/kg $CV^*_{(blank)} = 29$ %	SRM11-26	0.01	0.076
	SRM11-64	0.01	0.100
	SRM11-8	0.01	0.177
	SRM11-42	0.02	0.180
	SRM11-15	0.02	0.200
	SRM11-45	0.01	0.214
	SRM11-88	0.01	0.217
	SRM11-69	0.01	0.220
	SRM11-117	0.01	0.220
	SRM11-7	0.01	0.221
	SRM11-36	0.02	0.222
	SRM11-12	0.02	0.229
	SRM11-57	0.01	0.235
	SRM11-115	0.01	0.245
Perchlorate (cont.) (0.02 mg/kg)	SRM11-91	0.02	0.250
	SRM11-20	0.02	0.268
	SRM11-38	0.01	0.280
	SRM11-61	0.01	0.281
	SRM11-79	0.05	0.282
	SRM11-24	0.01	0.284
	SRM11-93	0.05	0.296
	SRM11-55	0.01	0.320
	SRM11-48	0.01	0.324
	SRM11-54	0.01	0.325
	SRM11-29	0.01	0.330
	SRM11-107	0.1	0.330
	SRM11-27	0.01	0.345
	SRM11-4	0.01	0.383
	SRM11-31	0.02	0.442
	SRM11-128	0.02	0.480
	SRM11-83	0.02	0.608
	SRM11-78	0.02	found
	SRM11-63	0.01	not quantified
Pymetrozine (0.01 mg/kg) Robust Mean$_{(blank)}$: 0.716 mg/kg $CV^*_{(blank)} = 53$ %	SRM11-98	0.01	0.070
	SRM11-107	0.01	0.131
	SRM11-31	0.01	0.197
	SRM11-64	0.01	0.270
	SRM11-7	0.01	0.274
	SRM11-72	0.01	0.341
	SRM11-55	0.01	0.420
	SRM11-4	0.01	0.423
	SRM11-36	0.01	0.431
	SRM11-93	0.01	0.464
	SRM11-60	0.01	0.473
	SRM11-57	0.01	0.475
	SRM11-128	0.01	0.560
	SRM11-115	0.005	0.566
	SRM11-53	0.01	0.582
	SRM11-48	0.01	0.602
	SRM11-15	0.01	0.624
	SRM11-54	0.01	0.662
	SRM11-81	0.01	0.692
	SRM11-8	0.01	0.704
	SRM11-12	0.01	0.723
	SRM11-79	0.01	0.734
	SRM11-117	0.01	0.740
	SRM11-61	0.01	0.765
	SRM11-18	0.01	0.840
	SRM11-39	0.01	0.841
	SRM11-33	0.01	0.853
	SRM11-62	0.01	0.857
	SRM11-76	0.02	0.870
	SRM11-24	0.01	0.894
	SRM11-25	0.01	0.990
	SRM11-91	0.01	1.10
	SRM11-42	0.02	1.12
	SRM11-16	0.01	1.141
	SRM11-110	0.01	1.25
	SRM11-20	0.01	1.38
	SRM11-74	0.01	1.41
	SRM11-69	0.01	1.50
	SRM11-83	0.01	1.58
	SRM11-5	<0.01	< 0.01
	SRM11-78	0.01	found
	SRM11-63	0.01	not quantified

Table 4-4: Assigned values, uncertainties of assigned values and CV^* values calculated for all compounds present in the test item

	Calculations based on the Entire Population of Results from EU and EFTA Laboratories							
	Compound	No. of FNs	No. of numerical results (EU+EFTA)	Assigned Value (AV) [mg/kg]	$u(x_{pt})$ [1] [mg/kg]	$u(x_{pt})$ Tolerance [mg/kg]	Judgement for UAV-test	CV^* [2] [%]
Compulsory Compounds	Cyromazine	2	86	1.512	+/-0.0648	0.1134	passed	31.8
	Dithiocarbamates	1	94	1.297	+/-0.0579	0.0973	passed	34.6
	Dodine		83	1.243	+/-0.0447	0.0932	passed	26.2
	TFNA	1	62	0.756	+/-0.0240	0.0567	passed	20.0
	TFNG		63	0.448	+/-0.0146	0.0336	passed	20.7
	Tolylfluanid	4	83	0.598 [4]	+/-0.0471	0.0448	failed	57.4 [4]
	Average [3] CV^*							**26.7**
Optional Compounds	BAC-C14		58	0.285	+/-0.0121	0.0213	passed	25.8
	Chlorate	3	43	2.033	+/-0.1730	0.1525	failed	44.6
	Dithianon	3	36	1.729 [4]	+/-0.3397	0.1297	failed	94.3 [4]
	Phosphonic acid	2	38	9.831	+/-0.5884	0.7373	passed	29.5
	Perchlorate	2	43	0.260	+/-0.0178	0.0195	passed	35.9
	Pymetrozine	2	60	0.432	+/-0.0295	0.0324	passed	42.3
	Quizalofop	6	52	0.171	+/-0.0073	0.0128	passed	24.6
	Triclopyr	2	61	0.177	+/-0.0053	0.0133	passed	18.7
	Average [3] CV^* (without dithianon and chlorate)							**31.6 (29.5)**
	Alternative calculations based on Results Using ILIS [5]							
	Compound	**No. of FNs**	**No. of numerical results (EU+EFTA)**	**Alternative AV [mg/kg]**	**$u(x_{pt})$ [1] [mg/kg]**	**$u(x_{pt})$ Tolerance [mg/kg]**	**Judgement for UAV-test**	**CV^* [2] [%]**
	Cyromazine [5]		12	1.647	+/-0.1175	0.1235	passed	19.8
	Chlorate [5]		22	2.468	+/-0.1024	0.1851	passed	15.5
	Perchlorate [5]		23	0.234	+/-0.0143	0.0176	passed	23.5
	Pymetrozine [6]		21	0.532	+/-0.0382	0.0399	passed	26.3

1: $u(x_{pt})$: Uncertainty of assigned value based on robust estimate of participant mean, calculated as shown under **Section 2.2 (p. 30)**
2: CV^*: Relative standard deviation based on robust statistics
3: The average CV^* is given for information purpose only. CV^*s of individual compounds or average CV^*s of individual compounds or related compounds over many PTs are more meaningfull and conclusive.
4: Excluded from the calculation of the average CV^*s and the assigned values were calculated for informative purpose only.
5: For cyromazine, chlorate and perchlorate alternative assigned values were calculated based on results reported by the sub-population using ILISs.
6: For pymetrozine, alternative assigned values were calculated based on results of sub-population having used approached entailing correction of result for recovery.

in terms of statistical certainty. Considering these facts the Scientific Committee decided that z-scores of ***tolylfluanid*** should be calculated for informative purposes only. The ***tolylfluanid*** z-scores are furthermore disregarded when calculating the participants' overall performance (via AAZ).

Although the CV^*-value of ***dithiocarbamates*** (34.6 %) was higher than the FFP-RSD of 25 % the uncertainty of the assigned value passed the test (**Table 4-4**). The wide distribution of the results in this case was related to the use of propineb, which obviously needs more harsch conditions for the release of CS_2 compared to, e.g., thiram (**Section 4.5.9, p. 79**). In the case of ***chlorate*** the statistical uncertainty of the assigned value also did not pass the threshold due to the broad distriburion of the participants' results (CV^* = 44.6 %). Looking at the sub-population of results submitted by participants using chlorate-ILIS the distribution was much narrower (CV^* = 15.6 %) and the robust mean was slightly shifted (2.47 vs. 2.03). Based on these

facts, Scientific Committee decided that z-scores for ***chlorate*** should be calculated for information only and based on both the robust mean of the entire population (of EU and EFTA labs) as well as the robust mean of the sub-population using ILIS.

The compounds ***cyromazine*** (CV^* = 31.8 %) and ***perchlorate*** (CV^* = 35.9 %) also showed a relatively broad distribution of results, but still all passed the test for the uncertainty of the robust mean. The broad results distribution of these compounds was mainly attributed to the non-use of ILIS by a significant population of laboratories and in the case of ***perchlorate*** also due to the absence of a proper blank material. In the case of ***cyromazine*** errors were also due to an improper correction of results for recovery by several laboratories having employed the QuEChERS method (QuEChERS recovery rates typically range between 30 and 50 %). For these two compounds the Scientific Committee decided to normally evaluate the results using the robust mean of the entire population of EU and EFTA laboratories as assigned value and to additionally calculate, for information only, alternative z-scores based on the robust mean of the sub-population of laboratories having used ILIS in analysis. Considering only the sub-population of results submitted by labs using ILISs, the CV^*-values of these two compounds dropped impressively to 19.8 % for ***cyromazine*** and 23.5 % for ***perchlorate*** (**Table 4-4, p. 34** and **Section 4.5.4, p. 67**).

In the case of ***pymetrozine*** the wide distribution of results (CV^* = 42.3 %) was attributed to three main facors: a) the non-suitability of the blank material for calibration purposes (as it also contained pymetrozine); b) the high and pH-dependent polarity of the compound, causing low recovery rates with multiresiue methods if pH was not adjusted and biased results if not properly corrected for recovery; and c) the non-existence of an isotope labelled internal standard to correct for low recovery and matrix effects. The Scientific Committee decided to evaluate ***pymetrozine*** normally and to additionally evaluate alternative z-scores, for information only, using the results of the sub-population having corrected the results for recovery using internal standards added at the beginning of the sample preparation.

The CV^*-values of all other compulsory analytes were lower or slightly higher than 25 %. The average CV^* of compulsory analytes, based on the entire population excluding ***tolylfluanid***, was 26.7 %. The average CV^* of optional analytes based on the entire population of results excluding ***dithianon*** was 31.6 %. All these values exceed the FFP-RSD of 25 %. Considering the alternative assigned values based on only results obtained using ILISs for ***cyromazine***, ***chlorate***, ***perchlorate***, the average CV^* of compulsory (excluding tolylfluanid) was 24.3 %. In the case optional compounds the average CV^* excluding ***dithianon*** was 25.7 %. These average values are given for information only and are less conclusive compared to CV^*s of the individual or related compounds over one or many PTs.

4.4 Assessment of Laboratory Performance

4.4.1 False Positives

Two laboratories (SRM11-88 and 102) reported numerical results for *ethephon* at levels exceeding the MRRL. These results were judged as false positives. One laboratory (SRM11-88) reported a numerical result for *glyphosate* equal to the MRRL. This results was also judged as a false positive according to the rules in the General Protocol. *ethephon* and *glyphosate* were neither applied in the field, nor spiked to the sample material, nor detected by the organisers and the overwhelming majority of the participants (**Table 4-5, p. 36**). As these three results exceeded or were equal to the respective MRRLs in the Target Pesticides List and also exceeded the respective reporting limits (RLs) of the laboratories, they were therefore clearly judged as false positives.

Table 4-5: Overview of false positive and potentially false positive results reported by participating laboratories

Compound	PT-Code	Analysed	Reported Result [mg/kg]	RL [mg/kg]	MRRL [mg/kg]	Judgement
Ethephon	SRM11-88	Yes	0.131	0.01	0.02	FP
	SRM11-102	Yes	1.2	0.05	0.02	FP
Glyphosate	SRM11-29	Yes	< 0.03	0.01	0.03	–
	SRM11-88	Yes	0.03	0.01	0.03	FP
BAC-C12	SRM11-53	Yes	< 0.020	0.02	0.02	–
BAC-C16	SRM11-53	Yes	< 0.020	0.02	0.02	–
DDAC-C10	SRM11-53	Yes	< 0.020	0.02	0.01	–
Fosetyl	SRM11-68	Yes	0.01	0.01	0.02	–

In three cases laboratories reported < MRRL for *glyphosate*, *BAC-C12* and *BAC-C16*. One further laboratory (SRM11-68) reported a numerical result lower than the MRRL for *fosetyl*. Following the General Protocol these results were not judged as false positives.

4.4.2 False Negatives

Among the compulsory compounds there were 9 cases (2× ***cyromazine***, 2× ***dithiocarbamates***, 1× ***TFNA*** and 4× ***tolylfluanid***) where the participants reported "analysed, but not detected" for target compounds applied in the field and detected by the majority of the laboratories targeting them (**Table 4-6, p. 37**). All these results were reported by laboratories from EU and EFTA countries. As the assigned values for these four analytes were sufficiently distant from the MRRLs, these results were judged as false negatives. These 9 false negative results represented 1.8 % of the 479 results reported from EU/EFTA labs for compulsory target compounds present in the test item. Among EU/EFTA labs the FN-rate for COMPULSORY compounds was 0.6 % (4 out of 611 results).

Among the optional compounds there were 20 cases (6× ***quizalofop***, 4× ***phosphonic acid***, 3× ***chlorate***, 3× ***dithianon***, 2× ***pymetrozine*** and 2× ***triclorpyr***) where the participants reported "analysed, but not detected" for target compounds that were either applied in the field, contained in the irrigation water or spiked to the test item and detected by the majority of the laboratories targeting them (**Table 4-5**). All of them were reported by participants from EU and EFTA laboratories. These 20 false negative results accounted for 4.9 % of the 411 results reported by EU and EFTA laboratories for optional target compounds present in the test item.

Table 4-6: Overview of false negative results reported by participating laboratories (including 3rd country laboratories)

	Compound	MRRL [mg/kg]	Assigned Value [mg/kg]	Lab-Code	Analysed	Detected	RL [mg/kg]	Judgement
Compulsory Compounds	Cyromazine	0.01	1.512 [1)]	SRM11-83	Yes	No	0.01	False Negative
				SRM11-43	Yes	No	0.01	False Negative
	Dithiocarbamates	0.03	1.297	SRM11-55	Yes	No	0.03	False Negative
				SRM11-77	Yes	No	0.3	False Negative
	TFNA	0.01	0.756	SRM11-114	Yes	No	0.03	False Negative
	Tolylfluanid	0.01	0.598 [1)]	SRM11-19	Yes	No	0.01	False Negative
				SRM11-35	Yes	No	0.01	False Negative
				SRM11-70	Yes	No	0.01	False Negative
				SRM11-96	Yes	No	0.005	False Negative
Optional Compounds	Chlorate	0.02	2.033 [1)]	SRM11-18	Yes	No	0.01	False Negative
				SRM11-49	Yes	No	0.02	False Negative
				SRM11-107	Yes	No	0.1	False Negative
	Dithianon	0.01	*1.729* [2)]	SRM11-7	Yes	No	0.01	False Negative
				SRM11-88	Yes	No	0.01	False Negative
				SRM11-107	Yes	No	0.01	False Negative
	Phosphonic acid	0.05	9.831	SRM11-5	Yes	No	< 0.01	False Negative
				SRM11-43	Yes	No	0.01	False Negative
	Perchlorate	0.02	0.260 [1)]	SRM11-18	Yes	No	0.01	False Negative
				SRM11-49	Yes	No	0.02	False Negative
	Pymetrozine	0.01	0.432	SRM11-49	Yes	No	0.01	False Negative
				SRM11-96	Yes	No	0.005	False Negative
	Quizalofop	0.01	0.171	SRM11-4	Yes	No	0.01	False Negative
				SRM11-14	Yes	No	0.01	False Negative
				SRM11-32	Yes	No	0.01	False Negative
				SRM11-81	Yes	No	0.01	False Negative
				SRM11-91	Yes	No	0.01	False Negative
				SRM11-98	Yes	No	0.01	False Negative
	Triclopyr	0.01	0.177	SRM11-14	Yes	No	0.01	False Negative
				SRM11-118	Yes	No	0.01	False Negative

1: Robust mean derived from the entire population of results received by EU and EFTA laboratories. An alternative robust mean derived from results reported by a sub-population of labs was also calculated for information purposes (see **Section 4.3, p. 32**)
2: Robust mean derived from the entire population of results received by EU and EFTA laboratories (for information only)

4.4.3 Laboratory Performance Based on z-Scores

For all compounds except dithianon, individual z-scores were calculated using the FFP-RSD of 25 % and assigned values based on the entire population. For ***dithianon*** no z-scores were calculated due to the large uncertainty of the assigned value. For ***tolylfluanid*** z-scores based on the robust mean of the entire population of results reproted by EU/EFTA labs were calculated for information only. For ***chlorate***, ***tolylfluanid***, ***cyromazine***, ***perchlorate*** and ***pymetrozine*** alternative z-scores based on sub-populations of results were aditionally calculated.

Table 4-7 shows the overall classification of z-scores achieved by all laboratories for compulsory and optional compounds. The respective rules are shown in **Section 2.4 (p. 14)**. Looking only at the entire population of results submitted by laboratories from EU and EFTA countries, and excluding ***dithianon*** as well as ***tolylfluanid***, which was evaluated for information only, "acceptable" z-scores were achieved by 82 – 94 % (87 % on average) of the labs in the case of compulsory compounds and by 72 – 95 % (84 % on average) in the case of optional compounds. Overall 85 % of the results submitted by EU- and EFTA-countries were acceptable, 5 % questionable and 9 % unacceptable (including false negatives). The respective overall figures of 3rd country labs were 89 %, 0 % and 11 %. Deviations of the sum from 100 % are due to rounding.

(Conti. **p. 52**)

Table 4-7: Overall classification of z-scores calculated using assinged values based on the entire population and FFP-RSD of 25 %

EU and EFTA laboratories						
	Compound	No. of results	Acceptable No. (%)	Questionable No. (%)	Unacceptable [1] No. (%)	FNs No.
Compulsory Compounds	Cyromazine [2]	88	73 (83 %)	9 (10 %)	6 (7 %)	2
	Dithiocarbamates	95	78 (82 %)	6 (6 %)	11 (12 %)	1
	Dodine	83	73 (88 %)	3 (4 %)	7 (8 %)	
	TFNA	63	59 (94 %)	0 (0 %)	4 (6 %)	1
	TFNG	63	58 (92 %)	3 (5 %)	1 (2 %)	
	Tolylfluanid [3]	*87*	*54 (62 %)*	*11 (13 %)*	*22 (25 %)*	*4*
	Subtotal (excl. tolyfluanid)	**392**	**341 (87 %)**	**21 (5 %)**	**29 (7 %)**	**8 [5]**
Optional Compounds	BAC-C14	58	55 (95 %)	0 (0 %)	3 (5 %)	
	Chlorate [2]	46	33 (72 %)	6 (13 %)	7 (15 %)	3
	Dithianon [4]	39				3
	Phosphonic acid	40	35 (88 %)	1 (3 %)	4 (10 %)	2
	Perchlorate [2]	45	34 (76 %)	4 (9 %)	7 (16 %)	2
	Pymetrozine [2]	62	47 (76 %)	4 (6 %)	11 (18 %)	2
	Quizalofop	58	49 (84 %)	1 (2 %)	8 (14 %)	6
	Triclopyr	63	59 (94 %)	0 (0 %)	3 (5 %)	2
	Subtotal (excl. dithianon)	**372**	**312 (84 %)**	**16 (4 %)**	**43 (12 %)**	**20 [5]**
Overall EU/EFTA (Average) (excl. tolyfluanid and dithianon)		**764**	**653 (85 %)**	**37 (5 %)**	**72 (9 %)**	**28 [5]**

3rd country laboratories						
	Compound	No. of results	Acceptable	Questionable	Unacceptable [1]	FNs
Compulsory Compounds	Cyromazine [2]	1	(0 %)	(0 %)	1 (100 %)	
	Dithiocarbamates	2	2 (100 %)	(0 %)	(0 %)	
	Dodine	1	1 (100 %)	(0 %)	(0 %)	
	TFNA	1	1 (100 %)	(0 %)	(0 %)	
	TFNG	1	1 (100 %)	(0 %)	(0 %)	
	Tolylfluanid [3]	*2*	*2 (100 %)*	*(0 %)*	*(0 %)*	
	Subtotal (excl. tolyfluanid)	**6**	**5 (83 %)**	**0 (0 %)**	**1 (17 %)**	**0**
Optional Compounds	BAC-C14	2	2 (100 %)	(0 %)	(0 %)	
	Chlorate [2]	0				
	Dithianon [4]	1				
	Phosphonic acid	0				
	Perchlorate [2]	0				
	Pymetrozine [2]	0				
	Quizalofop	0				
	Triclopyr	1	1 (100 %)	(0 %)	(0 %)	
	Subtotal (excl. dithianon)	**3**	**3 (100 %)**	**0 (0 %)**	**0 (0 %)**	**0**
Overall 3rd country (Average) (excl. tolyfluanid and dithianon)		**9**	**8 (89 %)**	0 (0 %)	**1 (11 %)**	**0**

1) including false negatives (FNs)
2) Z-scores calculated based on assigned values derived from entire population of results by EU and EFTA labs. Alternative z-scores calculated based on results of a sub-population and for information only can be found in **Table 4-8 (p. 40)**.
3) Z-scores calculated based on assigned values derived from entire population of results by EU and EFTA labs. Due to the large uncertainty of the assigned value this data is FOR INFORMATION ONLY. Alternative z-scores calculated based on results of a sub-population, also for information only, can be found in Appendix.
4) No assigned value and z-scores were calculated.
5) including tolyfluanid and/or dithianon

Table 4-8: Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

COMPULSORY Compound				Cyromazine			Dithiocarbamates		Dodine	
Assigned Value / Robust Mean [mg/kg] based on					1.512 entire population	*1.647 § sub-population*	1.297		1.243	
MRRL [mg/kg]					0.010	*0.010*	0.030		0.010	
*CV**					31.8 %	*19.8 %*	34.6 %		26.2 %	
Lab code SRM11-	NRL-SRM	Analysed / corr. found, max. 11 / 6	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	*z-score § (FFP-RSD = 25 %)*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
1		4 / 3	B				0.835	-1.4	1.180	-0.2
2	x	11 / 6	A	0.700	-2.1	*-2.3*	0.275	-3.2	1.170	-0.2
3		11 / 6	A	1.290	-0.6	*-0.9*	0.885	-1.3	1.030	-0.7
4		11 / 6	A	2.120	1.6	*1.1*	1.610	1.0	1.430	0.6
5		9 / 5	B	0.730	-2.1	*-2.2*	0.310	-3.0	1.260	0.1
6		11 / 6	A	2.200	1.8	*1.3*	0.730	-1.7	1.100	-0.5
7	x	11 / 6	A	1.270	-0.6	*-0.9*	1.470	0.5	0.929	-1.0
8		11 / 6	A	1.260	-0.7	*-0.9*	1.933	2.0	1.070	-0.6
9	x	11 / 6	A	1.600	0.2	*-0.1*	1.000	-0.9	1.100	-0.5
11		9 / 6	B	1.500	0.0	*-0.4*	1.770	1.5	0.872	-1.2
12	x	11 / 6	A	1.620	0.3	*-0.1*	0.058	-3.8	1.260	0.1
13	x	10 / 5	A	1.790	0.7	*0.3*			1.330	0.3
14		11 / 6	A	0.510	-2.7	*-2.8*	0.950	-1.1	1.050	-0.6
15		11 / 6	A	1.670	0.4	*0.1*	1.460	0.5	1.190	-0.2
16	x	11 / 6	A	1.550	0.1	*-0.2*	0.994	-0.9	0.742	-1.6
17		3 / 2	B	1.450	-0.2	*-0.5*	1.340	0.1		
18		11 / 6	A	1.740	0.6	*0.2*	1.630	1.0	1.520	0.9
19	x	5 / 1	B				1.200	-0.3		
20		11 / 6	A	1.750	0.6	*0.3*	0.993	-0.9	1.380	0.4
21		7 / 3	B	3.790	6.0	*5.2*	1.530	0.7	2.200	3.1
22		11 / 6	A	1.170	-0.9	*-1.2*	1.530	0.7	1.100	-0.5
23	x	8 / 5	B	1.940	1.1	*0.7*	1.720	1.3	1.850	2.0
24		11 / 6	A	1.955	1.2	*0.7*	1.247	-0.2	1.234	0.0
25		6 / 3	B	2.210	1.8	*1.4*	1.820	1.6	1.610	1.2
26	x	3 / 3	B	1.320	-0.5	*-0.8*	1.290	0.0		
27		11 / 6	A	0.948	-1.5	*-1.7*	2.327	3.2	0.146	-3.5
28		11 / 6	A	1.536	0.1	*-0.3*	1.667	1.1	1.022	-0.7
29		11 / 6	A	0.960	-1.5	*-1.7*	1.800	1.6	1.000	-0.8
30	x	5 / 2	B				1.722	1.3		
31		11 / 6	A	0.108	-3.7	*-3.7*	0.571	-2.2	1.010	-0.7
32		10 / 6	A	1.160	-0.9	*-1.2*	0.230	-3.3	1.500	0.8
33	x	9 / 4	B	1.383	-0.3	*-0.6*	1.462	0.5		
34		11 / 6	A	1.480	-0.1	*-0.4*	1.390	0.3	1.650	1.3
35	x	11 / 5	A	2.610	2.9	*2.3*	3.790	7.7	1.140	-0.3
36		11 / 6	A	1.270	-0.6	*-0.9*	1.460	0.5	1.090	-0.5
37		6 / 3	B	1.584	0.2	*-0.2*			1.454	0.7
38		11 / 6	A	1.630	0.3	*0.0*	1.420	0.4	1.070	-0.6
39	x	11 / 6	A	1.081	-1.1	*-1.4*	0.876	-1.3	0.998	-0.8
40		11 / 6	A	1.900	1.0	*0.6*	1.800	1.6	1.400	0.5
41		11 / 6	A	0.957	-1.5	*-1.7*	1.480	0.6	0.961	-0.9
42		9 / 4	B	1.690	0.5	*0.1*	1.560	0.8	3.020	5.7

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 10 out of the 11 compulsory compounds on the Target Pesticides List, corretly detected at least 5 out of the 6 compulsory compounds present in the test item and not reported any false positive result)
# This laboratory had a sufficient scope but was classified into Category B due to the submission of false positive results.
§ Assigned value was based on only results obtained using ILIS and the z-scores were for informative purpose only.
‡ Assigned value with high uncertainty and the z-scores calculated therefrom were for informative purpose only.

Table 4-8 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

	COMPULSORY Compound				TFNA		TFNG		Tolylfluanid	
	Assigned Value / Robust Mean [mg/kg] based on				0.756		0.448		*0.598‡*	
	MRRL [mg/kg]				0.010		0.010		0.010	
	*CV**				20.0 %		20.7 %		57.5 %	
	Lab code SRM11-	NRL-SRM	Analysed / corr. found, max. 11 / 6	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	*z-score‡ (FFP-RSD = 25 %)*
	1		4 / 3	B					0.726	*0.9*
	2	x	11 / 6	A	0.808	0.3	0.735	2.6	2.080	*9.9*
	3		11 / 6	A	0.921	0.9	0.505	0.5	0.685	*0.6*
	4		11 / 6	A	0.891	0.7	0.473	0.2	0.821	*1.5*
	5		9 / 5	B	0.570	-1.0	0.400	-0.4		
	6		11 / 6	A	0.750	0.0	0.180	-2.4	0.570	*-0.2*
	7	x	11 / 6	A	0.788	0.2	0.487	0.3	0.599	*0.0*
	8		11 / 6	A	0.755	0.0	0.436	-0.1	0.538	*-0.4*
	9	x	11 / 6	A	0.785	0.2	0.343	-0.9	0.351	*-1.7*
	11		9 / 6	B	0.565	-1.0	0.382	-0.6	0.653	*0.4*
	12	x	11 / 6	A	0.875	0.6	0.467	0.2	0.754	*1.0*
	13	x	10 / 5	A	0.799	0.2	0.408	-0.4	0.560	*-0.3*
	14		11 / 6	A	0.420	-1.8	0.110	-3.0	0.650	*0.4*
	15		11 / 6	A	0.659	-0.5	0.530	0.7	0.268	*-2.2*
	16	x	11 / 6	A	0.861	0.6	0.460	0.1	1.123	*3.5*
	17		3 / 2	B						
	18		11 / 6	A	0.642	-0.6	0.418	-0.3	0.446	*-1.0*
	19	x	5 / 1	B					FN	*-3.9*
	20		11 / 6	A	0.983	1.2	0.337	-1.0	0.812	*1.4*
	21		7 / 3	B						
	22		11 / 6	A	0.700	-0.3	0.350	-0.9	1.170	*3.8*
	23	x	8 / 5	B	1.880	5.9			0.250	*-2.3*
	24		11 / 6	A	0.823	0.4	0.484	0.3	0.924	*2.2*
	25		6 / 3	B						
	26	x	3 / 3	B					0.438	*-1.1*
	27		11 / 6	A	0.503	-1.3	0.363	-0.8	0.738	*0.9*
	28		11 / 6	A	0.810	0.3	0.496	0.4	0.860	*1.8*
	29		11 / 6	A	0.770	0.1	0.470	0.2	0.720	*0.8*
	30	x	5 / 2	B					0.778	*1.2*
	31		11 / 6	A	0.561	-1.0	0.465	0.1	0.635	*0.3*
	32		10 / 6	A	0.740	-0.1	0.289	-1.4	0.038	*-3.7*
	33	x	9 / 4	B			0.627	1.6	0.250	*-2.3*
	34		11 / 6	A	0.617	-0.7	0.379	-0.6	1.010	*2.8*
	35	x	11 / 5	A	0.980	1.2	0.458	0.1	FN	*-3.9*
	36		11 / 6	A	0.753	0.0	0.434	-0.1	0.671	*0.5*
	37		6 / 3	B					0.524	*-0.5*
	38		11 / 6	A	0.887	0.7	0.445	0.0	0.295	*-2.0*
	39	x	11 / 6	A	0.623	-0.7	0.408	-0.4	0.501	*-0.6*
	40		11 / 6	A	0.850	0.5	0.520	0.6	0.400	*-1.3*
	41		11 / 6	A	0.619	-0.7	0.436	-0.1	0.310	*-1.9*
	42		9 / 4	B					0.460	*-0.9*

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 10 out of the 11 compulsory compounds on the Target Pesticides List, corretly detected at least 5 out of the 6 compulsory compounds present in the test item and not reported any false positive result)
# This laboratory had a sufficient scope but was classified into Category B due to the submission of false positive results.
§ Assigned value was based on only results obtained using ILIS and the z-scores were for informative purpose only.
‡ Assigned value with high uncertainty and the z-scores calculated therefrom were for informative purpose only.

Table 4-8 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

COMPULSORY Compound				Cyromazine			Dithiocarbamates		Dodine	
Assigned Value / Robust Mean [mg/kg] based on					1.512 entire population	1.647 § sub-population	1.297		1.243	
MRRL [mg/kg]					0.010	0.010	0.030		0.010	
*CV**					31.8 %	19.8 %	34.6 %		26.2 %	
Lab code SRM11-	NRL-SRM	Analysed / corr. found, max. 11 / 6	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	*z-score § (FFP-RSD = 25 %)*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
43		3 / 0	B	FN	-4.0	*-4.0*				
45		2 / 0	B							
46		1 / 1	B				1.350	0.2		
47		1 / 1	B				1.810	1.6		
48		11 / 6	A	1.600	0.2	*-0.1*	1.338	0.1	1.290	0.2
49		11 / 6	A	1.380	-0.4	*-0.6*	1.810	1.6	1.430	0.6
50	x	8 / 5	B	1.640	0.3	*0.0*			0.920	-1.0
51		1 / 1	B				1.340	0.1		
52	x	5 / 2	B				0.870	-1.3		
53		11 / 6	A	0.818	-1.8	*-2.0*	1.750	1.4	1.290	0.2
54		11 / 6	A	2.478	2.6	*2.0*	1.758	1.4	1.572	1.1
55		11 / 6	A	1.570	0.2	*-0.2*	1.070	-0.7	1.250	0.0
56		10 / 5	A	1.838	0.9	*0.5*	1.565	0.8	1.414	0.6
57		11 / 6	A	1.670	0.4	*0.1*	1.225	-0.2	1.450	0.7
58		9 / 5	B	1.150	-1.0	*-1.2*	0.252	-3.2	1.020	-0.7
59		1 / 1	B				1.650	1.1		
60		11 / 6	A	1.630	0.3	*0.0*	1.480	0.6	0.698	-1.8
61		11 / 6	A	1.699	0.5	*0.1*	1.419	0.4	1.356	0.4
62	x	5 / 2	B	1.015	-1.3	*-1.5*				
63		8 / 3	B	2.021	1.3	*0.9*			1.717	1.5
64		11 / 6	A	1.352	-0.4	*-0.7*	0.690	-1.9	1.030	-0.7
65		1 / 1	B				1.480	0.6		
66	x	5 / 2	B	1.270	-0.6	*-0.9*				
67		10 / 5	A				1.577	0.9	1.628	1.2
68	x	10 / 5	A	1.160	-0.9	*-1.2*			0.950	-0.9
69		11 / 6	A	2.030	1.4	*0.9*	1.650	1.1	1.280	0.1
70		4 / 1	B						1.717	1.5
71		11 / 6	A	2.120	1.6	*1.1*	0.434	-2.7	1.100	-0.5
72		11 / 6	A	1.210	-0.8	*-1.1*	1.470	0.5	0.848	-1.3
73		5 / 2	B	0.880	-1.7	*-1.9*				
74		4 / 2	B	2.380	2.3	*1.8*				
75		9 / 4	B	1.420	-0.2	*-0.6*	1.240	-0.2	1.130	-0.4
76	x	9 / 4	B	0.530	-2.6	*-2.7*	1.510	0.7	1.010	-0.7
77		1 / 0	B				FN	-3.9		
78	x	11 / 6	A	1.660	0.4	*0.0*	1.160	-0.4	1.110	-0.4
79	x	10 / 5	A	1.690	0.5	*0.1*	1.150	-0.5	1.120	-0.4
80	x	4 / 1	B	2.750	3.3	*2.7*				
81		11 / 6	A	1.967	1.2	*0.8*	1.438	0.4	1.241	0.0
82		6 / 2	B	0.483	-2.7	*-2.8*				
83		9 / 3	B	FN	-4.0	*-4.0*	1.070	-0.7	1.020	-0.7
84		4 / 2	B				1.400	0.3	1.370	0.4

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 10 out of the 11 compulsory compounds on the Target Pesticides List, corretly detected at least 5 out of the 6 compulsory compounds present in the test item and not reported any false positive result)
# This laboratory had a sufficient scope but was classified into Category B due to the submission of false positive results.
§ Assigned value was based on only results obtained using ILIS and the z-scores were for informative purpose only.
‡ Assigned value with high uncertainty and the z-scores calculated therefrom were for informative purpose only.

Table 4-8 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

COMPULSORY Compound				TFNA		TFNG		Tolylfluanid	
Assigned Value / Robust Mean [mg/kg] based on				0.756		0.448		*0.598‡*	
MRRL [mg/kg]				0.010		0.010		0.010	
*CV**				20.0 %		20.7 %		57.5 %	
Lab code SRM11-	NRL-SRM	Analysed / corr. found, max. 11 / 6	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	*z-score‡ (FFP-RSD = 25 %)*
43		3 / 0	B						
45		2 / 0	B						
46		1 / 1	B						
47		1 / 1	B						
48		11 / 6	A	0.625	-0.7	0.564	1.0	0.870	*1.8*
49		11 / 6	A	1.380	3.3	0.910	4.1	0.433	*-1.1*
50	x	8 / 5	B	0.625	-0.7	0.369	-0.7	0.609	*0.1*
51		1 / 1	B						
52	x	5 / 2	B					0.350	*-1.7*
53		11 / 6	A	0.696	-0.3	0.469	0.2	1.170	*3.8*
54		11 / 6	A	0.757	0.0	0.350	-0.9	0.185	*-2.8*
55		11 / 6	A	0.710	-0.2	0.500	0.5	0.670	*0.5*
56		10 / 5	A	0.870	0.6	0.578	1.2		
57		11 / 6	A	0.790	0.2	0.510	0.5	0.055	*-3.6*
58		9 / 5	B	0.710	-0.2			1.040	*3.0*
59		1 / 1	B						
60		11 / 6	A	0.817	0.3	0.543	0.8	0.127	*-3.1*
61		11 / 6	A	0.775	0.1	0.418	-0.3	0.882	*1.9*
62	x	5 / 2	B					0.470	*-0.9*
63		8 / 3	B					0.748	*1.0*
64		11 / 6	A	0.689	-0.4	0.418	-0.3	1.200	*4.0*
65		1 / 1	B						
66	x	5 / 2	B					0.430	*-1.1*
67		10 / 5	A	0.462	-1.6	0.345	-0.9	1.069	*3.2*
68	x	10 / 5	A	0.820	0.3	0.420	-0.3	0.550	*-0.3*
69		11 / 6	A	0.902	0.8	0.334	-1.0	0.434	*-1.1*
70		4 / 1	B					FN	*-3.9*
71		11 / 6	A	0.445	-1.6	0.356	-0.8	0.384	*-1.4*
72		11 / 6	A	0.773	0.1	0.375	-0.7	0.624	*0.2*
73		5 / 2	B					0.500	*-0.7*
74		4 / 2	B					1.640	*7.0*
75		9 / 4	B					0.910	*2.1*
76	x	9 / 4	B					0.550	*-0.3*
77		1 / 0	B						
78	x	11 / 6	A	0.713	-0.2	0.471	0.2	0.321	*-1.9*
79	x	10 / 5	A			0.495	0.4	0.189	*-2.7*
80	x	4 / 1	B						
81		11 / 6	A	0.777	0.1	0.476	0.2	0.691	*0.6*
82		6 / 2	B					0.160	*-2.9*
83		9 / 3	B					3.250	*17.8*
84		4 / 2	B						

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 10 out of the 11 compulsory compounds on the Target Pesticides List, corretly detected at least 5 out of the 6 compulsory compounds present in the test item and not reported any false positive result)
# This laboratory had a sufficient scope but was classified into Category B due to the submission of false positive results.
§ Assigned value was based on only results obtained using ILIS and the z-scores were for informative purpose only.
‡ Assigned value with high uncertainty and the z-scores calculated therefrom were for informative purpose only.

Table 4-8 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

COMPULSORY Compound				Cyromazine			Dithiocarbamates		Dodine	
Assigned Value / Robust Mean [mg/kg] based on					1.512 entire population	1.647§ sub-population	1.297		1.243	
MRRL [mg/kg]					0.010	0.010	0.030		0.010	
*CV**					31.8 %	19.8 %	34.6 %		26.2 %	
Lab code SRM11-	NRL-SRM	Analysed / corr. found, max. 11 / 6	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	*z-score§ (FFP-RSD = 25 %)*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
86	x	4 / 4	B	1.570	0.2	*-0.2*	1.670	1.2	0.900	-1.1
87		2 / 1	B				1.417	0.4		
88		11 / 6	B#	1.850	0.9	*0.5*	1.110	-0.6	2.127	2.8
89		1 / 1	B				0.270	-3.2		
90		1 / 1	B						2.400	3.7
91		11 / 6	A	1.410	-0.3	*-0.6*	1.220	-0.2	1.290	0.2
92		1 / 1	B				1.420	0.4		
93	x	11 / 6	A	1.700	0.5	*0.1*	0.960	-1.0	24.100	73.6
94		11 / 6	A	1.260	-0.7	*-0.9*	1.140	-0.5	0.979	-0.8
95		1 / 1	B				1.440	0.4		
96	x	7 / 3	B	1.050	-1.2	*-1.4*	0.526	-2.4	0.960	-0.9
97		4 / 3	B	1.350	-0.4	*-0.7*	1.050	-0.8		
98		6 / 3	B	1.000	-1.4	*-1.6*			1.200	-0.1
100		1 / 1	B				1.830	1.6		
101		1 / 1	B				1.650	1.1		
102	x	4 / 1	B				2.500	3.7		
103		1 / 1	B				1.340	0.1		
104		1 / 0	B							
105		4 / 2	B	1.300	-0.6	*-0.8*			1.140	-0.3
106		11 / 6	A	1.800	0.8	*0.4*	1.500	0.6	1.300	0.2
107		5 / 2	B	0.360	-3.0	*-3.1*			0.136	-3.6
108		1 / 1	B				1.610	1.0		
109		4 / 0	B							
110		2 / 2	B						1.090	-0.5
111		10 / 5	A	2.360	2.2	*1.7*			1.370	0.4
112		1 / 1	B				1.430	0.4		
114		9 / 5	B	1.147	-1.0	*-1.2*	0.564	-2.3	0.592	-2.1
115	x	11 / 6	A	1.820	0.8	*0.4*	1.135	-0.5	0.954	-0.9
116		4 / 2	B				0.797	-1.5		
117		11 / 6	A	2.080	1.5	*1.1*	1.170	-0.4	1.690	1.4
118		9 / 5	B	1.600	0.2	*-0.1*			1.810	1.8
119	x	11 / 6	A	1.880	1.0	*0.6*	0.579	-2.2	1.940	2.2
120		5 / 2	B	1.120	-1.0	*-1.3*				
121		1 / 1	B				0.620	-2.1		
122		1 / 1	B				1.603	0.9		
123		3 / 2	B				1.510	0.7	1.230	0.0
127	x	10 / 5	A	1.770	0.7	*0.3*			1.330	0.3
128		11 / 6	A	1.650	0.4	*0.0*	0.302	-3.1	2.540	4.2
3rd-44		7 / 3	B	0.221	-3.4	*-3.5*	1.050	-0.8		
3rd-126		6 / 5	B				0.990	-0.9	0.833	-1.3

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 10 out of the 11 compulsory compounds on the Target Pesticides List, corretly detected at least 5 out of the 6 compulsory compounds present in the test item and not reported any false positive result)
# This laboratory had a sufficient scope but was classified into Category B due to the submission of false positive results.
§ Assigned value was based on only results obtained using ILIS and the z-scores were for informative purpose only.
‡ Assigned value with high uncertainty and the z-scores calculated therefrom were for informative purpose only.

Table 4-8 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

	COMPULSORY Compound				TFNA		TFNG		Tolylfluanid	
	Assigned Value / Robust Mean [mg/kg] based on				0.756		0.448		*0.598*‡	
	MRRL [mg/kg]				0.010		0.010		0.010	
	*CV**				20.0 %		20.7 %		57.5 %	
	Lab code SRM11-	NRL-SRM	Analysed / corr. found, max. 11 / 6	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	*z-score‡ (FFP-RSD = 25 %)*
	86	x	4 / 4	B					0.490	*-0.7*
	87		2 / 1	B						
	88		11 / 6	B#	1.009	1.3	0.383	-0.6	0.124	*-3.2*
	89		1 / 1	B						
	90		1 / 1	B						
	91		11 / 6	A	1.520	4.0	0.492	0.4	1.100	*3.4*
	92		1 / 1	B						
	93	x	11 / 6	A	0.398	-1.9	0.316	-1.2	0.451	*-1.0*
	94		11 / 6	A	0.757	0.0	0.471	0.2	0.665	*0.5*
	95		1 / 1	B						
	96	x	7 / 3	B					FN	*-4.0*
	97		4 / 3	B					0.299	*-2.0*
	98		6 / 3	B					1.300	*4.7*
	100		1 / 1	B						
	101		1 / 1	B						
	102	x	4 / 1	B						
	103		1 / 1	B						
	104		1 / 0	B						
	105		4 / 2	B						
	106		11 / 6	A	0.530	-1.2	0.450	0.0	0.110	*-3.3*
	107		5 / 2	B						
	108		1 / 1	B						
	109		4 / 0	B						
	110		2 / 2	B					0.242	*-2.4*
	111		10 / 5	A	0.728	-0.1	0.531	0.7	1.130	*3.6*
	112		1 / 1	B						
	114		9 / 5	B	FN	-3.9	0.261	-1.7	0.864	*1.8*
	115	x	11 / 6	A	0.725	-0.2	0.492	0.4	0.364	*-1.6*
	116		4 / 2	B					0.680	*0.6*
	117		11 / 6	A	0.923	0.9	0.580	1.2	0.183	*-2.8*
	118		9 / 5	B	0.750	0.0	0.540	0.8	0.800	*1.4*
	119	x	11 / 6	A	0.916	0.8	0.698	2.2	0.439	*-1.1*
	120		5 / 2	B					0.119	*-3.2*
	121		1 / 1	B						
	122		1 / 1	B						
	123		3 / 2	B						
	127	x	10 / 5	A	0.873	0.6	0.577	1.1	0.494	*-0.7*
	128		11 / 6	A	0.663	-0.5	0.489	0.4	0.604	*0.0*
	3rd-44		7 / 3	B					0.670	*0.5*
	3rd-126		6 / 5	B	0.959	1.1	0.637	1.7	0.320	*-1.9*

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 10 out of the 11 compulsory compounds on the Target Pesticides List, corretly detected at least 5 out of the 6 compulsory compounds present in the test item and not reported any false positive result)
# This laboratory had a sufficient scope but was classified into Category B due to the submission of false positive results.
§ Assigned value was based on only results obtained using ILIS and the z-scores were for informative purpose only.
‡ Assigned value with high uncertainty and the z-scores calculated therefrom were for informative purpose only.

Table 4-9: Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

OPTIONAL Compound				BAC-C14		Chlorate			Dithia-non	Phosphonic acid	
Assigned Value / Robust Mean [mg/kg] based on				0.285			*1.512‡* entire population	*1.647§* sub-population	1.729	9.831	
MRRL [mg/kg]				0.020			*0.020*	*0.020*	0.010	0.050	
*CV**				25.8 %			*44.6 %*	*15.6 %*	94.3 %	29.5 %	
Lab code SRM11-	NRL-SRM	Analysed / corr. found max. 16 /8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	*z-score‡ (FFP-RSD = 25 %)*	*z-score§ (FFP-RSD = 25 %)*	Conc. [mg/kg]	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
1		7 / 1	B	0.158	-1.8						
2	x	11 / 4	A	0.599	4.4				0.266		
3		13 / 6	A	0.208	-1.1	2.430	*0.8*	*-0.1*		5.870	-1.6
4		14 / 7	A	0.352	0.9	2.750	*1.4*	*0.5*	2.090	17.300	3.0
5		11 / 4	B	0.350	0.9	2.600	*1.1*	*0.2*		FN	-4.0
6		15 / 8	A	0.330	0.6	2.300	*0.5*	*-0.3*	1.300	10.200	0.2
7	x	16 / 7	A	0.286	0.0	1.740	*-0.6*	*-1.2*	FN	10.570	0.3
8		14 / 7	A	0.286	0.0	2.650	*1.2*	*0.3*	3.290		
9	x	11 / 5	A	0.290	0.1	3.100	*2.1*	*1.0*			
11		11 / 5	B	0.210	-1.0				2.900		
12	x	15 / 8	A	0.343	0.8	2.270	*0.5*	*-0.3*	4.110	8.130	-0.7
13	x	8 / 0	A								
14		6 / 2	A						0.130		
15		15 / 7	A	0.317	0.5	1.300	*-1.4*	*-1.9*		5.680	-1.7
16	x	4 / 2	A								
17		2 / 1	B								
18		15 / 5	A	0.349	0.9	FN	*-4.0*	*-4.0*		6.030	-1.5
19	x	0 / 0	B								
20		8 / 5	A			2.240	*0.4*	*-0.4*		10.100	0.1
21		8 / 2	B	0.315	0.4						
22		6 / 3	A						5.620		
23	x	9 / 4	B	0.250	-0.5				0.490		
24		16 / 8	A	0.285	0.0	2.197	*0.3*	*-0.4*	3.792	11.444	0.7
25		1 / 1	B								
26	x	6 / 3	B	0.319	0.5	0.380	*-3.3*	*-3.4*			
27		5 / 3	A			0.650	*-2.7*	*-2.9*		5.528	-1.8
28		16 / 8	A	0.349	0.9	2.741	*1.4*	*0.4*	3.340	11.658	0.7
29		16 / 8	A	0.400	1.6	3.000	*1.9*	*0.9*	0.910	10.500	0.3
30	x	0 / 0	B								
31		7 / 6	A			0.298	*-3.4*	*-3.5*	0.991	1.206	-3.5
32		16 / 7	A	0.355	1.0	1.100	*-1.8*	*-2.2*	1.000	10.800	0.4
33	x	2 / 1	B								
34		11 / 3	A	0.180	-1.5	1.390	*-1.3*	*-1.7*			
35	x	1 / 0	A								
36		14 / 7	A	0.298	0.2	1.810	*-0.4*	*-1.1*		9.980	0.1
37		8 / 2	B	0.358	1.0						
38		16 / 8	A	0.273	-0.2	2.700	*1.3*	*0.4*	1.640	11.000	0.5
39	x	11 / 3	A	0.239	-0.6						
40		13 / 5	A	0.403	1.7					10.600	0.3
41		3 / 1	A								

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 9 compulsory compounds on the Target Pesticides List, corretly detected 5 or more out of the 6 compulsory compounds and that have not reported any false positive result)

This laboratory had a sufficient scope but were classified into Category B due to the submission of false positive results.

‡, § In the cases of chlorate and perchlorate: ‡ assigned value was based on entire population with wide distribution, the z-scores were for informative purpose only; ‡ assigned value based on only results obtained using ILIS and the z-scores were for informative purpose only.

† Assigned value based on results obtained using ISs added at the beginning of sample preparation, the z-scores calculated therefrom were for informative purpose only.

Table 4-9 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

	OPTIONAL Compound			Perchlorate			Pymetrozine			Quizalofop		Triclopyr	
	Assigned Value / Robust Mean [mg/kg] based on			*0.260*[‡] entire population	*0.234*[§] sub-population		0.432 entire population	*0.361*[†] sub-population		0.171		0.177	
	MRRL [mg/kg]			*0.020*	*0.020*		0.010	*0.020*		0.010		0.010	
	*CV**			*35.9 %*	*23.5 %*		42.3 %	*54.8 %*		24.6 %		17.7 %	
	Lab code SRM11-	NRL-SRM	Analysed / corr. found max. 16 / 8	Cat.*	Conc. [mg/kg]	*z-score*[‡] *(FFP-RSD =25 %)*	*z-score*[§] *(FFP-RSD =25 %)*	Conc. [mg/kg]	z-score (FFP-RSD =25 %)	*z-score*[†] *(FFP-RSD =25 %)*	Conc. [mg/kg]	z-score (FFP-RSD =25 %)	Conc. [mg/kg]	z-score (FFP-RSD =25 %)
	1		7 / 1	B										
	2	x	11 / 4	A							0.208	0.9	0.402	5.1
	3		13 / 6	A	0.240	*-0.3*	*0.1*				0.165	-0.1	0.191	0.3
	4		14 / 7	A	0.361	*1.5*	*2.2*	0.371	-0.6	*0.1*	FN	-3.8	0.097	-1.8
	5		11 / 4	B	0.390	*2.0*	*2.7*	0.170	-2.4	*-2.1*				
	6		15 / 8	A	0.076	*-2.8*	*-2.7*	1.200	7.1	*9.3*	0.130	-1.0	0.210	0.7
	7	x	16 / 7	A	0.220	*-0.6*	*-0.2*	0.285	-1.4	*-0.8*	0.204	0.8	0.181	0.1
	8		14 / 7	A	0.164	*-1.5*	*-1.2*	0.319	-1.0	*-0.5*	0.129	-1.0	0.153	-0.5
	9	x	11 / 5	A	0.240	*-0.3*	*0.1*				0.160	-0.3	0.207	0.7
	11		11 / 5	B				0.435	0.0	*0.8*	0.129	-1.0	0.123	-1.2
	12	x	15 / 8	A	0.190	*-1.1*	*-0.8*	0.461	0.3	*1.1*	0.164	-0.2	0.172	-0.1
	13	x	8 / 0	A										
	14		6 / 2	A				0.180	-2.3	*-2.0*	FN	-3.8	FN	-3.8
	15		15 / 7	A	0.194	*-1.0*	*-0.7*	0.628	1.8	*2.9*	0.177	0.1	0.190	0.3
	16	x	4 / 2	A				0.700	2.5	*3.7*	0.267	2.3		
	17		2 / 1	B				0.306	-1.2	*-0.6*				
	18		15 / 5	A	FN	*-3.8*	*-3.8*	0.522	0.8	*1.8*	0.167	-0.1	0.165	-0.3
	19	x	0 / 0	B										
	20		8 / 5	A	0.240	*-0.3*	*0.1*	0.479	0.4	*1.3*	0.131	-0.9		
	21		8 / 2	B									0.207	0.7
	22		6 / 3	A							0.084	-2.0	0.160	-0.4
	23	x	9 / 4	B							0.200	0.7	0.190	0.3
	24		16 / 8	A	0.230	*-0.5*	*-0.1*	0.564	1.2	*2.2*	0.206	0.8	0.179	0.0
	25		1 / 1	B				0.332	-0.9	*-0.3*				
	26	x	6 / 3	B	0.086	*-2.7*	*-2.5*							
	27		5 / 3	A	0.326	*1.0*	*1.6*							
	28		16 / 8	A	0.258	*0.0*	*0.4*	0.451	0.2	*1.0*	0.191	0.5	0.194	0.4
	29		16 / 8	A	0.330	*1.1*	*1.6*	0.540	1.0	*2.0*	0.170	0.0	0.150	-0.6
	30	x	0 / 0	B										
	31		7 / 6	A	0.865	*9.3*	*10.8*	0.113	-3.0	*-2.7*			0.143	-0.8
	32		16 / 7	A	0.410	*2.3*	*3.0*	1.105	6.2	*8.2*	FN	-3.8	0.159	-0.4
	33	x	2 / 1	B				0.423	-0.1	*0.7*				
	34		11 / 3	A									0.167	-0.2
	35	x	1 / 0	A										
	36		14 / 7	A	0.203	*-0.9*	*-0.5*	0.216	-2.0	*-1.6*	0.187	0.4	0.175	-0.1
	37		8 / 2	B									0.195	0.4
	38		16 / 8	A	0.270	*0.1*	*0.6*	0.402	-0.3	*0.4*	0.140	-0.7	0.213	0.8
	39	x	11 / 3	A				0.491	0.6	*1.4*			0.191	0.3
	40		13 / 5	A				0.410	-0.2	*0.5*	0.175	0.1	0.180	0.1
	41		3 / 1	A									0.178	0.0

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 9 compulsory compounds on the Target Pesticides List, corretly detected 5 or more out of the 6 compulsory compounds and that have not reported any false positive result)

[#] This laboratory had a sufficient scope but were classified into Category B due to the submission of false positive results.

[‡], [§] In the cases of chlorate and perchlorate: [‡] assigned value was based on entire population with wide distribution, the z-scores were for informative purpose only; [‡] assigned value based on only results obtained using ILIS and the z-scores were for informative purpose only.

[†] Assigned value based on results obtained using ISs added at the beginning of sample preparation, the z-scores calculated therefrom were for informative purpose only.

Table 4-9 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

OPTIONAL Compound				BAC-C14		Chlorate			Dithia-non	Phosphonic acid	
Assigned Value / Robust Mean [mg/kg] based on				0.285			1.512‡ entire population	1.647§ sub-population	1.729	9.831	
MRRL [mg/kg]				0.020			0.020	0.020	0.010	0.050	
*CV**				25.8 %			44.6 %	15.6 %	94.3 %	29.5 %	
Lab code SRM11-	NRL-SRM	Analysed / corr. found max. 16 /8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score‡ (FFP-RSD = 25 %)	z-score§ (FFP-RSD = 25 %)	Conc. [mg/kg]	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
42		13 / 7	B	0.360	1.1	1.640	-0.8	-1.3	0.200	12.300	1.0
43		4 / 2	B			0.450	-3.1	-3.3		FN	-4.0
45		3 / 1	B								
46		0 / 0	B								
47		0 / 0	B								
48		10 / 7	A			1.300	-1.4	-1.9	2.520	5.650	-1.7
49		14 / 3	A	0.271	-0.2	FN	-4.0	-4.0		5.060	-1.9
50	x	9 / 3	B	0.217	-1.0						
51		0 / 0	B								
52	x	1 / 0	B								
53		12 / 5	A	0.283	0.0				2.800		
54		16 / 8	A	0.344	0.8	0.694	-2.6	-2.9	0.434	10.970	0.5
55		13 / 6	A	0.041	-3.4	0.720	-2.6	-2.8		3.510	-2.6
56		4 / 2	A								
57		16 / 8	A	0.255	-0.4	2.250	0.4	-0.4	0.150	13.500	1.5
58		12 / 5	B	0.256	-0.4				1.440		
59		0 / 0	B								
60		5 / 3	A								
61		15 / 8	A	0.143	-2.0	2.550	1.0	0.1	10.170	12.350	1.0
62	x	2 / 1	B								
63		12 / 5	B	0.365	1.1	2.664	1.2	0.3			
64		13 / 8	A	0.209	-1.1	0.883	-2.3	-2.6	0.470	8.810	-0.4
65		0 / 0	B								
66	x	6 / 1	B	0.330	0.6						
67		9 / 5	A	0.272	-0.2				0.293	9.807	0.0
68	x	7 / 4	A			2.900	1.7	0.7		8.200	-0.7
69		9 / 6	A			2.250	0.4	-0.4		12.030	0.9
70		1 / 0	B								
71		10 / 3	A	0.249	-0.5						
72		6 / 4	A						0.302		
73		2 / 1	B								
74		2 / 1	B								
75		12 / 5	B	0.192	-1.3				3.440	9.340	-0.2
76	x	10 / 4	B	0.190	-1.3						
77		0 / 0	B								
78	x	14 / 7	A	0.266	-0.3	2.120	0.2	-0.6		10.000	0.1
79	x	10 / 7	A			2.520	1.0	0.1	1.080	10.700	0.4
80	x	0 / 0	B								
81		5 / 2	A						2.399		
82		1 / 1	B								

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 9 compulsory compounds on the Target Pesticides List, corretly detected 5 or more out of the 6 compulsory compounds and that have not reported any false positive result)

This laboratory had a sufficient scope but were classified into Category B due to the submission of false positive results.

‡, § In the cases of chlorate and perchlorate: ‡ assigned value was based on entire population with wide distribution, the z-scores were for informative purpose only; ‡ assigned value based on only results obtained using ILIS and the z-scores were for informative purpose only.

† Assigned value based on results obtained using ISs added at the beginning of sample preparation, the z-scores calculated therefrom were for informative purpose only.

Table 4-9 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

	OPTIONAL Compound				Perchlorate			Pymetrozine			Quizalofop		Triclopyr	
	Assigned Value / Robust Mean [mg/kg] based on				*0.260* ‡ entire population	*0.234* § sub-population		0.432 entire population	*0.361* † sub-population		0.171		0.177	
	MRRL [mg/kg]				*0.020*	*0.020*		0.010	*0.020*		0.010		0.010	
	*CV**				*35.9 %*	*23.5 %*		42.3 %	*54.8 %*		24.6 %		17.7 %	
	Lab code SRM11-	NRL-SRM	Analysed / corr. found max. 16 / 8	Cat.*	Conc. [mg/kg]	*z-score* ‡ *(FFP-RSD =25 %)*	*z-score* § *(FFP-RSD =25 %)*	Conc. [mg/kg]	z-score (FFP-RSD =25 %)	*z-score* † *(FFP-RSD =25 %)*	Conc. [mg/kg]	z-score (FFP-RSD =25 %)	Conc. [mg/kg]	z-score (FFP-RSD =25 %)
	42		13 / 7	B	0.230	*-0.5*	*-0.1*	0.590	1.5	*2.5*	0.190	0.5		
	43		4 / 2	B									0.165	-0.3
	45		3 / 1	B	0.183	*-1.2*	*-0.9*							
	46		0 / 0	B										
	47		0 / 0	B										
	48		10 / 7	A	0.247	*-0.2*	*0.2*	0.304	-1.2	*-0.6*	0.101	-1.6	0.117	-1.4
	49		14 / 3	A	FN	*-3.7*	*-3.7*	FN	-3.9	*-3.9*			0.133	-1.0
	50	x	9 / 3	B				0.412	-0.2	*0.6*			0.175	-0.1
	51		0 / 0	B										
	52	x	1 / 0	B										
	53		12 / 5	A				0.348	-0.8	*-0.1*	0.238	1.6	0.210	0.7
	54		16 / 8	A	0.334	*1.1*	*1.7*	0.662	2.1	*3.3*	0.149	-0.5	0.258	1.8
	55		13 / 6	A	0.360	*1.5*	*2.1*	0.260	-1.6	*-1.1*			0.210	0.7
	56		4 / 2	A				0.503	0.7	*1.6*			0.193	0.4
	57		16 / 8	A	0.235	*-0.4*	*0.0*	0.475	0.4	*1.3*	0.180	0.2	0.230	1.2
	58		12 / 5	B				0.379	-0.5	*0.2*	0.150	-0.5	0.173	-0.1
	59		0 / 0	B										
	60		5 / 3	A				0.529	0.9	*1.9*	0.224	1.2	0.177	0.0
	61		15 / 8	A	0.235	*-0.4*	*0.0*	0.374	-0.5	*0.1*	0.153	-0.4	0.138	-0.9
	62	x	2 / 1	B				0.625	1.8	*2.9*				
	63		12 / 5	B	0.236	*-0.4*	*0.0*	0.532	0.9	*1.9*	0.349	4.2		
	64		13 / 8	A	0.882	*9.6*	*11.1*	0.232	-1.8	*-1.4*	0.137	-0.8	0.257	1.8
	65		0 / 0	B										
	66	x	6 / 1	B										
	67		9 / 5	A							0.144	-0.6	0.148	-0.7
	68	x	7 / 4	A							0.110	-1.4	0.130	-1.1
	69		9 / 6	A	0.254	*-0.1*	*0.3*	0.864	4.0	*5.6*	0.218	1.1	0.186	0.2
	70		1 / 0	B										
	71		10 / 3	A							0.148	-0.5	0.173	-0.1
	72		6 / 4	A				0.218	-2.0	*-1.6*	0.180	0.2	0.181	0.1
	73		2 / 1	B							1.940	41.5		
	74		2 / 1	B				0.580	1.4	*2.4*				
	75		12 / 5	B							0.161	-0.2	0.156	-0.5
	76	x	10 / 4	B				0.520	0.8	*1.8*	0.140	-0.7	0.240	1.4
	77		0 / 0	B										
	78	x	14 / 7	A	0.210	*-0.8*	*-0.4*	0.304	-1.2	*-0.6*	0.193	0.5	0.182	0.1
	79	x	10 / 7	A	0.232	*-0.4*	*0.0*	0.406	-0.2	*0.5*	0.111	-1.4	0.146	-0.7
	80	x	0 / 0	B										
	81		5 / 2	A				0.353	-0.7	*-0.1*	FN	-3.8		
	82		1 / 1	B	0.070	*-2.9*	*-2.8*							

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 9 compulsory compounds on the Target Pesticides List, corretly detected 5 or more out of the 6 compulsory compounds and that have not reported any false positive result)

This laboratory had a sufficient scope but were classified into Category B due to the submission of false positive results.

‡, § In the cases of chlorate and perchlorate: ‡ assigned value was based on entire population with wide distribution, the z-scores were for informative purpose only; ‡ assigned value based on only results obtained using ILIS and the z-scores were for informative purpose only.

† Assigned value based on results obtained using ISs added at the beginning of sample preparation, the z-scores calculated therefrom were for informative purpose only.

Table 4-9 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

OPTIONAL Compound				BAC-C14		Chlorate			Dithia-non	Phosphonic acid	
Assigned Value / Robust Mean [mg/kg] based on				0.285			1.512‡ entire population	1.647§ sub-population	1.729	9.831	
MRRL [mg/kg]				0.020			0.020	0.020	0.010	0.050	
*CV**				25.8 %			44.6 %	15.6 %	94.3 %	29.5 %	
Lab code SRM11-	NRL-SRM	Analysed / corr. found max. 16 /8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score‡ (FFP-RSD = 25 %)	z-score§ (FFP-RSD = 25 %)	Conc. [mg/kg]	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
83		12 / 5	B	0.307	0.3	2.260	0.4	-0.3			
84		0 / 0	B								
86	x	0 / 0	B								
87		0 / 0	B								
88		16 / 7	B#	0.518	3.3	2.024	0.0	-0.7	FN	12.115	0.9
89		0 / 0	B								
90		5 / 1	B	0.241	-0.6						
91		15 / 6	A	0.332	0.7	2.350	0.6	-0.2		11.400	0.6
92		0 / 0	B								
93	x	12 / 6	A	0.219	-0.9	3.200	2.3	1.2	1.960		
94		8 / 3	A	0.234	-0.7						
95		0 / 0	B								
96	x	9 / 3	B	0.309	0.3				2.810		
97		2 / 1	B								
98		6 / 3	B						0.110		
100		0 / 0	B								
101		0 / 0	B								
102	x	0 / 0	B								
103		0 / 0	B								
104		0 / 0	B								
105		0 / 0	B								
106		15 / 7	A	0.230	-0.8	2.600	1.1	0.2	0.056	10.300	0.2
107		4 / 2	B			FN	-4.0	-4.0	FN		
108		0 / 0	B								
109		4 / 2	B								
110		6 / 2	B	0.223	-0.9						
111		8 / 5	A			2.460	0.8	0.0		12.600	1.1
112		0 / 0	B								
114		14 / 7	B	0.227	-0.8	0.251	-3.5	-3.6	0.227		
115	x	14 / 7	A	0.322	0.5	2.590	1.1	0.2		14.000	1.7
116		1 / 1	B								
117		16 / 8	A	0.262	-0.3	2.720	1.4	0.4	0.125	10.600	0.3
118		3 / 0	B								
119	x	10 / 3	A	0.195	-1.3						
120		0 / 0	B								
121		0 / 0	B								
122		0 / 0	B								
123		6 / 2	B	0.310	0.4				2.770		
127	x	3 / 2	A								
128		16 / 8	A	0.388	1.5	3.050	2.0	0.9	4.060	10.200	0.2
3rd-44		6 / 2	B	0.281	0.0				1.940		
3rd-126		6 / 2	B	0.290	0.1						

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 9 compulsory compounds on the Target Pesticides List, corretly detected 5 or more out of the 6 compulsory compounds and that have not reported any false positive result)

This laboratory had a sufficient scope but were classified into Category B due to the submission of false positive results.

‡, § In the cases of chlorate and perchlorate: ‡ assigned value was based on entire population with wide distribution, the z-scores were for informative purpose only; ‡ assigned value based on only results obtained using ILIS and the z-scores were for informative purpose only.

† Assigned value based on results obtained using ISs added at the beginning of sample preparation, the z-scores calculated therefrom were for informative purpose only.

Table 4-9 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

	OPTIONAL Compound				Perchlorate			Pymetrozine			Quizalofop		Triclopyr	
	Assigned Value / Robust Mean [mg/kg] based on				*0.260*[‡] entire population	*0.234*[§] sub-population		0.432 entire population	*0.361*[†] sub-population		0.171		0.177	
	MRRL [mg/kg]				*0.020*	*0.020*		0.010	*0.020*		0.010		0.010	
	*CV**				*35.9 %*	*23.5 %*		42.3 %	*54.8 %*		24.6 %		17.7 %	
	Lab code SRM11-	NRL-SRM	Analysed / corr. found max. 16 / 8	Cat.*	Conc. [mg/kg]	*z-score*[‡] *(FFP-RSD =25 %)*	*z-score*[§] *(FFP-RSD =25 %)*	Conc. [mg/kg]	z-score (FFP-RSD =25 %)	*z-score*[†] *(FFP-RSD =25 %)*	Conc. [mg/kg]	z-score (FFP-RSD =25 %)	Conc. [mg/kg]	z-score (FFP-RSD =25 %)
	83		12 / 5	B	0.598	*5.2*	*6.2*	0.949	4.8	*6.5*			0.170	-0.2
	84		0 / 0	B										
	86	x	0 / 0	B										
	87		0 / 0	B										
	88		16 / 7	B[#]	0.179	*-1.2*	*-0.9*	0.763	3.1	*4.4*	0.210	0.9	0.154	-0.5
	89		0 / 0	B										
	90		5 / 1	B										
	91		15 / 6	A	0.224	*-0.6*	*-0.2*	0.511	0.7	*1.7*	FN	-3.8	0.160	-0.4
	92		0 / 0	B										
	93	x	12 / 6	A	0.275	*0.2*	*0.7*	0.338	-0.9	*-0.3*	0.249	1.8		
	94		8 / 3	A							0.182	0.3	0.180	0.1
	95		0 / 0	B										
	96	x	9 / 3	B				FN	-4.0	*-3.9*			0.172	-0.1
	97		2 / 1	B				0.310	-1.1	*-0.6*				
	98		6 / 3	B				0.070	-3.4	*-3.2*	FN	-3.8	0.110	-1.5
	100		0 / 0	B										
	101		0 / 0	B										
	102	x	0 / 0	B										
	103		0 / 0	B										
	104		0 / 0	B										
	105		0 / 0	B										
	106		15 / 7	A	0.250	*-0.2*	*0.3*				0.150	-0.5	0.160	-0.4
	107		4 / 2	B	0.276	*0.2*	*0.7*	0.045	-3.6	*-3.5*				
	108		0 / 0	B										
	109		4 / 2	B							0.181	0.2	0.187	0.2
	110		6 / 2	B				1.310	8.1	*10.5*				
	111		8 / 5	A	0.177	*-1.3*	*-1.0*				0.204	0.8	0.255	1.8
	112		0 / 0	B										
	114		14 / 7	B	0.821	*8.6*	*10.0*	0.351	-0.7	*-0.1*	0.149	-0.5	0.105	-1.6
	115	x	14 / 7	A	0.212	*-0.7*	*-0.4*	0.365	-0.6	*0.0*	0.154	-0.4	0.228	1.1
	116		1 / 1	B				0.292	-1.3	*-0.8*				
	117		16 / 8	A	0.223	*-0.6*	*-0.2*	0.376	-0.5	*0.2*	0.170	0.0	0.177	0.0
	118		3 / 0	B									FN	-3.8
	119	x	10 / 3	A				0.267	-1.5	*-1.0*	0.129	-1.0		
	120		0 / 0	B										
	121		0 / 0	B										
	122		0 / 0	B										
	123		6 / 2	B										
	127	x	3 / 2	A				0.582	1.4	*2.4*	0.121	-1.2		
	128		16 / 8	A	0.502	*3.7*	*4.6*	0.504	0.7	*1.6*	0.222	1.2	0.205	0.6
	3rd-44		6 / 2	B										
	3rd-126		6 / 2	B									0.158	0.0

* Category A/B classification (Cat A was assigned to laboratories that have correctly analysed at least 9 compulsory compounds on the Target Pesticides List, corretly detected 5 or more out of the 6 compulsory compounds and that have not reported any false positive result)

[#] This laboratory had a sufficient scope but were classified into Category B due to the submission of false positive results.

[‡], [§] In the cases of chlorate and perchlorate: [‡] assigned value was based on entire population with wide distribution, the z-scores were for informative purpose only; [‡] assigned value based on only results obtained using ILIS and the z-scores were for informative purpose only.

[†] Assigned value based on results obtained using ISs added at the beginning of sample preparation, the z-scores calculated therefrom were for informative purpose only.

4.4.4 Laboratory Classification Based on Scope

All participating laboratories having reported results were classified into categories A or B based on their "scope", as reflected by the number of target analytes sought for and correctly detected by the laboratory among the COMPULSORY pesticides. Following the rules defined in the General Protocol (6th Edition, see **Appendix 8**), a laboratory had to fulfill the following conditions in order to be classified into Category A in the present PT: a) analysis of at least ten out of the eleven compulsory pesticides on the Target Pesticides List; b) correct detection of at least five out of the six compulsory pesticides present in the test item, and c) no false positive results. One laboratory (SRM11-88) had a sufficient analytical scope (analysing all 11 and correctly detecting all 6 compulsory pesticides present in the test item) but was still classified into Category B due to the submission of false positive results.

A total of 56 EU and EFTA laboratories (47 %) were classified into Category A and 64 (53 %) into Category B. Both of the third-country laboratories were classified into Category B. Considering only the compulsory compounds (excluding ***tolylfluanid***) the laboratories from EU and EFTA countries classified into Category A achieved an overall AAZ of 0.9 (n = 274), whereas those classified into Category B achieved an overall AAZ of 1.3 (n = 118).

Table 4-10 and **Table 4-11 (p. 54)** show the details of laboratories classified into Category A and B, respectively. For informative purposes, the AAZ was calculated for laboratories with 5 or more individual z-scores. For the AAZ calculation any z-scores > 5 were set at 5.

Table 4-10: Category A laboratories ordered by lab-codes

COMPULSORY Compounds			Cyromazine		Dithiocarbamates	Dodine	TFNA	TFNG	*Tolylfluanid*[3]		
Assigned Value [mg/kg]			1.512	*1.647*[2]	1.297	1.243	0.756	0.448	*0.598*		
MRRL [mg/kg]			0.010	*0.010*	0.030	0.010	0.010	0.010	0.010		
*CV**			31.8 %	*25.0 %*	34.6 %	26.2 %	20.0 %	20.7 %	*57.5 %*		
Lab code SRM11-	NRL-SRM	Analysed / corr. found[1]	z-scores	*z-scores*[2]	z-scores	z-scores	z-scores	z-scores	*z-scores*	AAZ[4]	*AAZ*[5]
2	x	11 / 6	-2.1	*-2.3*	-3.2	-0.2	0.3	2.6	*9.9*	1.7	*1.7*
3		11 / 6	-0.6	*-0.9*	-1.3	-0.7	0.9	0.5	*0.6*	0.8	*0.9*
4		11 / 6	1.6	*1.1*	1.0	0.6	0.7	0.2	*1.5*	0.8	*0.7*
6		11 / 6	1.8	*1.3*	-1.7	-0.5	0.0	-2.4	*-0.2*	1.3	*1.2*
7	x	11 / 6	-0.6	*-0.9*	0.5	-1.0	0.2	0.3	*0.0*	0.5	*0.6*
8		11 / 6	-0.7	*-0.9*	2.0	-0.6	0.0	-0.1	*-0.4*	0.7	*0.7*
9	x	11 / 6	0.2	*-0.1*	-0.9	-0.5	0.2	-0.9	*-1.7*	0.5	*0.5*
12	x	11 / 6	0.3	*-0.1*	-3.8	0.1	0.6	0.2	*1.0*	1.0	*1.0*
13	x	10 / 5	0.7	*0.3*		0.3	0.2	-0.4	*-0.3*	0.4	*0.3*
14		11 / 6	-2.7	*-2.8*	-1.1	-0.6	-1.8	-3.0	*0.4*	1.8	*1.9*
15		11 / 6	0.4	*0.1*	0.5	-0.2	-0.5	0.7	*-2.2*	0.5	*0.4*
16	x	11 / 6	0.1	*-0.2*	-0.9	-1.6	0.6	0.1	*3.5*	0.7	*0.7*
18		11 / 6	0.6	*0.2*	1.0	0.9	-0.6	-0.3	*-1.0*	0.7	*0.6*
20		11 / 6	0.6	*0.3*	-0.9	0.4	1.2	-1.0	*1.4*	0.8	*0.8*
22		11 / 6	-0.9	*-1.2*	0.7	-0.5	-0.3	-0.9	*3.8*	0.7	*0.7*
24		11 / 6	1.2	*0.7*	-0.2	0.0	0.4	0.3	*2.2*	0.4	*0.3*

1) Referring to compulsory compounds only (max. 11/6)
2) Assigned value was based on only results obtained using ILIS, the z-scores were calculated for informative purpose only.
3) Both the assigned value and the z-score of tolylfluanid were for information only and the z-scores were excluded from the AAZ-calcualtaion.
4) AAZ: Average of Absolute z-scores, is given for informative purposes. It was calculated using all z-scores of each lab using assigned values based on the entire population.
For the calculation of the AAZ of all compulsory compounds except tolylfluanid the value "5" was applied where the z-score was higher than 5 (shown in square brackets).
5) AAZ calculated using for dithiocarbamates, dodine, TFNA, and TFNG the z-scores based on the assigned value derived from the entire population of results submitted by EU and EFTA laboratories, for cyromazine based on the assigned value derived from the sub-population using ILIS and for tolylfluanid based the assigned value derived from the sub-population.
FN = false negative results

Table 4-10 (cont.): Category A laboratories ordered by lab-codes

COMPULSORY Compounds			Cyromazine		Dithiocar-bamates	Dodine	TFNA	TFNG	*Tolylflu-anid*[3]		
Assigned Value [mg/kg]			1.512	*1.647*[2]	1.297	1.243	0.756	0.448	*0.598*		
MRRL [mg/kg]			0.010	*0.010*	0.030	0.010	0.010	0.010	0.010		
*CV**			31.8 %	*25.0 %*	34.6 %	26.2 %	20.0 %	20.7 %	*57.5 %*		
Lab code SRM11-	NRL-SRM	Analysed / corr. found[1]	z-scores	*z-scores*[2]	z-scores	z-scores	z-scores	z-scores	*z-scores*	AAZ[4]	*AAZ*[5]
27		11 / 6	-1.5	*-1.7*	3.2	-3.5	-1.3	-0.8	*0.9*	2.1	*2.1*
28		11 / 6	0.1	*-0.3*	1.1	-0.7	0.3	0.4	*1.8*	0.5	*0.6*
29		11 / 6	-1.5	*-1.7*	1.6	-0.8	0.1	0.2	*0.8*	0.8	*0.9*
31		11 / 6	-3.7	*-3.7*	-2.2	-0.7	-1.0	0.1	*0.3*	1.5	*1.5*
32		10 / 6	-0.9	*-1.2*	-3.3	0.8	-0.1	-1.4	*-3.7*	1.3	*1.4*
34		11 / 6	-0.1	*-0.4*	0.3	1.3	-0.7	-0.6	*2.8*	0.6	*0.7*
35	x	11 / 5	2.9	*2.3*	[7.7]	-0.3	1.2	0.1	*-3.9*[FN]	1.9	*1.8*
36		11 / 6	-0.6	*-0.9*	0.5	-0.5	0.0	-0.1	*0.5*	0.3	*0.4*
38		11 / 6	0.3	*0.0*	0.4	-0.6	0.7	0.0	*-2.0*	0.4	*0.3*
39	x	11 / 6	-1.1	*-1.4*	-1.3	-0.8	-0.7	-0.4	*-0.6*	0.9	*0.9*
40		11 / 6	1.0	*0.6*	1.6	0.5	0.5	0.6	*-1.3*	0.8	*0.8*
41		11 / 6	-1.5	*-1.7*	0.6	-0.9	-0.7	-0.1	*-1.9*	0.8	*0.8*
48		11 / 6	0.2	*-0.1*	0.1	0.2	-0.7	1.0	*1.8*	0.4	*0.4*
49		11 / 6	-0.4	*-0.6*	1.6	0.6	3.3	4.1	*-1.1*	2.0	*2.0*
53		11 / 6	-1.8	*-2.0*	1.4	0.2	-0.3	0.2	*3.8*	0.8	*0.8*
54		11 / 6	2.6	*2.0*	1.4	1.1	0.0	-0.9	*-2.8*	1.2	*1.1*
55		11 / 6	0.2	*-0.2*	-0.7	0.0	-0.2	0.5	*0.5*	0.3	*0.3*
56		10 / 5	0.9	*0.5*	0.8	0.6	0.6	1.2		0.8	*0.7*
57		11 / 6	0.4	*0.1*	-0.2	0.7	0.2	0.5	*-3.6*	0.4	*0.3*
60		11 / 6	0.3	*0.0*	0.6	-1.8	0.3	0.8	*-3.1*	0.8	*0.7*
61		11 / 6	0.5	*0.1*	0.4	0.4	0.1	-0.3	*1.9*	0.3	*0.3*
64		11 / 6	-0.4	*-0.7*	-1.9	-0.7	-0.4	-0.3	*4.0*	0.7	*0.8*
67		10 / 5			0.9	1.2	-1.6	-0.9	*3.2*	1.2	*1.2*
68	x	10 / 5	-0.9	*-1.2*		-0.9	0.3	-0.3	*-0.3*	0.6	*0.7*
69		11 / 6	1.4	*0.9*	1.1	0.1	0.8	-1.0	*-1.1*	0.9	*0.8*
71		11 / 6	1.6	*1.1*	-2.7	-0.5	-1.6	-0.8	*-1.4*	1.4	*1.3*
72		11 / 6	-0.8	*-1.1*	0.5	-1.3	0.1	-0.7	*0.2*	0.7	*0.7*
78	x	11 / 6	0.4	*0.0*	-0.4	-0.4	-0.2	0.2	*-1.9*	0.3	*0.2*
79	x	10 / 5	0.5	*0.1*	-0.5	-0.4		0.4	*-2.7*	0.5	*0.4*
81		11 / 6	1.2	*0.8*	0.4	0.0	0.1	0.2	*0.6*	0.4	*0.3*
91		11 / 6	-0.3	*-0.6*	-0.2	0.2	4.0	0.4	*3.4*	1.0	*1.1*
93	x	11 / 6	0.5	*0.1*	-1.0	[73.6}	-1.9	-1.2	*-1.0*	1.9	*1.8*
94		11 / 6	-0.7	*-0.9*	-0.5	-0.8	0.0	0.2	*0.5*	0.4	*0.5*
106		11 / 6	0.8	*0.4*	0.6	0.2	-1.2	0.0	*-3.3*	0.6	*0.5*
111		10 / 5	2.2	*1.7*		0.4	-0.1	0.7	*3.6*	0.9	*0.7*
115	x	11 / 6	0.8	*0.4*	-0.5	-0.9	-0.2	0.4	*-1.6*	0.6	*0.5*
117		11 / 6	1.5	*1.1*	-0.4	1.4	0.9	1.2	*-2.8*	1.1	*1.0*
119	x	11 / 6	1.0	*0.6*	-2.2	2.2	0.8	2.2	*-1.1*	1.7	*1.6*
127	x	10 / 5	0.7	*0.3*		0.3	0.6	1.1	*-0.7*	0.7	*0.6*
128		11 / 6	0.4	*0.0*	-3.1	4.2	-0.5	0.4	*0.0*	1.7	*1.6*

1) Referring to compulsory compounds only (max. 11/6)
2) Assigned value was based on only results obtained using ILIS, the z-scores were calculated for informative purpose only.
3) Both the assigned value and the z-score of tolylfluanid were for information only and the z-scores were excluded from the AAZ-calcualtaion.
4) AAZ: Average of Absolute z-scores, is given for informative purposes. It was calculated using all z-scores of each lab using assigned values based on the entire population.
For the calculation of the AAZ of all compulsory compounds except tolylfluanid the value "5" was applied where the z-score was higher than 5 (shown in square brackets).
5) AAZ calculated using for dithiocarbamates, dodine, TFNA, and TFNG the z-scores based on the assigned value derived from the entire population of results submitted by EU and EFTA laboratories, for cyromazine based on the assigned value derived from the sub-population using ILIS and for tolylfluanid based the assigned value derived from the sub-population.
FN = false negative results

Table 4-11: Category B laboratories ordered by lab-codes

COMPULSORY Compounds			Cyromazine		Dithiocar-bamates	Dodine	TFNA	TFNG	*Tolylflu-anid*[3]		
Assigned Value [mg/kg]			1.512	*1.647*[2]	1.297	1.243	0.756	0.448	*0.598*		
MRRL [mg/kg]			0.010	*0.010*	0.030	0.010	0.010	0.010	0.010		
*CV**			31.8 %	*25.0 %*	34.6 %	26.2 %	20.0 %	20.7 %	*57.5 %*		
Lab code SRM11-	NRL-SRM	Analysed / corr. found[1]	z-scores	*z-scores*[2]	z-scores	z-scores	z-scores	z-scores	*z-scores*	AAZ[4]	*AAZ*[5]
1		4 / 3			-1.4	-0.2			*0.9*		
5		9 / 5	-2.1	*-2.2*	-3.0	0.1	-1.0	-0.4		1.3	*1.3*
11		9 / 6	0.0	*-0.4*	1.5	-1.2	-1.0	-0.6	*0.4*	0.9	*0.9*
17		3 / 2	-0.2	*-0.5*	0.1						
19	x	5 / 1			-0.3				*-3.9*[FN]		
21		7 / 3	[6.0]	*[5.2]*	0.7	3.1					
23	x	8 / 5	1.1	*0.7*	1.3	2.0	[5.9]		*-2.3*	2.4	*2.3*
25		6 / 3	1.8	*1.4*	1.6	1.2					
26	x	3 / 3	-0.5	*-0.8*	0.0				*-1.1*		
30	x	5 / 2			1.3				*1.2*		
33	x	9 / 4	-0.3	*-0.6*	0.5			1.6	*-2.3*		
37		6 / 3	0.2	*-0.2*		0.7			*-0.5*		
42		9 / 4	0.5	*0.1*	0.8	[5.7]			*-0.9*		
43		3 / 0	-4.0[FN]	*-4.0*[FN]							
45		2 / 0									
46		1 / 1			0.2						
47		1 / 1			1.6						
50	x	8 / 5	0.3	*0.0*		-1.0	-0.7	-0.7	*0.1*	0.7	*0.6*
51		1 / 1			0.1						
52	x	5 / 2			-1.3				*-1.7*		
58		9 / 5	-1.0	*-1.2*	-3.2	-0.7	-0.2		*3.0*	1.3	*1.3*
59		1 / 1			1.1						
62	x	5 / 2	-1.3	*-1.5*					*-0.9*		
63		8 / 3	1.3	*0.9*		1.5			*1.0*		
65		1 / 1			0.6						
66	x	5 / 2	-0.6	*-0.9*					*-1.1*		
70		4 / 1				1.5			*-3.9*[FN]		
73		5 / 2	-1.7	*-1.9*					*-0.7*		
74		4 / 2	2.3	*1.8*					*7.0*		
75		9 / 4	-0.2	*-0.6*	-0.2	-0.4			*2.1*		
76	x	9 / 4	-2.6	*-2.7*	0.7	-0.7			*-0.3*		
77		1 / 0			-3.9[FN]						
80	x	4 / 1	3.3	*2.7*							

1) Referring to compulsory compounds only (max. 11/6)
2) Assigned value was based on only results obtained using ILIS, the z-scores were calculated for informative purpose only.
3) Both the assigned value and the z-score of tolylfluanid were for information only and the z-scores were excluded from the AAZ-calcualtaion.
4) AAZ: Average of Absolute z-scores, is given for informative purposes. It was calculated using all z-scores of each lab using assigned values based on the entire population.
   For the calculation of the AAZ of all compulsory compounds except tolylfluanid the value "5" was applied where the z-score was higher than 5 (shown in square brackets).
5) AAZ calculated using for dithiocarbamates, dodine, TFNA, and TFNG the z-scores based on the assigned value derived from the entire population of results submitted by EU and EFTA laboratories, for cyromazine based on the assigned value derived from the sub-population using ILIS and for tolylfluanid based the assigned value derived from the sub-population.

[#] = Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
[FN] = false negative results

Table 4-11 (cont.): Category B laboratories ordered by lab-codes

COMPULSORY Compounds			Cyromazine		Dithiocar-bamates	Dodine	TFNA	TFNG	*Tolylflu-anid*[3]		
Assigned Value [mg/kg]			1.512	*1.647*[2]	1.297	1.243	0.756	0.448	*0.598*		
MRRL [mg/kg]			0.010	*0.010*	0.030	0.010	0.010	0.010	0.010		
*CV**			31.8 %	*25.0 %*	34.6 %	26.2 %	20.0 %	20.7 %	*57.5 %*		
Lab code SRM11-	NRL-SRM	Analysed / corr. found[1]	z-scores	*z-scores*[2]	z-scores	z-scores	z-scores	z-scores	*z-scores*	AAZ[4]	*AAZ*[5]
82		6 / 2	-2.7	*-2.8*					*-2.9*		
83		9 / 3	-4.0[FN]	*-4.0[FN]*	-0.7	-0.7			*17.8*		
84		4 / 2			0.3	0.4					
86	x	4 / 4	0.2	*-0.2*	1.2	-1.1			*-0.7*		
87		2 / 1			0.4						
88#		11 / 6	0.9	*0.5*	-0.6	2.8	1.3	-0.6	*-3.2*	1.2	*1.2*
89		1 / 1			-3.2						
90		1 / 1				3.7					
92		1 / 1			0.4						
95		1 / 1			0.4						
96	x	7 / 3	-1.2	*-1.4*	-2.4	-0.9			*-4.0[FN]*		
97		4 / 3	-0.4	*-0.7*	-0.8				*-2.0*		
98		6 / 3	-1.4	*-1.6*		-0.1			*4.7*		
100		1 / 1			1.6						
101		1 / 1			1.1						
102	x	4 / 1			3.7						
103		1 / 1			0.1						
104		1 / 0									
105		4 / 2	-0.6	*-0.8*		-0.3					
107		5 / 2	-3.0	*-3.1*		-3.6					
108		1 / 1			1.0						
109		4 / 0									
110		2 / 2				-0.5			*-2.4*		
112		1 / 1			0.4						
114		9 / 5	-1.0	*-1.2*	-2.3	-2.1	-3.9	-1.7	*1.8*	2.2	*2.2*
116		4 / 2			-1.5				*0.6*		
118		9 / 5	0.2	*-0.1*		1.8	0.0	0.8	*1.4*	0.7	*0.7*
120		5 / 2	-1.0	*-1.3*					*-3.2*		
121		1 / 1			-2.1						
122		1 / 1			0.9						
123		3 / 2			0.7	0.0					
3rd-44		7 / 3	-3.4	*-3.5*	-0.8				*0.5*		
3rd-126		6 / 5			-0.9	-1.3	1.1	1.7	*-1.9*		

1) Referring to compulsory compounds only (max. 11/6)
2) Assigned value was based on only results obtained using ILIS, the z-scores were calculated for informative purpose only.
3) Both the assigned value and the z-score of tolylfluanid were for information only and the z-scores were excluded from the AAZ-calcualtaion.
4) AAZ: Average of Absolute z-scores, is given for informative purposes. It was calculated using all z-scores of each lab using assigned values based on the entire population.
For the calculation of the AAZ of all compulsory compounds except tolylfluanid the value "5" was applied where the z-score was higher than 5 (shown in square brackets).
5) AAZ calculated using for dithiocarbamates, dodine, TFNA, and TFNG the z-scores based on the assigned value derived from the entire population of results submitted by EU and EFTA laboratories, for cyromazine based on the assigned value derived from the sub-population using ILIS and for tolylfluanid based the assigned value derived from the sub-population.
# = Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
FN = false negative results

4.4.5 Laboratory Feedback in Case of Poor Results

As a follow-up measure to this EUPT, all participating laboratories that had achieved questionable ($2 < |z\text{-score}| < 3$) or unacceptable ($|z\text{-score}| \geq 3$) results were asked to investigate the reasons for their poor performance and to report them to the organisers. This was done in order to sensibilize the laboratories to investigate the sources of errors. A compilation of the feedback received by the laboratories is given in **Appendix 7**. Where the feedback received from the participants was not conclusive or contradictory to the methodology information, the organizers contacted the laboratories, asked specific questions to clarify the information and to help the laboratories better localize the sources of errors. Where the methodology data suggested different sources of errors, this was communicated, too. The information received from this interaction with the laboratories has been also integrated in the feeback-compilation in **Appendix 7**. To improve clarity, the various types of errors were coded. Where the error sources reported was only a weak suggestion or not supported by the methodology data, this was marked by placing it in brackets. Where the methodology or the additional feedback received through e-mails suggested additional or alternative sources of errors, this was communicated. The compilation of the feedback information and the conclusions about the error sources provide valuable input not only to the laboratories but also to NRLs and can them better assist OfLs in improving their performance.

In the current PT and excluding ***dithianon*** that achived a CV^*-value of 94 % and an assigned value with high uncertainty, in total, 144 results reported by 67 laboratories were evaluated with $|z| > 2$, thereof 96 results reported by 53 laboratories being evaluated with $|z| \geq 3$ (please see **Table 4-6, p. 37**). As regards EU and EFTA laboratories $|z| > 2$ was assigned to 143 results with 95 of them being evaluated with $|z| \geq 3$. Following intensive correspondence with the participants, all regarding laboratories responded to the organisers with (possible) reasons for their poor performance in all cases but one. In 52 of those case the real reasons could not be clarified inspite of intensive investigation. All of the 6 false negative results concerning ***quizalofop*** resulted from misunderstanding of the definition of the target analyte: Instead of ***quizalofop*** its ethylester was sought for. The most frequently reported error source (136 cases) layed in the erroneous or inappropriate calibration, e.g., error in concentration of stock or working standard solution. In 127 cases the participants' poor performance may have resulted from the presence of the analytes in the EUPT-Blank material and the assosiated difficulties in dealing with the matrix effects. Matrix effect not properly compensated (33 cases), degradation prior to analysis due to inappropiated storage or per-treatment (32 cases), results not properly corrected for recovery (29 cases), lack of experience (26 cases), application of inappropiate analytical procedures 22 cases), errors in transcription, documentation and calculation (19 cases) and QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results (17 cases) were the other frequently reasons for the poor performance. In a few cases the participants reported problems with measurement (7 cases), procedure not properly conducted (6 cases), misinterpretation of data (5 cases) and inter-portion variabilities (3 cases) as the reasons.

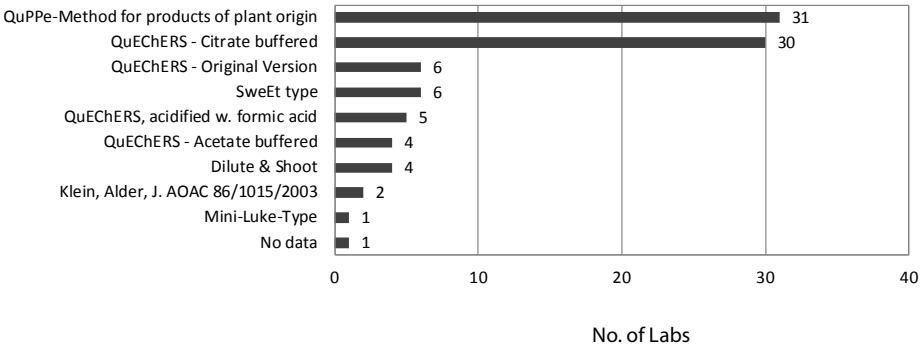
The two laboratories that have reported false positive results were also asked to provide feedback. One of them stated lacking of experience with the commodity, lacking of validation of the analytical method used for the PT-commodity and misintepretation of the chromatographical signal as the main error source in its false positive result of *ethephon*. The other laboratory reported interference in the method applied and misinterpretation of the data for *ethephon* and *glyphosate* as possible reason for the false positives results.

4.5 Methodological Information

4.5.1 Analytical methods used

An overview of the methods used by the participating labs for sample preparation and determination for each analyte present in the test item can be seen in **Figure 4-1**. No specific recommendations on the analytical procedure to be used were made by the organiser, as the laboratories were prompted to use the procedures employed or intended to be employed for official controls in their laboratories.

Cyromazine: Sample preparation



Cyromazine: Determinative technique

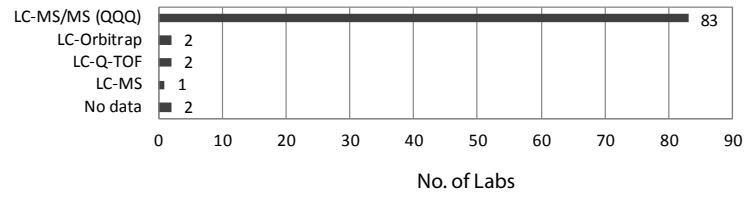
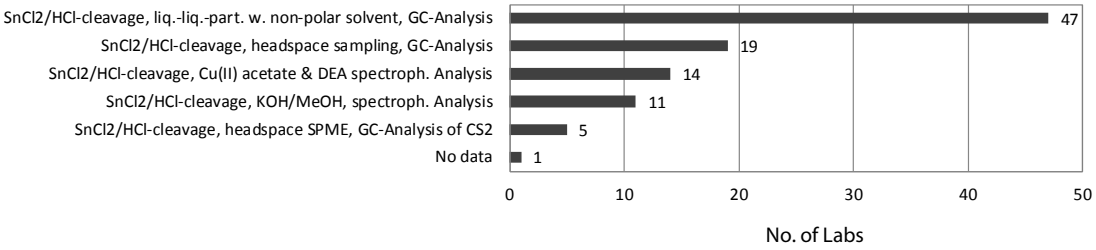
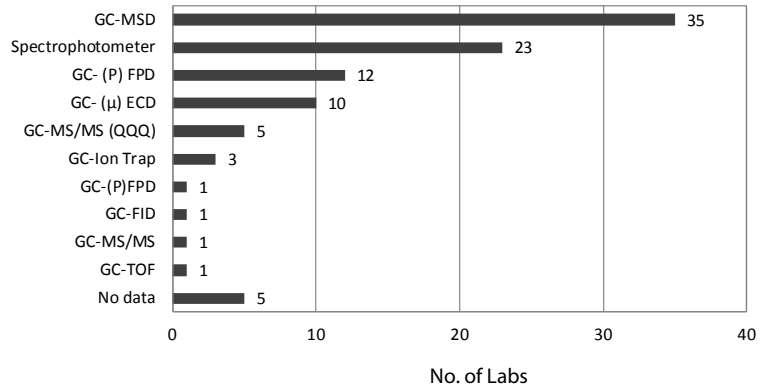


Figure 4-1: Methods applied for sample preparation and determinative technique by laboratories as reported

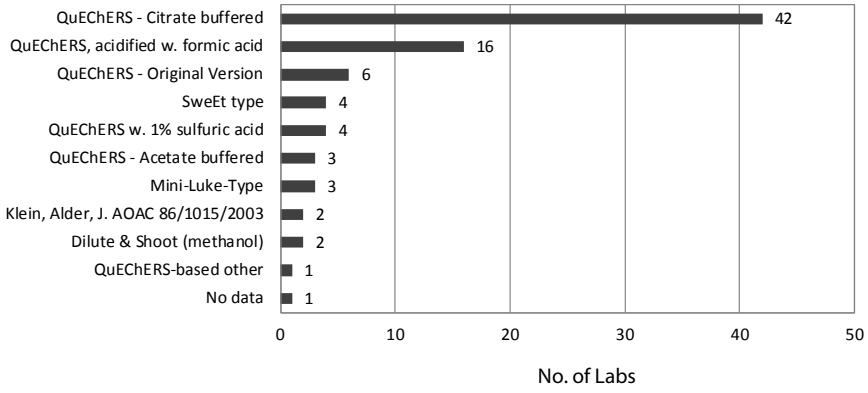
Dithiocarbamates: Sample preparation



Dithiocarbamates: Determinative technique



Dodine: Sample preparation



Dodine: Determinative technique

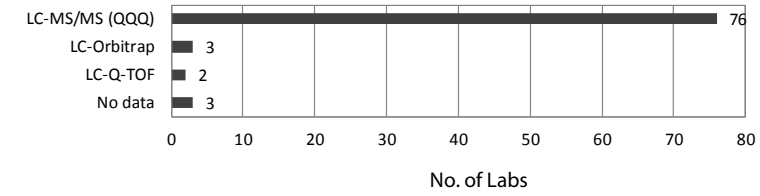
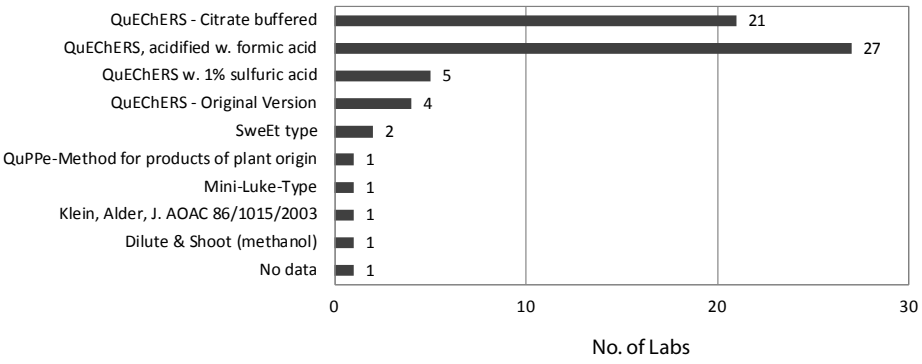
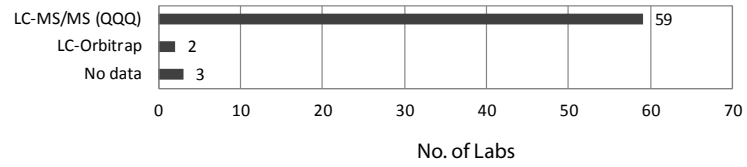


Figure 4-1 (cont.): Methods applied for sample preparation and determinative technique by laboratories as reported

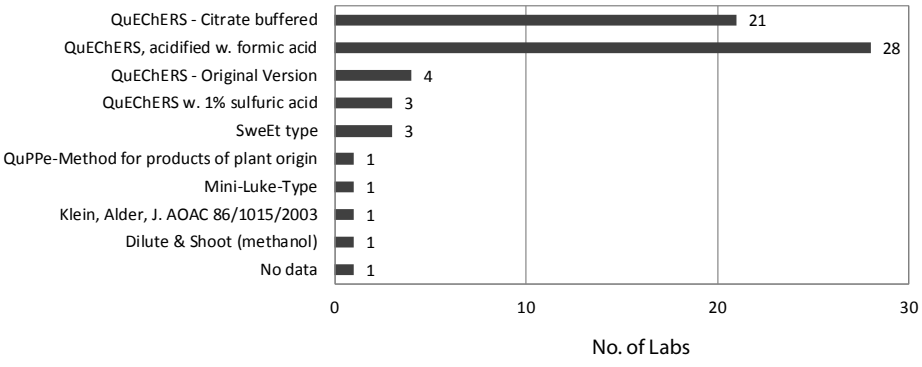
TFNA: Sample preparation



TFNA: Determinative technique



TFNG: Sample preparation



TFNG: Determinative technique

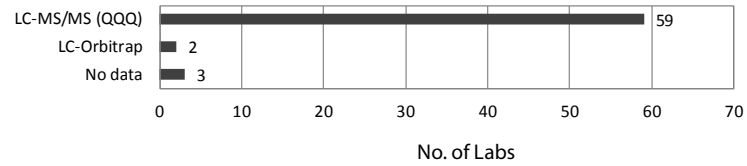
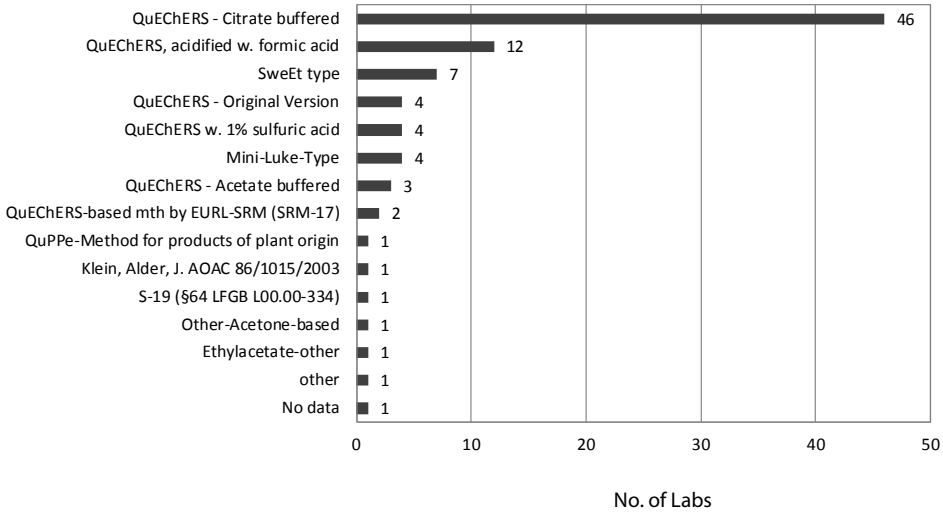
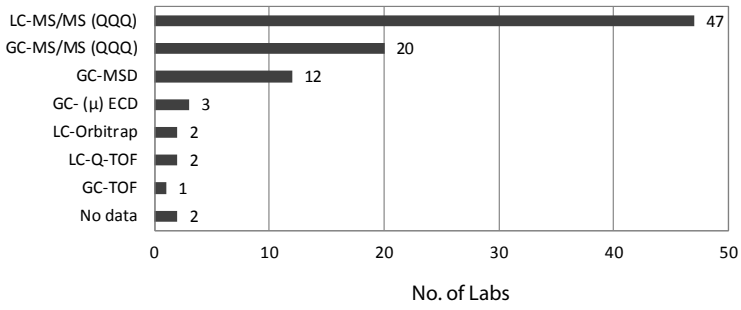


Figure 4-1 (cont.): Methods applied for sample preparation and determinative technique by laboratories as reported

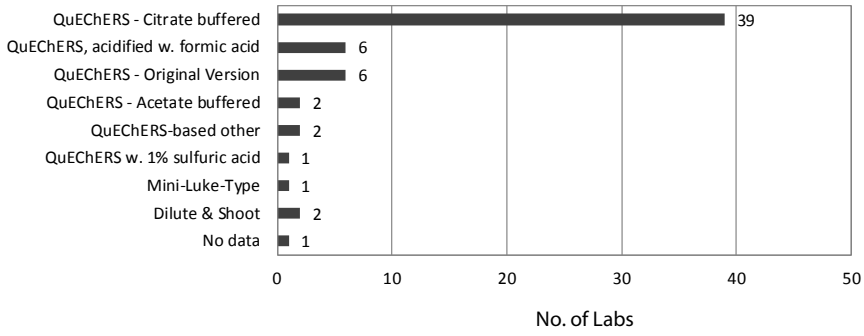
Tolylfluanid: Sample preparation



Tolylfluanid: Determinative technique



BAC-C14: Sample preparation



BAC-C14: Determinative technique

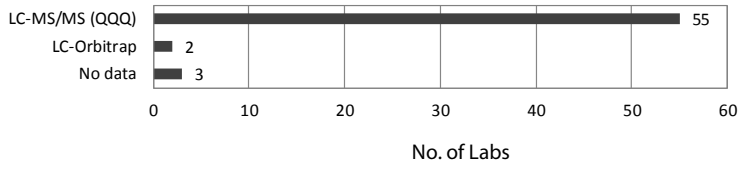
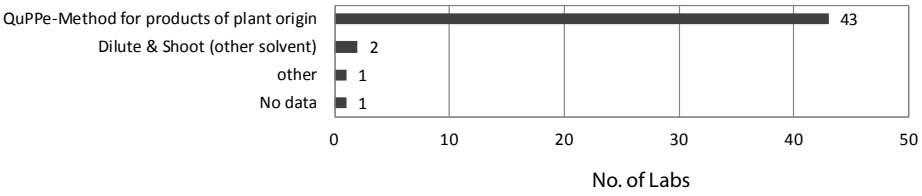
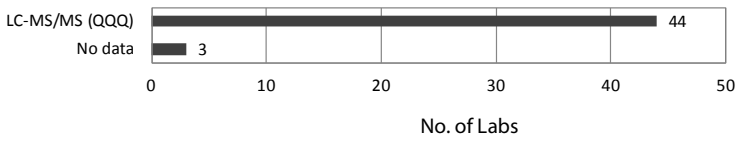


Figure 4-1 (cont.): Methods applied for sample preparation and determinative technique by laboratories as reported

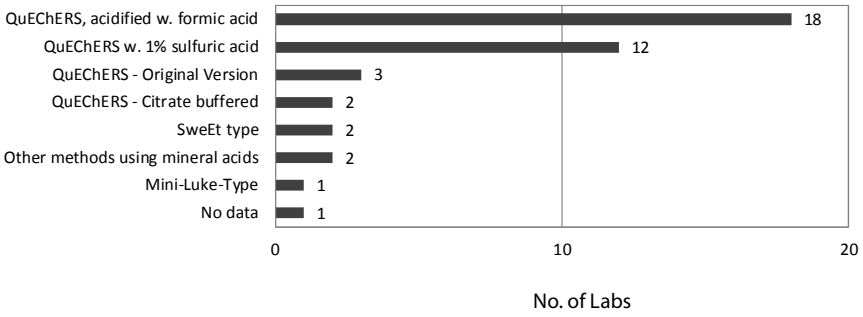
Chlorate: Sample preparation



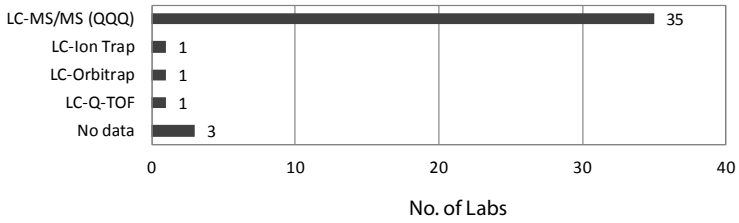
Chlorate: Determinative technique



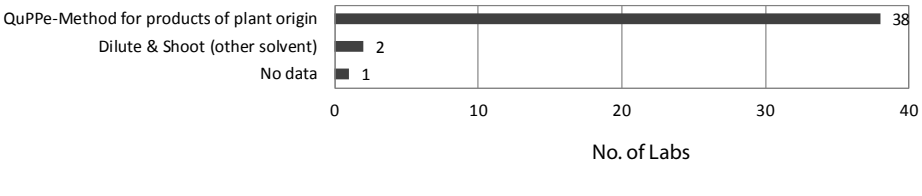
Dithianon: Sample preparation



Dithianon: Determinative technique



Phosphonic acid: Sample preparation



Phosphonic acid: Determinative technique

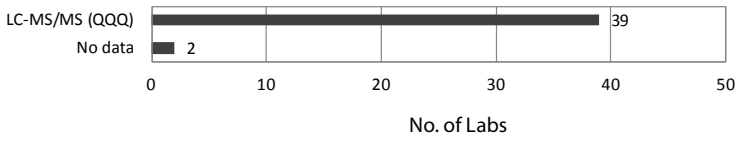
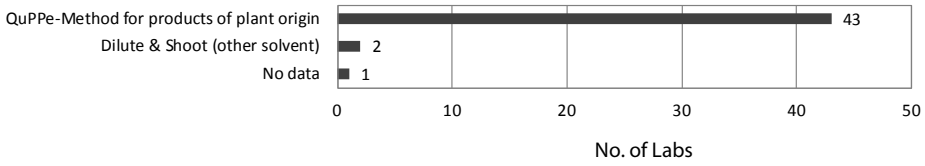
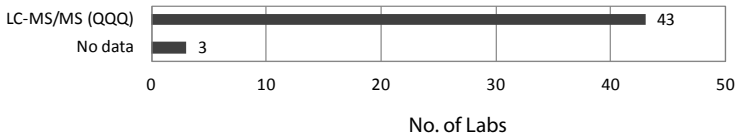


Figure 4-1 (cont.): Methods applied for sample preparation and determinative technique by laboratories as reported

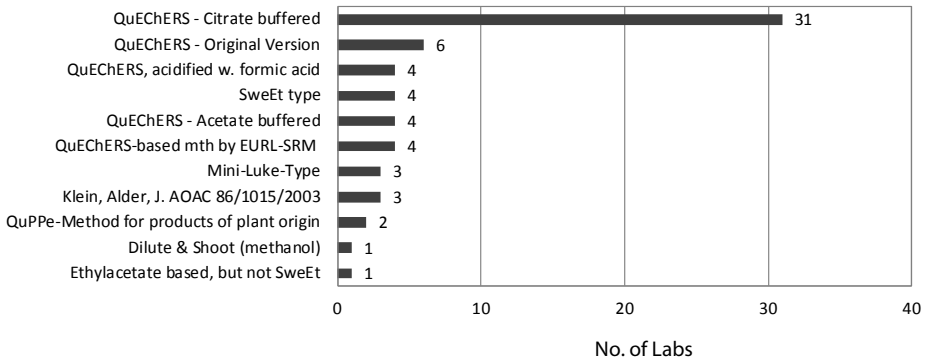
Perchlorate: Sample preparation



Perchlorate: Determinative technique



Pymetrozine: Sample preparation



Pymetrozine: Determinative technique

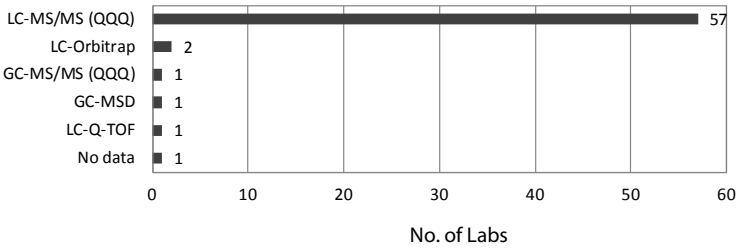
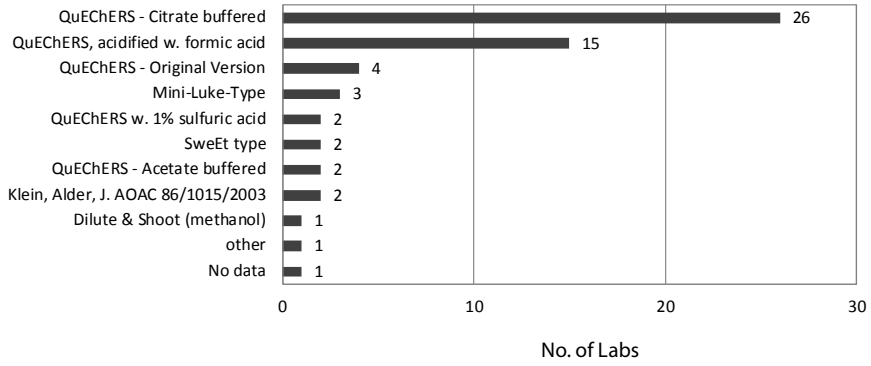
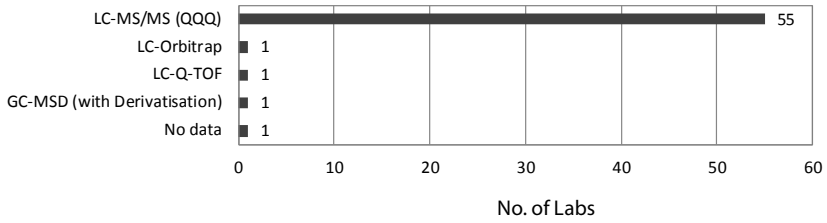


Figure 4-1 (cont.): Methods applied for sample preparation and determinative technique by laboratories as reported

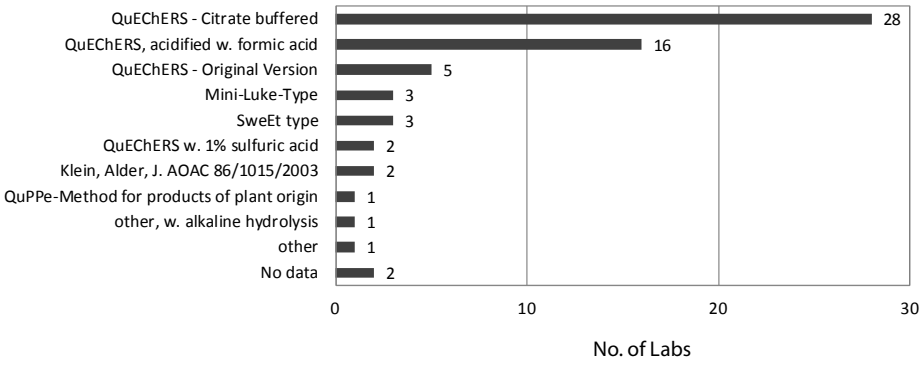
Quizalofop: Sample preparation



Quizalofop: Determinative technique



Triclopyr: Sample preparation



Triclopyr: Determinative technique

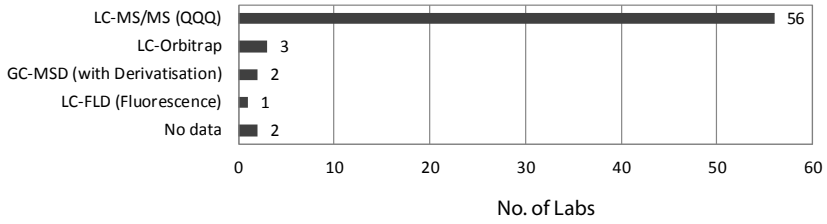


Figure 4-1 (cont.): Methods applied for sample preparation and determinative technique by laboratories as reported

4.5.2 Initial Sample Temperature and Extraction Time

Since both temperature and extraction time can influence the stability and/or the extractability of certain pesticides. Therefore, the participants were asked to indicate the initial temperature as well as the extraction times entailed in their procedure. Experiments by the organizers have shown that for the compounds present in the test item there were no issues with retarded extractability. The participants' results were thus not evaluated regarding this issue. The experiments have, however, shown that extraction time and temperature have a strong influence of ***dithianon*** and ***tolylfluaid***.

Table 4-12 gives an overview of the extraction times and initial sample temperatures employed by the various participating laboratories using QuEChERS and QuPPe. As can be seen in this table, laboratories have left their analytical portions to reach room temperature before starting analysis in roughly one out of four cases in the case of QuEChERS and in one out of three cases in case of QuPPe. In total, laboratories have started their QuEChERS extraction in a defrosted state in more than 60 % of the cases. Not distinguishable in this table are the cases where labs have left the test items to initially defrost in order to easily proceed with the preparation of the analytical portions foreseen to be processed within the PT, followed by a re-freezing of these portions until analysis.

Various tests by the organizers, including the transport simulation stability tests (see **Section 1.8, p. 7**) demonstrated that the levels of ***dithianon*** and ***tolylfluaid*** drop rapidly when sample homogenates of high pH (such as spinach) are left to defrost. The influence on the other compounds present in the test item was insignifficant if the material was not let in a defrosted state for many days. **Table 4-12** shows also the data specifically for ***dithianon*** and ***tolylfluaid***.

Dithianon has a tendency to form radicals and to conjugate with matrix components. In thawed homogenates of commodities exhibiting high pH and poor antioxidative potential, its concentration declines rapidly. Losses are also noticed in frozen homogenates but at a much slower rate. To minimize losses samples should be immediately acidified (preferably during homogenization). The addition of antioxidants is also helpful. ***Tolylfluaid*** is mainly sensitive to hydrolysis at high pH with the hydrolysis rate being higher at higher temperatures.

Table 4-13 (p. 66) demonstrates how thawing the test item has caused a strong concentration drop of ***dithianon*** and ***tolylfluaid*** of many participants. To allow a comparison of the initial sample temperature, only results of laboratories having employed methods involving acidification are compared. Regarding ***dithianon***, the robust mean concentration of laboratories employing the sample in deep frozen conditions was more than double as high as the respective level determined by labs emplyoing the sample at ambient temperature. A similar effect was observed with ***tolylfluaid*** (see **Table 4-13**). In the case of ***tolylfluaid*** the results confirm organizer's own observations that acidification is not absolutely necessary when samples are analyzed in frozen condition.

Even though the sub-populations compared here are small and the statistical certainty is therefore poor, the general trend is evident.

In the case of ***dithiocarbamates***, the influence of the reaction time on the determined levels of CS_2 is discussed in **Section 4.5.9 (p. 79)**.

Table 4-12: Initial temperature and extraction time for sample preparation using QuEChERS and QuPPe methods

Extraction time	Initial sample temperature													
	deep frozen (- 18 °C)	slightly frozen (- 8 °C – 0 °C)	just thawed	cold (4 °C – 10 °C)	ambient (20 °C – 24 °C)	No data	Sum	deep frozen (- 18 °C)	slightly frozen (- 8 °C – 0 °C)	just thawed	cold (4 °C – 10 °C)	ambient (20 °C – 24 °C)	No data	Sum
	QuEChERS (all analytes)							QuPPe (all analytes)						
0.5 min					3		3							
1 min	25	10	36	40	24		135	6	6	6	10	12		40
2 min	7	26	1	16	22	1	73		2		11	5		18
3 min	13		5				18	3						3
5 min		12			9	8	29	2				9		11
10 min	9	19	9	15	31		83	4	6	3	4	13		30
15 min	30			29	37		96	7			7	7		21
20 min		12	12	7	2		33	4	4	3		3		14
25 min	12			6			18							
30 min	13	8	5		3		29	3	2	3	3			11
60 min										1				1
No data				10	8	3	21	1			3	3	3	10
Sum	**109**	**87**	**68**	**123**	**139**	**12**	**538**	**30**	**20**	**16**	**38**	**52**	**3**	**159**

Extraction time	Initial sample temperature													
	deep frozen (- 18 °C)	slightly frozen (- 8 °C – 0 °C)	just thawed	cold (4 °C – 10 °C)	ambient (20 °C – 24 °C)	No data	Sum	deep frozen (- 18 °C)	slightly frozen (- 8 °C – 0 °C)	just thawed	cold (4 °C – 10 °C)	ambient (20 °C – 24 °C)	No data	Sum
	QuEChERS (Dithianon)							QuEChERS (Tolyfluanid)						
0.5 min					1		1							
1 min	3		4	2	1		10	2	2	4	5	5		18
2 min	1	2			1		4		3		4	1	1	9
3 min	1						1	3		1				4
5 min		1			1		2		2			1	1	4
10 min		2	1		1		4	1	3	1	2	4		11
15 min	3			3	3		9	4			4	4		12
20 min			1				1		2	1	1	1		5
25 min								1			1			2
30 min								2	1	1				4
No data				1	1		2				1	1		2
Sum	**8**	**5**	**6**	**6**	**9**	**0**	**34**	**13**	**13**	**8**	**18**	**17**	**2**	**71**

Table 4-13: Impact of initial temperature on the results of dithianon and tolylfluanid. Due to the insufficient number of data, an evaluation of dithianon results reported by labs not acidifying the samples during analysis was not deemed reasonable.

	Dithianon (Sample preparation involving acidification)		
	Entire Population	**Initial sample temperature: Ambient**	**Initial sample temperature: Deeply frozen**
No. of Results (total)	30	8	8
No. of Results (numerical)	29	8	8
No. of FN	1	0	0
Robust Mean [mg/kg]	**1.862**	**1.278**	**3.357**
*CV**	89.0 %	103.9 %	71.7 %
	Tolylfluanid (Sample preparation without acidification)		
	Entire Population	**Initial sample temperature: Ambient**	**Initial sample temperature: Deeply frozen**
No. of Results (total)	60	14	11
No. of Results (numerical)	57	14	11
No. of FN	3	0	0
Robust Mean [mg/kg]	**0.576**	**0.447**	**0.824**
*CV**	62.5 %	67.3 %	39.7 %
	Tolylfluanid (Sample preparation involving acidification)		
	Entire Population	**Initial sample temperature: Ambient**	**Initial sample temperature: Deeply frozen**
No. of Results (total)	26	8	5
No. of Results (numerical)	26	0	0
No. of FN	0	0	0
Robust Mean [mg/kg]	**0.621**	**0.556**	**0.827**
*CV**	50.1 %	55.0 %	33.5 %

4.5.3 Calibration Approaches

Table 4-14 gives an overview of the calibration types as well as the use or non-use of internal standards by the participants within this PT. The standard additions approach was employed in 24 % of the cases (14 % with additions to the sample portions at the beginning of extraction and 10 % with addition to the extract aliquots). 46 % of the results were generated using matrix-matched calibration. 16 % of the results were generated using solvent-based calibrations and 12 % of the results were generated using procedural calibration. Among the 368 cases where matrix-based calibrations were employed only in 7 cases blank material other than the EUPT-Blank was used.

Among the 129 cases where calibration solutions were prepared in pure solvent ILISs were applied in 15 cases (ca. 2 % of the cases). 9 % of the results (69 cases) were generated without the use of internal standards, and 44 (5 %) using other internal standards.

Table 4-14: Calibration approaches employed for the analysis of the target compounds combined with the internal standards used in the EUPT-SRM11 (excluded dithiocarbamates)

	Internal Standard used?										Internal Standard used?				
	COMPULSORY COMPOUNDS					OPTIONAL COMPOUNDS					Overall				
Calibration type	ILIS was used	Other IS was used	No IS was used	No data	Sum	ILIS was used	Other IS was used	No IS was used	No data	Sum	ILIS was used	Other IS was used	No IS was used	No data	Sum
Matrix-based (mainly matrix-matched)	7 (2 %)	82 (21 %)	97 (25 %)	6 (2 %)	**192 (49 %)**	16 (4 %)	59 (14 %)	98 (24 %)	3 (1 %)	**176 (43 %)**	23 (6 %)	141 (34 %)	195 (24 %)	9 (1 %)	**368 (46 %)**
Pure solvent based	1 (0 %)	24 (6 %)	27 (7 %)	0 (0 %)	**52 (13 %)**	14 (3 %)	20 (5 %)	42 (10 %)	1 (0 %)	**77 (19 %)**	15 (4 %)	44 (11 %)	69 (9 %)	1 (0 %)	**129 (16 %)**
Procedural	1 (0 %)	18 (5 %)	26 (7 %)	0 (0 %)	**45 (12 %)**	12 (3 %)	16 (4 %)	24 (6 %)	0 (0 %)	**52 (13 %)**	13 (3 %)	34 (8 %)	50 (6 %)	0 (0 %)	**97 (12 %)**
Standard addition to extract aliquots	2 (1 %)	12 (3 %)	32 (8 %)	0 (0 %)	**46 (12 %)**	6 (1 %)	7 (2 %)	25 (6 %)	0 (0 %)	**38 (9 %)**	8 (2 %)	19 (5 %)	57 (7 %)	0 (0 %)	**84 (10 %)**
Standard addition to sample portions	1 (0 %)	25 (6 %)	21 (5 %)	3 (1 %)	**50 (13 %)**	15 (4 %)	20 (5 %)	19 (5 %)	7 (2 %)	**61 (15 %)**	16 (4 %)	45 (11 %)	40 (5 %)	10 (1 %)	**111 (14 %)**
no data	0 (0 %)	0 (0 %)	0 (0 %)	5 (1 %)	**5 (1 %)**	3 (1 %)	2 (0 %)	0 (0 %)	5 (1 %)	**10 (2 %)**	3 (1 %)	2 (0 %)	0 (0 %)	10 (1 %)	**15 (2 %)**
Overall	**12 (3 %)**	**161 (41 %)**	**203 (52 %)**	**14 (4 %)**	390 (100%)	**66 (16 %)**	**124 (30 %)**	**208 (50 %)**	**16 (4 %)**	414 (100%)	**78 (19 %)**	**285 (69 %)**	**411 (51 %)**	**30 (4 %)**	**804 (100%)**

* Percentages in parentheses based on total number of results = 804

4.5.4 Use of Internal standards (ISs)

ISs are typically applied to correct for recovery, volume deviations and/or to compensate for the influence of matrix on measurement or derivatisation. An overview of the ISs used by the participants in the present PT is shown in **Table 4-15**. Approximately 42 % of the results were generated using ISs, thereof ILISs were employed in only 9 % of the cases overall. In the case of compulsory compounds only 12 results (3 %) were generated using ILIS, all for ***cyromazine***. 2 laboratories used $^{13}CS_2$ as ILIS. Although ILISs of ***TFNA***, ***TFNG*** and ***tolyfluanid*** are commercially available, no participants reported their use. In the case of optional compounds ILISs were employed 9 % of the cases on average, with ***perchlorate*** (53 %), ***chlorate*** (48 %) and ***phosphonic acid*** (43 %) leading the list by far. This was not surprsing, since the ILISs of these compounds were provided by the organisers to the participants in order to assist the participating laboratories in analysis. ILISs offer the highest accuracy and are recommended for both recovery correction and matrix-effect correction. As demostrated in previous PTs and in **Table 4-16 (p. 69)**, the variability of the results of ***cyromazine***, ***perchlorate***, ***chlorate*** and ***phosphonic acid*** submitted by laboratories using ILISs was clearly narrower than those of laboratories not using them.

Table 4-15: Use of internal standards for the analysis of the compounds in the EUPT-SRM11

COMPULSORY COMPOUNDS								
Q: was IS used?	**ISs were added to...**	**Cyromazine**	**Dodine**	**Dithiocarbamates**	**TFNA**	**TFNG**	**Tolylfluanid**	**Sum**
Yes, ILIS was used	**Subtotal**	**12 (13 %)**	**–**	**2 (2 %)**	**–**	**–**	**–**	**14 (3 %)**
	1) at the beginning of procedure	12 (13 %)	–	1 (1 %)	–	–	–	13 (3 %)
	2) at an intermediate stage (between 1 and 3)	–	–	1 (1 %)	–	–	–	1 (< 1 %)
	3) to an aliquot of the final extract	–	–	–	–	–	–	–
Yes, other IS was used	**Subtotal**	**28 (31 %)**	**38 (45 %)**	**9 (9 %)**	**25 (39 %)**	**24 (38 %)**	**46 (52 %)**	**170 (35 %)**
	1) at the beginning of procedure	24 (27 %)	33 (39 %)	6 (6 %)	22 (34 %)	21 (33 %)	39 (44 %)	145 (30 %)
	2) at an intermediate stage (between 1 and 3)	2 (2 %)	2 (2 %)	–	2 (3 %)	2 (3 %)	1 (1 %)	9 (2 %)
	3) to an aliquot of the final extract	2 (2 %)	3 (4 %)	3 (3 %)	1 (2 %)	1 (2 %)	6 (7 %)	16 (3 %)
	No data	–	–	–	–	–	–	–
No	–	46 (52 %)	43 (51 %)	81 (84 %)	37 (58 %)	38 (59 %)	39 (44 %)	284 (58 %)
No data	–	3 (3 %)	3 (4 %)	5 (5 %)	2 (3 %)	2 (3 %)	4 (4 %)	19 (4 %)
Overall Sum		**89**	**84**	**97**	**64**	**64**	**89**	**487**

Table 4-16 shows for ***cyromazine***, ***phosphonic acid***, ***chlorate*** and ***perchlorate*** a comparison of the robust mean concentration derived from the entire population of data against the robust mean of the sub-populations using ILIS and not using ILIS. Setting the robust mean concentration of the entire population (which was used to calculate the z-scores) at 100 %, the distance of the robust mean of the sub-population using ILIS was +9 % in the case of ***cyromazine***, +7 % in the case of +20 % in the case of ***chlorate***, and -10 % in the case of ***perchlorate***. In addition to the regular evaluation using the entire dataset the EUPT-Scientific Committee decided to calculate for informative purposes the alternative assigned values based on the robust mean of the sub-population using ILIS in the case of ***cyromazine***, ***chlorate*** and ***perchlorate***. Interesting was the great distance between the robust mean concentrations of the sub-populations using and not using ILIS which was +10 percentage points in the case of ***cyromazine***, +13 percentage points in the case of ***phosphonic acid***, +38 percentage points in the case of ***chlorate*** and -28 percentage points in the case of ***perchlorate***.

Roughly, one out of three results (293 of 901) was generated using a generic IS. Thereof, triphenyl phosphate (73 cases) and nicarbazin (35 cases) were the are often used generic ISs. In the case of ***dithiocarbamates***, laboratories used thiophene (4 cases) or chloroform (3 cases) as ISs. Generic ISs mainly correct for volumetric errors, spills, and to some extend also for sensitivity drifts of instruments. They can even partly compensate for matrix effects for target analytes showing a similar matrix-effect trend as the IS. In general, generic IS are chosen to show little matrix effects and virtually quantitative recoveries. Recovery-based correction through generic ISs is thus typically minor. In case of significant matrix effects, specifically on the IS (e.g., in LC-analysis) a significant bias may be, however, added to all analytes which makes their use tricky.

	OPTIONAL COMPOUNDS										ALL
	Q: was IS used?	ISs were added to...	BAC–C14	Chlorate	Dithianon	Perchlorate	Phosphonic acid	Pymetrozine	Quizalofop	Triclopyr	Sum	Overall
	Yes, ILIS was used	**Sum**	**1 (2 %)**	**22 (48 %)**	**2 (5 %)**	**24 (53 %)**	**17 (43 %)**	**–**	**–**	**–**	**66 (16 %)**	**80 (9 %)**
		1) at the beginning of procedure	1 (2 %)	18 (39 %)	2 (5 %)	20 (44 %)	13 (33 %)	–	–	–	54 (13 %)	67 (7 %)
		2) at an intermediate stage (between 1 and 3)	–	1 (2 %)	–	1 (2 %)	2 (5 %)	–	–	–	4 (1 %)	5 (1 %)
		3) to an aliquot of the final extract	–	3 (7 %)	–	3 (7 %)	2 (5 %)	–	–	–	8 (2 %)	8 (1 %)
	Yes, other IS was used	**Sum**	**21 (35 %)**	**5 (11 %)**	**15 (38 %)**	**2 (4 %)**	**5 (13 %)**	**26 (43 %)**	**22 (38 %)**	**27 (42 %)**	**123 (30 %)**	**293 (33 %)**
		1) at the beginning of procedure	18 (30 %)	5 (11 %)	12 (30 %)	2 (4 %)	4 (10 %)	21 (34 %)	16 (28 %)	22 (34 %)	100 (24 %)	245 (27 %)
		2) at an intermediate stage (between 1 and 3)	–	–	–	–	1 (3 %)	1 (2 %)	2 (3 %)	1 (2 %)	5 (1 %)	14 (2 %)
		3) to an aliquot of the final extract	3 (5 %)	–	3 (8 %)	–	–	4 (7 %)	4 (7 %)	4 (6 %)	18 (4 %)	34 (4 %)
		No data	–	–	–	–	1 (3 %)	–	–	–	1 (< 1 %)	1 (< 1 %)
	no	–	36 (60 %)	18 (39 %)	21 (53 %)	18 (40 %)	15 (38 %)	35 (57 %)	31 (53 %)	34 (53 %)	208 (50 %)	492 (55 %)
	no data	–	2 (3 %)	1 (2 %)	2 (5 %)	1 (2 %)	2 (5 %)	–	5 (9 %)	3 (5 %)	16 (4 %)	35 (4 %)
	Overall		**60**	**46**	**40**	**45**	**40**	**61**	**58**	**64**	**414**	**901**

Table 4-16: Impact of ILISs on the distribution of results and the average bias (only results from EU and EFTA laboratories were taken into account)

	Cyromazine			Phosphonic acid		
	All Results	Results Obtained Using ILIS	Results Obtained without ILIS	All Results	Results Obtained Using ILIS	Results Obtained without ILIS
Robust Mean [mg/kg]	1.512	1.647	1.491	9.831	10.516	9.249
*CV**	31.8 %	**19.8 %**	33.3 %	29.5 %	**26.6 %**	31.1 %
AAZ [1] (average bias)	1.19	**0.66**	1.14	1.08	**0.79**	1.14
No. of results [2]	88	12	76	40	17	23
No. (%) of acceptable results	73 (83 %)	11 (92 %)	65 (86 %)	35 (88 %)	17 (100 %)	17 (74 %)
No. (%) of questionable results	9 (10 %)	1 (8 %)	6 (8 %)	1 (3 %)	0 (0 %)	3 (13 %)
No. (%) of unacceptable [2] results	6 (7 %)	0 (0 %)	5 (6 %)	4 (10 %)	0 (0 %)	3 (13 %)
	Chlorate			**Perchlorate**		
	All Results	Results Obtained Using ILIS	Results Obtained without ILIS	All Results	Results Obtained Using ILIS	Results Obtained without ILIS
Robust Mean [mg/kg]	2.033	2.443	1.668	0.260	0.234	0.307
*CV**	44.6 %	**15.5 %**	65.8 %	35.9 %	**23.5 %**	53.4 %
AAZ [1] (average bias)	1.56	**0.76**	1.81	1.75	**1.03**	1.97
No. of results [2]	46	22	24	45	24	21
No. (%) of acceptable results	33 (72 %)	20 (91 %)	14 (58 %)	34 (76 %)	20 (83 %)	11 (52 %)
No. (%) of questionable results	6 (13 %)	0 (0 %)	4 (17 %)	4 (9 %)	0 (0 %)	4 (19 %)
No. (%) of unacceptable [2] results	7 (15 %)	2 (9 %)	6 (25 %)	7 (16 %)	4 (17 %)	6 (29 %)

1) z-scores calculated using the robust mean in the corresponding population, "5" was used in case of the z-score was higher than 5
2) including false negative results

Table 4-17: Example of a negative impact of using a generic IS in the case of pymetrizine (only results from EU and EFTA laboratories were taken into account)

	Pymetrozine		
	All Results	**Results Obtained using ISs and added at Beginning of the procedure**	**Results obtained without using any ISs**
Robust Mean [mg/kg]	0.432	0.363	0.445
CV*	42.3 %	**52.5 %**	35.5 %
AAZ [1] (average bias)	1.80	**1.65**	1.31
No. of results [2]	62	21	35
No. (%) of acceptable results	47 (76 %)	14 (67 %)	29 (83 %)
No. (%) of questionable results	4 (6 %)	3 (14 %)	2 (6 %)
No. (%) of unacceptable [2] results	11 (18 %)	4 (19 %)	4 (11 %)

Table 4-17 shows, in the case of pymetrozine, a comparison of results reported by laboratories using various generic ISs with the results of laboratories not using IS. Overall the results of laboratories using generic ISs showed a broader sidtribution than the results of laboratories not using it.

Among the 293 cases where ISs were used they were added at the beginning of the procedure, in 245 cases (84 %), at an intermediate stage in 14 cases (5 %) and to an aliquot of the final extract in 34 cases (12 %).

4.5.5 Correction of Results for Recovery

The various approaches employed by the laboratories to correct their results for recovery are summerised in **Table 4-18**. Recovery corrections can be accomplished by using ILISs or other approaches. In many cases other approaches were combined with the use of ILISs for better accuracy. Regarding compulsory analytes and xcluding ***dithiocarbamates***, laboratories reported results which were corrected for recovery via various approaches in 129 out of 390 cases (33 % overall). Thereof, procedural calibrations were used in 45 cases (12 %), standard additions to sample portions in 50 cases (13 %) and recovery factors in 24 cases (6 %). ILISs were in 9 cases (2 %) used as the sole means of recovery-based result correction, and in 3 cases (< 1 %) in combination with other approaches correcting for recovery. Standard additions to extract aliquots, an approach only correcting results for matrix effects and not for recovery unless combined with other means for recovery correction, were used in 45 cases (12 %). Among the compulsory ones ***cyromazine*** was the compound most frequently corrected for recovery (48 %, 43 out of 89 cases), followed by ***dodine*** (30 %, 25 out of 84 cases), ***tolylfluanid*** (29 %, 26 out of 89 cases), ***TFNA*** (27 %, 17 out of 64 cases) and ***TFNG*** (28 %, 17 out of 64 cases). Among the optional compounds ***perchlorate*** was corrected for recovery in 29 out of 45 casess (64 %), followed by ***chlorate*** (61 %, 28 out of 46 cases), ***phosphonic acid*** (58 %, 23 out of 40 cases), ***pymetrozine*** (33 %, 20 out of 61 cases), ***BAC-14*** (30 %, 18 out of 60 cases), ***dithianon*** (30 %, 12 out of 40 cases), ***quizalofop*** (26 %, 15 out of 58 cases) and ***triclopyr*** (25 %, 16 out of 64 cases).

Figure 4-2 (p. 72) shows the distribution of the recovery figures used by the participants to correct results for recovery. In two out of three cases (16 out of 35) where results were corrected based on recovery figures the recovery figures used were within the range of 40 – 70%. In 5 cases (15 %) they were within the 70 to 100 % range and in another 5 cases below 40 %. Only two of the reported recovery figures exceeded 100 %. In 34 out of the 35 cases the respective experiments for establishing the recovery figures were conducted within the same batch, 26 using the blank material provided by the organiser and 8 using other matrices. In one case the recovery figure was derived from QC validation data. In 8 of the cases the recovery

Table 4-18: Overview of other means of correcting for recovery or matrix-effects used by the laboratory, excluding dithiocarbamates

	COMPULSORY COMPOUNDS					
Means of correcting for recovery or matrix-effects used	**Cyromazine**	**Dodine**	**TFNA**	**TFNG**	**Tolylfluanid**	**Overall**
1): Procedural calibration [combined with ILIS]	12 [1]	10	7	7	9	45 (12 %) [1] (< 1 %)
2): Std. additions to sample portions [combined with ILIS]	11 [1]	10	8	8	13	50 (13 %) [1] (< 1 %)
3): Std. additions to extract aliquots [combined with ILIS]	11 [1]	7	9	9	9	45 (12 %) [1] (< 1 %)
4): Use of recovery factor [combined with ILIS]	10	5	2	3	4	24 (6 %) [0] (0 %)
Via ILIS alone	[9]					[9] (2 %)
No data	2	1	1	1	1	6 (2 %) [0] (0 %)
Sum correcting for recovery	**43 (48 %)**	**25 (30 %)**	**17 (27 %)**	**18 (28 %)**	**26 (29 %)**	**129 (33 %)**
Overall SUM	**89**	**84**	**64**	**64**	**89**	**390**

	OPTIONAL COMPOUNDS								
Means of correcting for recovery or matrix-effects used	**BAC-C14**	**Chlorate**	**Dithianon**	**Perchlorate**	**Phosphonic acid**	**Pymetrozine**	**Quizalofop**	**Triclopyr**	**Overall**
1): Procedural calibration [combined with ILIS]	6	7 [4]	7 [1]	5 [3]	6 [4]	7	7	7	52 (13 %) [12] (3 %)
2): Std. additions to sample portions [combined with ILIS]	12 [1]	8 [5]	4	9 [6]	7 [3]	6	6	7	59 (14 %) [15] (4 %)
3): Std. additions to extract aliquots [combined with ILIS]	4	5 [2]	4	5 [1]	2	7	4	4	35 (8 %) [3] (1 %)
4): Use of recovery factor [combined with ILIS]			1			7	2	2	12 (3 %) [0] (0 %)
Via ILIS alone		[11]	[1]	[14]	[10]				[36] (9 %)
No data	1	0	1	0	2	0	7	2	13 (3 %) [0] (0 %)
Sum correcting for recovery	**18 (30 %)**	**28 (61 %)**	**12 (30 %)**	**29 (64 %)**	**23 (58 %)**	**20 (33 %)**	**15 (26 %)**	**16 (25 %)**	**161 (39 %)**
Overall SUM	**60**	**46**	**40**	**45**	**40**	**61**	**58**	**64**	**414**

figures were based on only one experimental recovery figure and in 14, 5, 4 and 3 cases it was based on two, three, four and more than five replicates respectively (**Table 4-19, p. 73**). As EURL-SRM has repeatedly emphasized in the EUPT-reports and at the EURL-Workshops, using a recovery figure obtained from single experiment may be critical due to the higher risk of spurious errors. The use of historical QC-data from basic and routine validations is also risky, especially if there is differences from matrix to matrix and if variability is high. Compared to previous EUPT-SRMs, the use of recovery figures for the correction of results has dropped. In addition, the percentage of cases where recovery figures between 70 and 120 % were used has dropped significantly.

Correction using a recovery factor will usually lead to a result that is closer to the assigned value compared to the result that would have been reported if no recovery correction had been applied (provided that the assigned value is not strongly biased from the real value itself). As in previous EUPT-SRMs the submitted data support this trend (**Table 4-19, p. 73**), but not as clearly. In 19 cases the absolute z-scores resulted

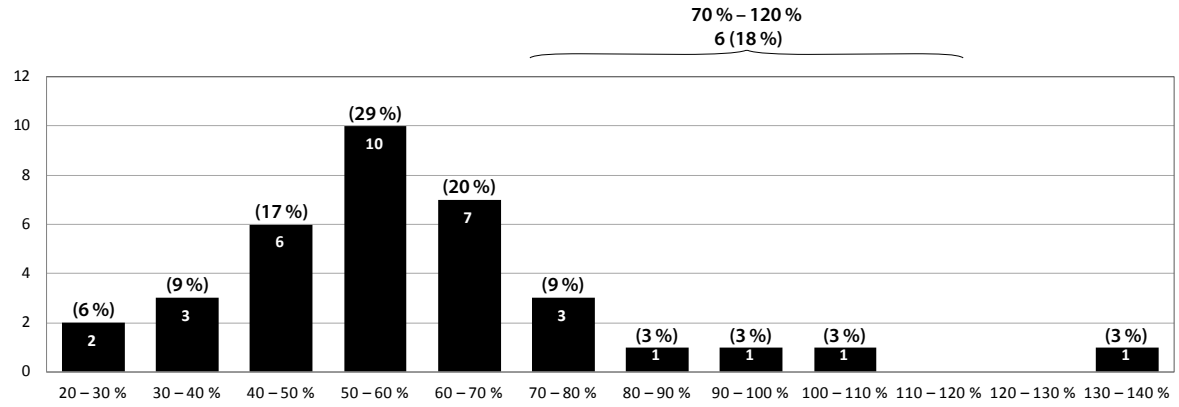


Figure 4-2: Distribution of recovery figures used for results correction for the recovery

from results with recovery correction were smaller than if the recovery correction was not applied. However, in 12 cases the opposite happened. In four cases the z-score paradoxically shifted from "acceptable" even to "unacceptable" following the correction for recovery. Besides the recovery itself there were obviously additional sources of errors leading to the bad scores that were not covered by applying a recovery figure (see also organisers' comments in **Appendix 7)**. Compared to other types of result correction such as the use of ILISs or standard addition to sample portions, recovery correction based on recovery figures is tricky and less accurate. This approach should be the last remedy.

4.5.6 Coverage of Compounds in Routine Scope and Analytical Experience of Laboratories

As can be seen in **Figure 4-3, p. 74** the percentage of participating laboratories (n = 122) that covered the various compounds in the EUPT-SRM11 Target Pesticides List varied greatly ranging from 52 % (***TFNA*** and ***TFNG***) to 80 % (***dithiocarbamates***) in the case of compulsory compounds and between 26 % (*BAC-C18*) and 70 % (*MCPA*) for the optional ones. Calculating based on the full number of laboratories that were finally considered as being obliged to take part in this test (n = 124), the percentages lower slightly further. Although introduced several years ago, ***ethephon*** and ***glyphosate*** are still analysed by less than 50 % of the participating laboratories.

Compounds reported as belonging to the routine scope of laboratories were also targeted within this EUPT with very few exceptions for which the organisers received explanations in almost all cases (**Table 4-20**). Among the COMPULSORY compounds, in the case of ***cyromazine*** one laboratory and in the case of ***dithiocarbamates*** 5 laboratories did not analyse for the pesticides although they were within their routine scope due to technical problems (5 cases) and shortage of personell. OPTIONAL compounds included in the routine scope of participating laboratories were in 96 % of the cases also targeted by those laboratories in this exercise (**Table 4-20**). In 17 out of the 19 cases, where the laboratories did not target the analytes belonging to the their routine scope, the reasons were reported. In four cases, the participants reported that those analytes are not routinely covered in spinach. In three cases (2× ***perchlorate*** and 1× ***chlorate***) the laboratories reported about technical problems and in the remaining 10 cases (3× ***dithianon***, 2× *BAC-C14*, 2× ***pymethrozine*** and 1x each ***chlorate***, ***perchlorate***, and ***triclopyr***) the laboratories could not perform the analysis due to personnel shortage.

Table 4-19: Compilation of results where RECOVERY-BASED CORRECTION OF RESULTS was applied and influence on the AAZ-scores (average bias)

Compounds	LabCode SRM11-	Submitted Recovery figure [%]	Recovery Replicates considered	Submitted Result [mg/kg]	z-score derived from submitted result	z-score (if non-corrected results were submitted)*
Cyromazine | AV = 1.512 mg/kg	8	45	1	1.26	-0.7	-2.5
	38	64	2	1.63	0.3	-1.2
	39	55	3	1.081	-1.1	-2.4
	58	54.9	2	1.15	-1.0	-2.3
	74	35	4	2.38	***2.3***	***-1.8***
	80	85	5	2.75	***3.3***	***2.2***
	88	75	2	1.85	0.9	-0.3
	94	56.2	3	1.26	-0.7	-2.1
	127	48	1	1.77	0.7	-1.8
Dodine | AV = 1.243 mg/kg	48	63	1	1.29	0.2	-1.4
	67	53	2	1.628	1.2	-1.2
	79	74.8	3	1.12	-0.4	-1.3
	127	50	1	1.33	0.3	-1.9
Dithiocarbamates | AV = 1.297 mg/kg	8	50	2	1.933	***2.0***	***-1.0***
	27	54	1	2.327	***3.2***	***-0.1***
	101	96	2	1.65	1.1	0.9
TFNA | AV = 0.756 mg/kg	38	52	2	0.887	0.7	-1.6
	88	45	5	1.009	1.3	-1.6
TFNG | AV = 0.448 mg/kg	38	73	2	0.445	0.0	-1.1
	48	62	1	0.564	1.0	-0.9
	88	40	5	0.383	-0.6	-2.6
Tolylfluanid | AV: uncertain	9	70	1	0.351	–	–
	67	51	2	1.069	–	–
	74	51	4	1.64	–	–
Dithianon | AV: uncertain	79	59.1	3	1.08	–	–
Pymetrozine | AV = 0.432 mg/kg	6	25	2	1.2	***7.1***	***-1.2***
	8	24	4	0.319	-1.0	-3.3
	38	57	2	0.402	-0.3	-1.9
	39	64	3	0.491	0.6	-1.1
	58	67.2	2	0.379	-0.5	-1.6
	74	40	4	0.58	1.4	-1.9
	127	50	1	0.582	1.4	-1.3
Quizalofop | AV = 0.171 mg/kg	67	104	2	0.144	-0.6	-0.5
Triclopyr | AV = 0.177 mg/kg	67	132	2	0.148	-0.7	0.4
	115	65	no data	0.228	1.1	-0.7
	17 labs	**35 cases**	no data (1×) 1 repl. (8×) 2 repl. (14×) 3 repl. (5×) 4 repl. (4×) 5 repl. (3×)		**AAZ = 1.2** 27 × Acceptable 1 × Questionable 3 × Unacceptable	**AAZ = 1.5** 24 × Acceptable 6 × Questionable 1 × Unacceptable

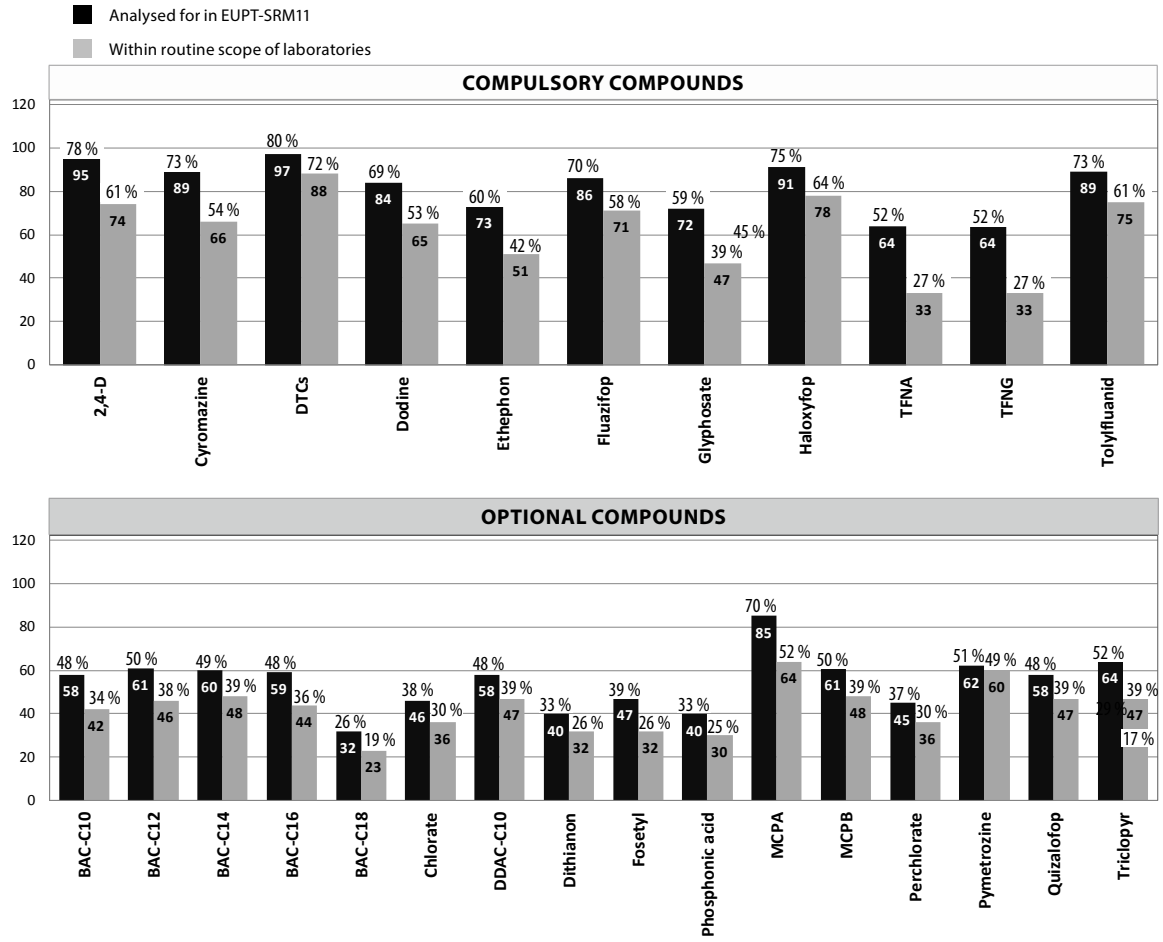


Figure 4-3: Number of laboratories targeting the various compounds of the EUPT-SRM11 target pesticides list and of laboratories covering those compounds routinely. The percentage figures are based on the total number of participating laboratories having submitted at least one resul (n = 122).

In 452 cases the participating laboratories even analysed for compounds in this exercize that are not yet included in their routine scopes, concerning compulsory compounds in 229 cases and optional ones in 223 cases. This indicates that many laboratories are in the position or even in the process of expanding their scope with additional SRM-compounds. The compounds most frequently analysed by laboratories although not yet included in their routine scope were ***TFNA*** and ***TFNG*** (31 laboratories each), followed by ***glyphosate*** (25 laboratories), ***cyromazine*** (24 laboratories) and ***ethephon*** (22 laboratories).

Asked about their analytical experinece with the various compounds, laboratories replied in 60 % of the cases that they have > 2 years of experience with compulsory compounds they reported results for. The respective figure for optional compounds was 49 %. In 21 % of the cases concerning compulsory compounds and in 28 % of the cases concerning optional compounds, laboratories reported very short (1 < year) or no experience with the analytes they reported results for. **Figure 4-4 (p. 76)** gives an overview of the analytical experinece reported by the laboratories.

Table 4-20: Inclusion of EUPT-SRM11 compounds in the laboratories' routine scope

		within routine scope of lab		NOT within routine scope of lab	
		analysed for in this EUPT	not analysed for	analysed for in this EUPT	not analysed for
COMPULSORY COMPOUNDS	**2,4-D**	74 (100 %)		21 (44 %)	27
	Cyromazine	65 (98 %)	1	24 (43 %)	32
	Dithiocarbamates	83 (94 %)	5	14 (41 %)	20
	Dodine	65 (100 %)		19 (33 %)	38
	Ethephon	51 (100 %)		22 (31 %)	49
	Fluazifop	71 (100 %)		15 (29 %)	36
	Glyphosate	47 (100 %)		25 (33 %)	50
	Haloxyfop	78 (100 %)		13 (30 %)	31
	TFNA	33 (100 %)		31 (35 %)	58
	TFNG	33 (100 %)		31 (35 %)	58
	Tolylfluanid	75 (100 %)		14 (30 %)	33
	Sum	**675 (99 %)**	**6 (1 %)**	**229 (35 %)**	**432 (65 %)**
OPTIONAL COMPOUNDS	**BAC-C10**	40 (95 %)	2	18 (23 %)	62
	BAC-C12	44 (96 %)	2	17 (22 %)	59
	BAC-C14	46 (96 %)	2	14 (19 %)	60
	BAC-C16	42 (95 %)	2	17 (22 %)	61
	BAC-C18	21 (91 %)	2	11 (11 %)	88
	Chlorate	34 (94 %)	2	12 (14 %)	74
	DDAC-C10	45 (96 %)	2	13 (17 %)	62
	Dithianon	25 (78 %)	7	15 (17 %)	75
	Fosetyl	32 (100 %)		15 (17 %)	75
	Phosphonic acid	30 (100 %)		10 (11 %)	82
	MCPA	64 (100 %)		21 (36 %)	37
	MCPB	48 (100 %)		13 (18 %)	61
	Perchlorate	33 (92 %)	3	12 (14 %)	74
	Pymetrozine	56 (93 %)	4	6 (10 %)	56
	Quizalofop	47 (100 %)		11 (15 %)	64
	Triclopyr	46 (98 %)	1	18 (24 %)	57
	Sum	**653 (96 %)**	**29 (4 %)**	**223 (18 %)**	**1047 (82 %)**

Excluding ***dithianon*** and tolylfluanid laboratories with longer experience with the analytes seem to achieve on average better z-scores than those having less experience (**Figure 4-5, p. 77**). However, the difference was moderate. In general differences could also result from different frequency with which compounds of varying analytical difficulty are represented in each group.

Table 4-21 gives an overview of laboratories' experience with the analysis of the individual compounds in the Target Pesticides List. Among the compulsory compounds present in the test item laboratories had the most experience with the analysis of ***dithiocarbamates***. 84 laboratories (87 %) indicated more than two years of experience with analysing ***dithiocarbamates***, followed by ***tolylfluanid***, ***cyromazine*** and ***dodine*** (75 %, 64 % and 62 %, respectively). Among the laboratories reporting results for ***TFNA*** and ***TFNG***, circa 25 % reported having experience of more than 2 years with the analysis of these compounds. Another 25 % of the labs reported not having any with those compounds prior to this exercize. This shows that the number of laboratories including these compounds in their analytical scope is increasing.

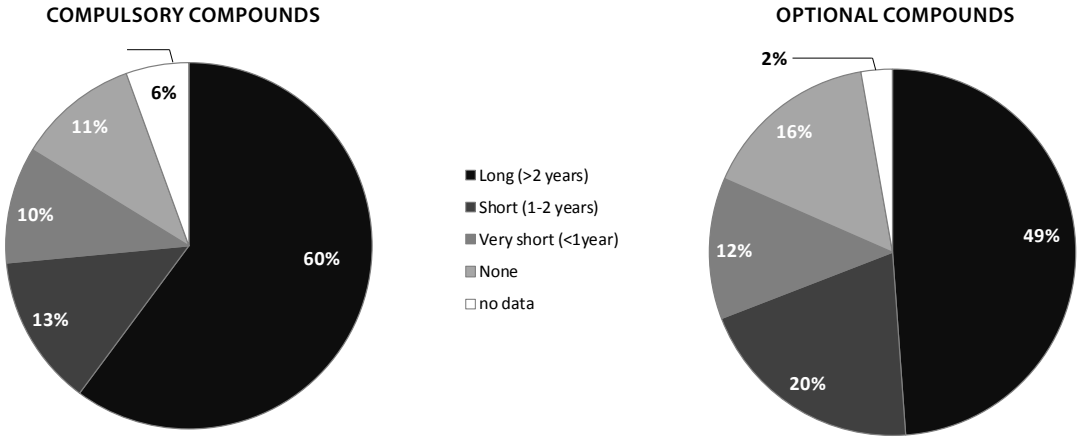


Figure 4-4: Experience of laboratories with the analysis of pesticides present in the test item for which they have reported results (overall)

For optional compounds the laboratories reported having overall less analytical experience compared to the compulsory ones. ***BAC-C14*** (77 %) and ***pymethrozine*** (76 %) were the optional compounds with which the laboratories had the most experience. Compared to the previous PTs the number of laboratories have analysed ***chlorate***, ***percchlorate*** and ***phosphonic acid*** and with experience more than 2 years increased strongly: ***chlorate*** 18 % in EUPT-SRM9 versus 52 % in EUPT-SRM11, ***perchloarte*** 3 % in EUPT-SRM9 versus 54 % in EUPT-SRM11 and ***phosphonic acid*** 17 % in EUPT-SRM10 versus 40 % in EUPT-SRM11. ***Dithianon*** is the optional compound with which the participating laboratories had the least experience: 15 % of the laboratories submitting results reporting no experience with its analysis and 15 % reported experience of less than 1 year.

Table 4-21 also gives an overview of the overall performance of the laboratories in correlation with their experience with the analysis of the various compounds. ***Dithianon*** and ***tolylfluanid*** were excluded from this evaluation due to their highly biased assigned valued. Overall, laboratories having longer experience with the analytes seem to achieve on average better z-scores than those having less experience. **Figure 4-5** gives an overall overview of this correlation. It should be noted, however, that differences could also result from different frequency with which compounds of varying analytical difficulty are represented in each group.

4.5.7 Size of Analytical Portions

The size of the analytical portions employed by the participants were in the range from 0.5 g to 200 g for ***dithiocarbamates***; from 2 g to 15 g for ***dodine***, from 2 to 20 g for ***tolylfluanid***, from 2 to 25 g for ***cyromazine***, and from 1 to 15 g for ***TFNA*** and ***TFNG*** (**Figure 4-6**). Not considerung ***dithiocarbamates*** the majority of the laboratories (84 %) employed analytical portions equal or larger than the analytical portion size of 10 g used by the organisers in the homogeneity test. In the case of ***dithiocarbamates*** 65 % were generated from sample size smaller than the 50 g used by the organisers for the homogeneity test.

The participating laboratories were informed via the Specific Protocol about the sample sizes (10 g and 50 g) used in the homogeneity tests and that sufficient homogeneity cannot be guaranteed when smaller analytical portions were used. In any case, the organisers recommended the participants in the Specific Protocol and in a short instruction accompanying the PT-materials thoroughly re-homogenising the en-

Table 4-21: Laboratories' experience with the analysis of individual compounds present in the test item and correlation with AAZ reflecting the average deviation from the assigned value. AAZs were calculated for population with at least 10 laboratories, CV^* were calculated for population with at least 10 laboratories. All participants, including laboratories from 3rd countries, were considered.

COMPULSORY COMPOUNDS				OPTIONAL COMPOUNDS			
Pesticides	**Experience**	**No. of Labs (%)**	**AAZ/CV^***	**Pesticides**	**Experience**	**No. of Labs (%)**	**AAZ/CV^***
Cyromazine AAZ: 1.1 CV^*: 31.8 %	> 2 years	57 (64 %)	0.9 / 28.4 %	**BAC-C14** AAZ: 0.9 CV^*: 25.8 %	> 2 years	46 (77 %)	0.9 / 29.2 %
	1 – 2 years	16 (18 %)	1.5 / 42.6 %		1 – 2 years	8 (13 %)	0.8 / 25.1 %
	< 1 year	6 (7 %)			< 1 year	4 (7 %)	
	None	5 (6 %)	1.6 / –		None	0 (0 %)	– / –
	no data	5 (6 %)	1.9 / –		no data	2 (3 %)	0.5 / –
Dithiocarbamates AAZ: 1.2 CV^*: 34.6 %	> 2 years	84 (87 %)	1.1 / 32.3 %	**Chlorate** AAZ: 1.6 CV^*: 44.6 %	> 2 years	24 (52 %)	1.2 / 23.7 %
	1 – 2 years	3 (3 %)	2.0 / –		1 – 2 years	10 (22 %)	1.6 / 66.6 %
	< 1 year	4 (4 %)			< 1 year	4 (9 %)	
	None	1 (1 %)	0.1 / –		None	3 (7 %)	1.6 / –
	no data	5 (5 %)	1.7 / –		no data	5 (11 %)	2.9 / –
Dodine AAZ: 1.0 CV^*: 26.2 %	> 2 years	52 (62 %)	1.0 / 27.5 %	**Phosphonic acid** AAZ: 1.1 CV^*: 29.5 %	> 2 years	16 (40 %)	0.9 / 32.2 %
	1 – 2 years	10 (12 %)	1.0 / 23.5 %		1 – 2 years	14 (35 %)	1.0 / 31.4 %
	< 1 year	11 (13 %)			< 1 year	4 (10 %)	
	None	8 (10 %)	1.0 / –		None	2 (5 %)	1.7 / –
	no data	3 (4 %)	1.2 / –		no data	4 (10 %)	2.2 / –
TFNA AAZ: 0.8 CV^*: 20.0 %	> 2 years	16 (25 %)	0.5 / 13.2 %	**Perchlorate** AAZ: 1.5 CV^*: 35.9 %	> 2 years	23 (51 %)	1.1 / 28.9 %
	1 – 2 years	15 (23 %)	0.9 / 21.9 %		1 – 2 years	8 (18 %)	1.9 / 69.1 %
	< 1 year	13 (20 %)			< 1 year	7 (16 %)	
	None	16 (25 %)	0.9 / 29 %		None	3 (7 %)	0.6 / –
	no data	4 (6 %)	1.1 / –		no data	4 (9 %)	2.6 / –
TFNG AAZ: 0.8 CV^*: 20.7 %	> 2 years	17 (27 %)	0.5 / 18.4 %	**Pymetrozine** AAZ: 1,6 CV^*: 42.3 %	> 2 years	47 (76 %)	1.4 / 44.2 %
	1 – 2 years	14 (22 %)	0.9 / 24.3 %		1 – 2 years	6 (10 %)	2.0 / 32.7 %
	< 1 year	12 (19 %)			< 1 year	4 (6 %)	
	None	18 (28 %)	0.7 / 23.2 %		None	2 (3 %)	1.0 / –
	no data	3 (5 %)	0.8 / –		no data	3 (5 %)	3.4 / –
				Quizalofop AAZ: 1,2 CV^*: 24.6 %	> 2 years	36 (62 %)	0.9 / 17.3 %
					1 – 2 years	9 (16 %)	1.0 / 16.6 %
					< 1 year	3 (5 %)	
					None	3 (5 %)	0.9 / –
					no data	7 (12 %)	3.4 / –
				Triclopyr AAZ: 0.8 CV^*: 18.7 %	> 2 years	39 (61 %)	0.6 / 18.4 %
					1 – 2 years	9 (14 %)	0.5 / 15.5 %
					< 1 year	7 (11 %)	
					None	5 (8 %)	1.7 / –
					no data	4 (6 %)	2.0 / –

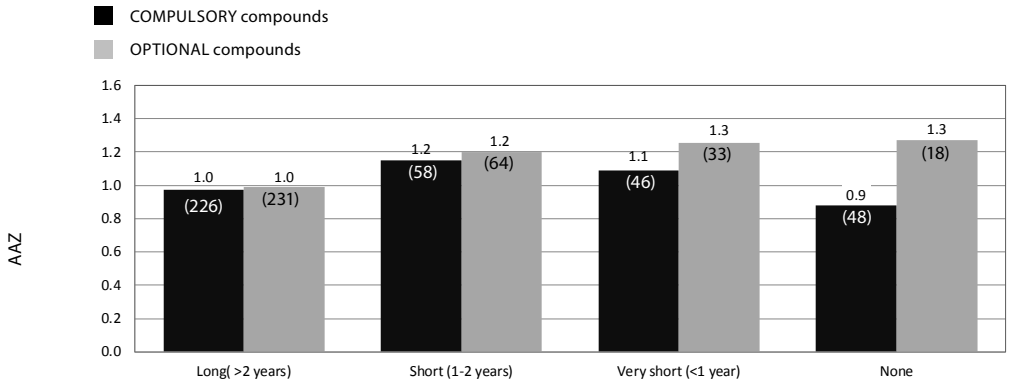


Figure 4-5: Correlation between the labs' experience with the analytes and the AAZ. (Dithianon and tolylfluanid were excluded; Number of data in each case in parentheses)

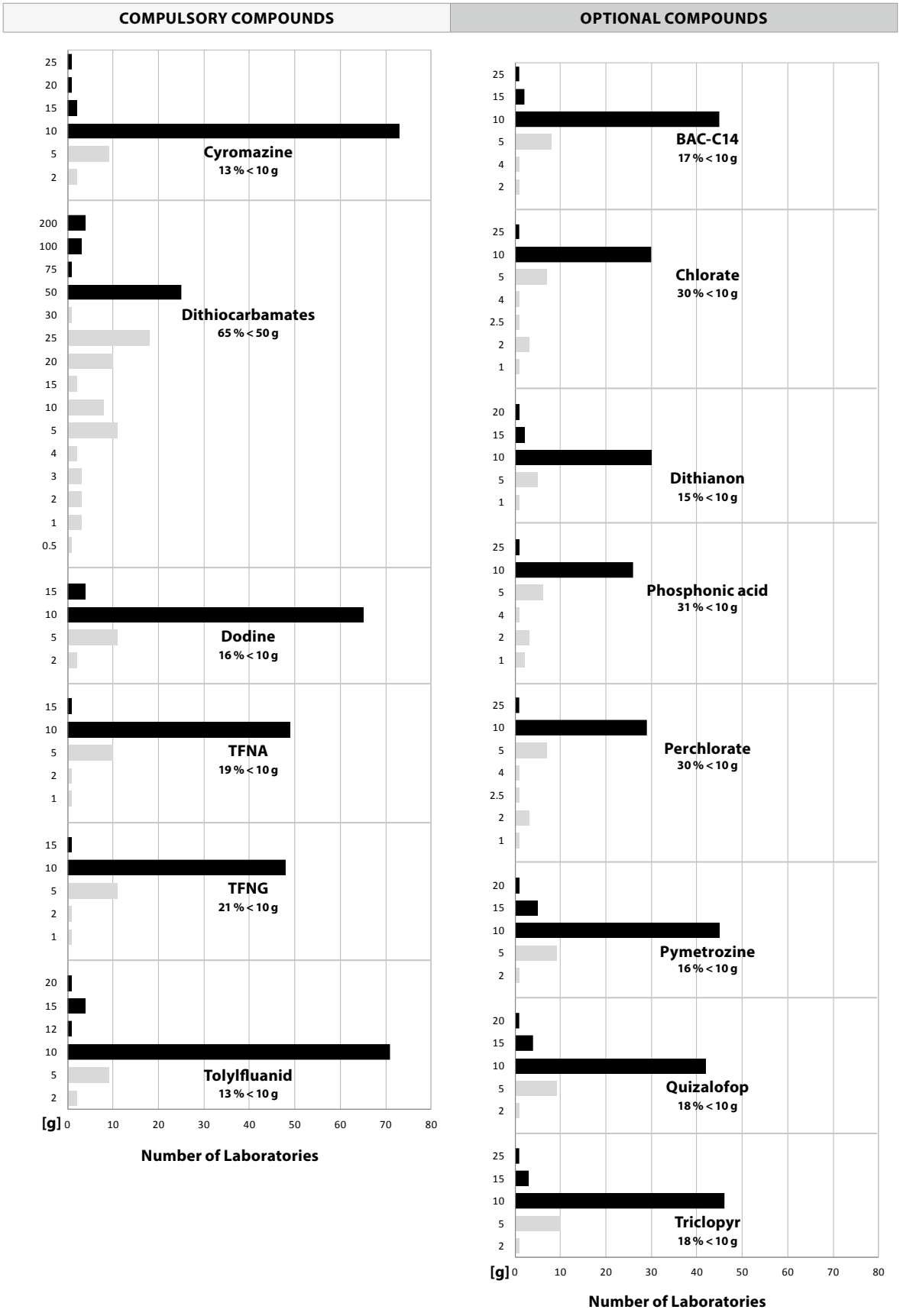


Figure 4-6: Size of analytical portions [g] employed by labs and percentage of analytical portions smaller than those used to test homogeneity by the organiser.

tire sample at low temperatures before any analytical portions were taken. If performed, this step might have improved homogeneity. Analyzing replicate analyses of small analytical portions and averaging can also help to reduce the influence of sub-sampling variability on the results.

4.5.8 Comparison of Reporting Limits, Assigned Values and MRRLs

Figure 4-7 (p. 80) shows a compilation of the reporting limits (RLs) reported by the laboratories for each of the compounds present in the test item. All reported RLs were clearly lower than the corresponding assigned values.

In the case of compulsory compounds present in the test item, the respective MRRLs were not met in 14 % of the cases by the participating laboratories on average. Among the compulsory analytes ***dithiocarbamates*** was the one, the MRRL of which (0.03 mg/kg) could not be met most frequently (45 % of the cases). Among the optional compounds present in the test item, on average there were also 9 % of the participating laboratories not meeting the MRRL, with the MRRL of ***phosphonic acid*** (0.05 mg/kg) not being met most frequently (33 % of the cases). For all other analytes present in the test item, the percentage of labs being not able to meet the corresponding MRRLs was lower than 10 %.

4.5.9 Special Case: Dithiocarbamates

The analysis of ***dithiocarbamates*** usually involves a chemical transformation of these compounds into CS_2 under acidic and reductive conditions ($SnCl_2$/HCl addition) and high temperatures. The CS_2 formed is either analyzed as such via GC (following partitioning into a non-polar solvent or following headspace sampling), or it is allowed to form complexes with xanthogenate or Cu-diethanolamine, which are measured spectrophotometrically. The concentration of ***dithiocarbamates*** is expressed as CS_2. The analytical approaches used can have an influence on the distribution of the results. As shown in **Table 4-22 (p. 81)** the results submitted by laboratories using spectrophotometric methods exhibited overall the narrowest distribution (CV^* 18.5 % on average) and those obtained by methods involving headspace sampling the broadest distribution (CV^* on average 42.2 %). The results of laboratories employing methods involving liquid-liquid partitioning were in-between (CV^* 32.5 % on average). The results generated by methods involving liquid-liquid partitioning showed typically the highest and those involving headspace sampling the lowest robust mean value. The present EUPT was, however, an exception in this regard, as spectrophotometric methods showed the highest robust mean. This may be related to the use of propineb for spiking, which was proven more difficult to transform into CS_2 compared to thiram that was used in all other EUPTs. A possible reason for the higher conversion yields achieved by spectrophotometric methods in the case of propineb might be the constant purging of the CS_2 formed out of the system, which drives the transformation reaction towards the educts side. The overall lower variability of the spectrophotometric methods and the overall higher variability of the headspace methods may be, among others, related to the higher variability of GC- compared to spectrophotometric measurements as well as to the size of the analytical portion employed (typically 25 – 100 g in spectrophotometric methods versus 1 – 5 g in headspace methods).

In this PT, the ***dithiocarbamates*** spiked to the test material was instead of thiram propineb. When validating their procedures (initially or routinely) laboratories typically spike with thiram which are easy to handle. High recovery rates with thiram do not necessarily translate to high recovery rates with all types of ***dithiocarbamates*** such as propineb, which is more stable than thiram and requires more harsh reaction conditions to quantitatively release CS_2.

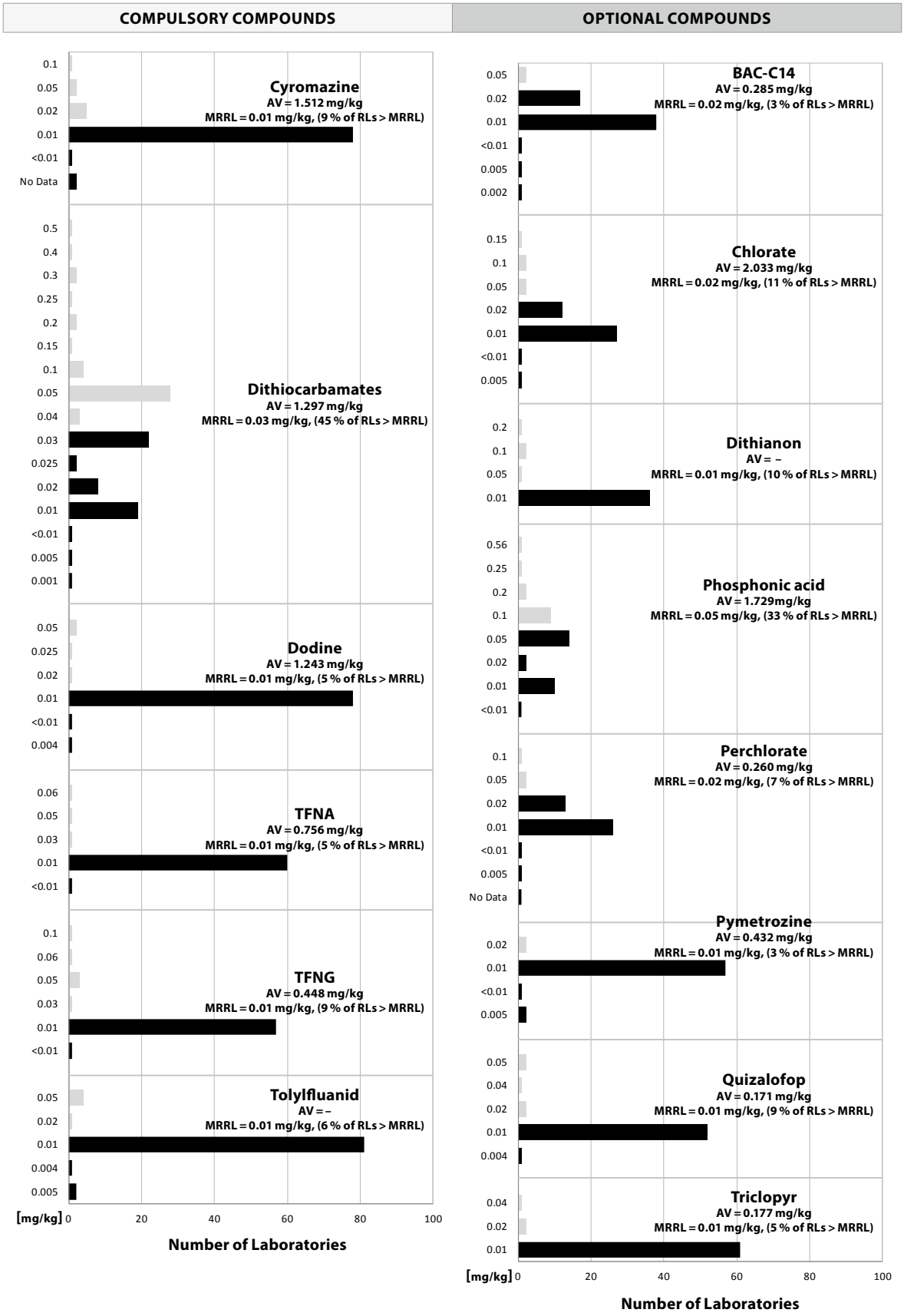


Figure 4-7: Distribution of laboratories' Reporting Limits (RLs) and comparison with the MRRLs and the assigned values (AV).

Table 4-22: Comparison of results of dithocarbamates obtained from different methods from EUPT-SRM6 till EUPT-SRM11.

		Entire Population (EU, EFTA)	Liq.-Liq. Partitioning	Headspace	Spectro-photometric	Other *
SRM6 (Rice, 2011)	No. of Results (numerical)	63	26	12	25	
	No. of FN	1	0	1	0	
	Robust Mean [mg/kg]	0.603	0.619	0.531	0.599	
	*CV**	24.2 %	27.9 %	44.4 %	20.4 %	
SRM7 (Lentils, 2012)	No. of Results (numerical)	83	32	16	35	
	No. of FN	4	1	0	3	
	Robust Mean [mg/kg]	0.615	0.658	0.660	0.577	
	*CV**	23.1 %	26.7 %	25.8 %	19.0 %	
SRM10 (Maize, 2015)	No. of Results (numerical)	85	33	27	25	
	No. of FN	1	1	0	0	
	Robust Mean [mg/kg]	0.559	0.656	0.525	0.548	
	*CV**	36.9 %	34.9 %	44.1 %	16.9 %	
SRM11 (Spinach, 2016)	No. of Results (numerical)	94	43	22	24	5 *
	No. of FN	1	0	0	1	0
	Robust Mean [mg/kg]	1.29	1.32	1.11	1.40	–
	*CV**	34.6 %	40.5 %	54.5 %	17.7 %	–
overall aversage CV*		29.7 %	32.5 %	42.2 %	18.5 %	–

* no data reported

According to the experience of the organizers temperature, time and amount of acid added to the samples are among the most important factors influencing the conversion rates of propineb to CS_2. Low final HCl concentrations in the reaction mixture (e.g. < 2 M), low temperatures (e.g. < 80 °C) and/or too short reaction duration (< 120 min) are considered critical. Confirming these statements by correlating the reaction conditions with the participants results is, however, difficult as there is many additional factors that may lead to systematic or spurious errors. CS_2 losses in the calibration standard will for example lead to overestimated results. Leaking reaction vessels may lead to underestimate results. In the case of methods involving liquid-liquid partitioning cooling down the reaction vessel prior to withdrawing the organic phase can be also critical. The headspace in the GC-vials in which extracts and calibration standards are filled can be also critical if too large or too different. Backgroung levels of CS_2 in the laboratory may influence the results, too, especially, when quantifying low concentrations of ***dithiocarbamates***.

Figure 4-8 (p. 82) shows the correlation between the reaction conditions applied by the various participants in ***dithiocarbamates*** analysis and the CS_2 results.

Dithiocarbamates, such as thiram, are known for being sensitive to decomposition. In the particular study, however, it was observed that propineb (or more precisely the determined CS_2 levels) were not markedly affected even when the test item was left to stand over 1 day at ambient temperature. This observation was also confirmed by a participant who reported good stability of the determined CS_2 levels that even after leaving the test item homogenate to thaw and reach ambient temperature for 4 times and for several hours. Studies on the impact of a contact with metals (e.g. during re-mixing of the material) were inconclusive and will be continued.

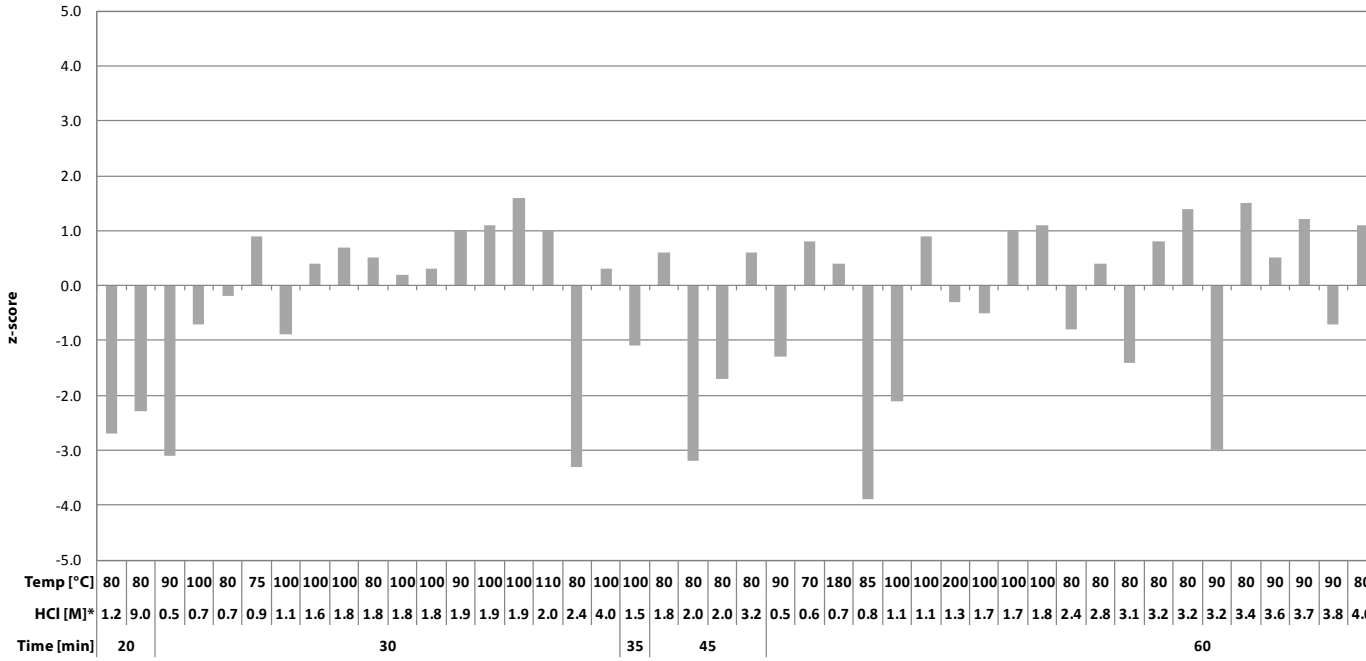
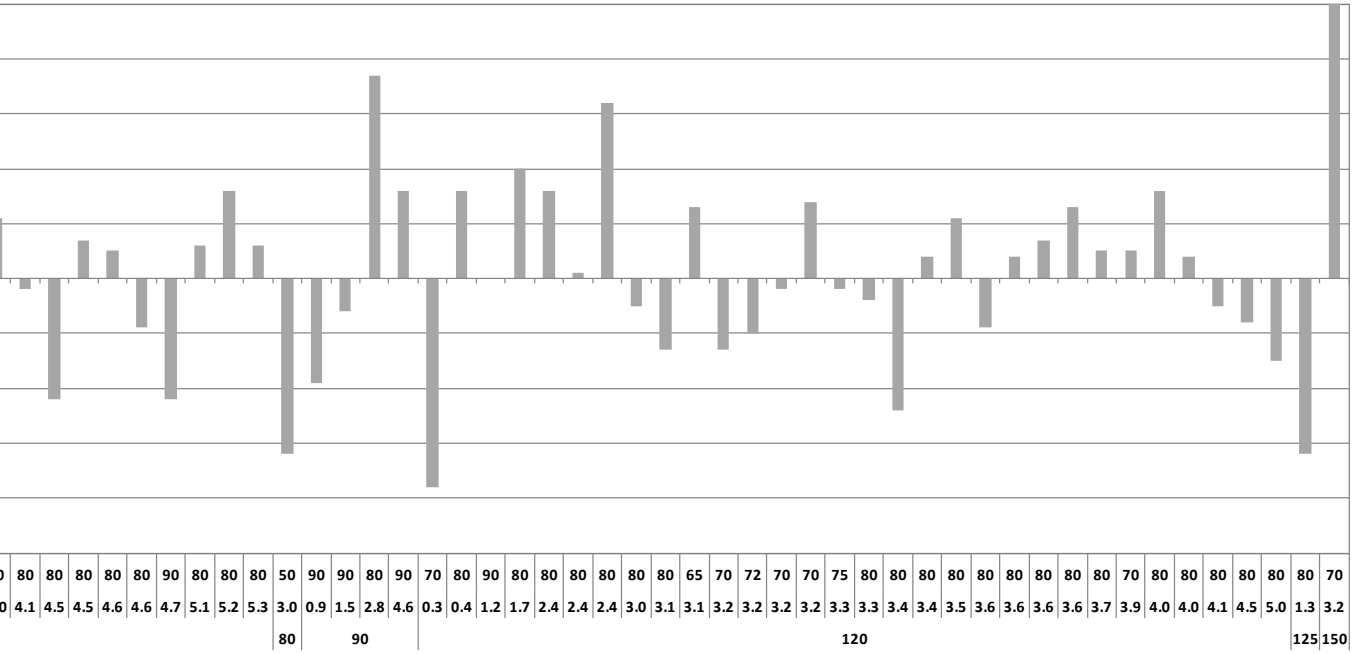


Figure 4-8: Correlation between the reaction conditions applied by the various participants in dithiocarbamate analysis and the CS_2 results. This compilation shows data from all participants having accurately reported their reaction conditions in a post PT-survey (n=90). *: HCl concentration in the reaction mixture calculated from information collected from the participants, regarding the weight of the analytical portion, the composition and amount of the $SnCl_2$/HCl reagent used and the volume of water added.

4.6 Critical Points in this PT and Post-PT Advices to Participants

- If your method forsees the use of very small analytical portions (e.g., < 5 g), be aware that sub-sampling variability become more critical. Averaging results of replicate analyses will reduce errors caused by the inhomogeneity of the test material.
- Due to the large number of participants the PT-material is often short. If your method uses very large analytical portions (e.g., > 50 g), try to modify them to also be valid for smaller portion sizes. This may be achieved, e.g., by scaling down the procedure or by diluting the sample with water prior to analysis.
- To avoid bias it is important to compensate for strongly deviating recovery rates and matrix effects:
  - ◊ Strongly deviating recovery rates: Employ procedures that adjust for recovery (e.g. ILIS added at the beginning of the procedure, standard addition to sample portions, procedural calibration); these approaches also correct for matrix effects.
  - ◊ Significant matrix effects: Use either the above mentioned procedures that also correct for recovery or procedures that compensate for matrix effects only (e.g. matrix-matched calibrations, ILISs added to the sample extract, standard addition to extract aliquots, analyte protectants in GC)
- In the case of ***dithiocarbamate*** analysis, make sure that your method involves reaction conditions (duration, temperature, concentration of reagent, pH) that are strong enough for achieving satisfactory conversion rates to CS_2 and also for ***dithiocarbamates*** that are more resistant such as propineb. Use different ***dithiocarbamates*** to check whether your method achieves good recoveries..
- If ***dithianon*** is among the target analytes, acidify the sample using strongly with mineral acid to make the compound remains stable.



- Avoid thawing the test material prior to analysis as many analytes can be sensitive to degradation (e.g., in the present PT ***dithianon*** and ***tolylfluanid***). Any degradation experienced at this stage cannot be compensated afterwards.
- Always refer to the analyte definition given on the Target Pesticides List and report the results correpsonding to the definition.
- Always submit all methodological data requested and check for correctness and plausibility. Posterior collection and correction of missing or contradictory input is very time consuming and delays the publication of the final report.

4.7 Summary, Conclusions, Retrospect and Prospect

The EUPT-SRM11 was the 11th scheduled EUPT focusing on pesticides requiring the use of "single" residue methods.

A total of 124 laboratories representing 28 EU countries and 1 EFTA country registered for the EUPT-SRM11, and 120 thereof submitted results. In addition, 2 laboratories from third countries registered for participation with all of them reporting results. Regarding NRL-SRMs two EU-countries (Croatia and Romania) were not represented in the EUPT-SRM11. The NRL-SRM in Croatia has not yet been designated, whereas the NRL-SRM in Romania reported that the commodity of the current PT is not part of its analytical scope. Malta was represented by the UK NRL-SRM acting as proxy-NRL-SRM for Malta.

Compared to the previous EUPT-SRMs using vegetable as commodity the number of laboratories that participated in this EUPT has increased significantly (**Table 4-23**). It should be noted that participation in EUPTs largely depends on the compounds included in the Target Pesticides List as well as the matrices concerned. The number of participants in EUPT-SRMs based on fruit or vegetables is generally higher compared to PTs based on cereals or feeding stuff. EUPTs entailing target compounds which are included in the scope of many laboratories, such as ***dithiocarbamates***, also tend to show an increased number of participants (**Table 4-24, p. 86**). The organisers would like to appeal to all laboratories to gradually expand their scope, so that more SRM compounds are covered among those included in EU-coordinated monitoring as well as the SANTE working document suggesting compouns to be included in the national programs. Where possible and reasonable, Member States may consider establishing OfLs specializing in the analysis of important SRM compounds that analyze those compounds also for other OfLs on a subcontract basis.

Table 4-23: Retrospective comparison of EUPT-SRMs (Statistical evaluation based on data from laboratories in EU and EFTA countries)

EUPT-	SRM1 (2007)	SRM2 (2008)	SRM3 (2009)	SRM4 (2009)	SRM5 (2010)	SRM6 (2011)
Test Item (Commodity)	Apple juice	Wheat flour	Carrot homogenate	Oat flour	Apple purée	Rice flour
Participants submitting results (EU/EFTA)	24	30	66	48	81	77
Participants submitting results (3rd and EU Candidate Countries)	–	–	–	–	2	2
Compounds in Target Pesticides List Compulsory / Optional	15 / –	8 / 3	8 / –	13 / 8	11 / –	13 / –
Compounds in test item Compulsory / Optional	3 [1] / –	3 / 2	5 / –	5 [2] / 2	5 [3] / –	7 / –
No. of results without false positives Compulsory / Optional	38 / –	56 / 22	193 / –	95 / 47	239 / –	291 / –
No. of false negative results Compulsory / Optional	0 / –	1 / 0	0 / –	3 / 2	5 / –	5 / –
Mean no. of results per lab Compulsory / Optional	1.58 / –	1.87 / 0.73	2.92 / –	1.97 / 0.98	2.95 / –	3.79 / –
Average of absolute z-scores (AAZ) Compulsory / Optional	0.57 / –	1.13 / 0.67	1.04 / –	0.98	1.11 / –	0.83 / –
Acceptable z-scores Compulsory / Optional	97 % / –	81 % / 100 %	87 % / –	89 % / 88 %	92 % / –	91 % / –
Questionable z-scores Compulsory / Optional	– / –	9 % / 0 %	7 % / –	5 % / 6 %	3 % / –	6 % / –
Unacceptable z-scores Compulsory / Optional (thereof false negatives)	3 % / –	10 % / 0 % (1.8 % / 0 %)	6 % / –	6 % / 6 % (3.7 % / 4 %)	5 % / – (0.6 % / –)	4 % / – (1.7 % / –)
Number of false positives Compulsory / Optional	0 / –	1 / –	0 / –	0 / –	3 / 3	0 / –
Category A laboratories [7]	–	–	–	31 %	19 %	25 %
CV^* (average) [8] Compulsory / Optional	25 % / –	37 % / 22 %	28 % / 24 %	27 %	22 % / –	23 % / –

1) One compound (fenbutatin oxide) was evaluated for information only due to insufficient number of participants.
2) Two compounds (ethephon and glyphosate) were evaluated for information only due to insufficient number of participants.
3) One compound (dithiocarbamates as CS_2) was evaluated for information only due to uncertain assigned value.
4) Three compounds (chlorothalonil, cyromazine and fenbutatin oxide) were evaluated for information only due to uncertain assigned value.
5) Two compounds (4-OH-chlorothalonil and trimesium) were evaluated for information only due to uncertain assigned value.
6) Three compounds (tolylfluanid, dithianon and pymethrozine) were evaluated for information only due to uncertain assigned value and excluded in the evaluation
7) The criteria applied to define Category A and B in EUPT-SRM4 and -SRM5 were different from those in EUPT-SRM6 – 10.
8) CV^* = robust relative standard dieviation, known as Qn-RSD in EUPT-SRM1 – 9 (calculated for informative purpose)

Judging from the number of participants, the average of absolute z-scores (AAZ) and the number of laboratories classified into Category A the quantity and quality of the results of the EUPT-SRM11 remained high (**Table 4-23**), but overall lower than in most previous EUPTs. This is due to the presence of several analytes that are difficult to analyze, such as ***pymetrozine***, ***tolylfliuanid***, ***dithianon*** and ***propineb*** as ***dithiocarbamate***.

The Target Pesticides List of EUPT-SRM11 (**Appendix 11**) contained in total 27 SRM-compounds. 11 of them were compulsory and the rest optional for the laboratories in terms of scope. All of the compulsory compounds (*2,4-D*, ***cyromazine***, ***dithiocarbamates***, ***dodine***, *ethephon*, *fluazifop*, *glyphosate*, *haloxyfop*, ***TFNA***, ***TFNG*** and ***tolylfluanid***) were relevant to the EU multiannual coordinated control program (MACP) for spinach and included in the MACP regulation. Two of the optional compounds, ***dithianon*** and ***pymetrozine***, were also included in the MACP regulation. Further 11 of the compounds on the target pesticides list are included in the SANTE working document for monitoring: *BAC-C10*, *BAC-C12*, ***BAC-C14***, *BAC-C16*, *BAC-C18*, ***chlorate***, *DDAC-C10*, *fosetyl*, *MCPA*, *MCPB*, ***perchlorate***, ***quizalofop***, ***triclopyr***.

EUPT-	SRM7 (2012)	SRM8 (2013)	SRM9 (2014)	SRM10 (2015)	SRM11 (2016)
Matrix of test item	Lentil flour	Potato homogenate	Cow's whole milk	Maize flour	Spinach homogenate
Participants submitting results (EU/EFTA)	110	110	62	104	120
Participants submitting results (3rd and EU Candidate Countries)	4	6	5	6	2
Compounds in Target Pesticide List Compulsory / Optional	16 / –	13 / 10	12 / 7	9 / 14	11 / 16
Compounds in test item Compulsory / Optional	8 [4] / –	8 [5] / 7	8 [5] / 6	8 / 5	6 [6] / 8 [6]
No. of results without false positives Compulsory / Optional	439 / –	604 / 212	361 / 132	461 / 135	479 / 411
No. of false negative results Compulsory / Optional	11 / –	14 / 8	3 / 4	4 / 2	8 / 20
Mean no. of results per lab Compulsory / Optional	4.12 / –	5.49 / 1.93	5.87 / 2.19	4.43 / 1.29	4.03 / 3.71
Average of absolute z-scores (AAZ) Compulsory / Optional	0.97 / –	0.98 / 1.06	0.75 / 0.80	0.9 / 0.7	1.0 [6] / 1.1 [6]
Acceptable z-scores Compulsory / Optional	90 % / –	88 % / 85 %	92 % / 71 %	87 % / 89 %	87 % [6] / 85 % [6]
Questionable z-scores Compulsory / Optional	3 % / –	6 % / 5 %	4 % / 5 %	8 % / 6 %	5 % [6] / 4 % [6]
Unacceptable z-scores Compulsory / Optional (thereof false negatives)	7 % / – (2.1 % / –)	6 % / 10 % (2.2 % / 3.6 %)	4 % / 3.5 % (0.8 % / 2.7 %)	5 % / 4 % (0.8 % / 2.9 %)	7 % [6] / 10 % [6] (1.0 % [6] / 4.8 % [6])
Number of false positives Compulsory / Optional	0 / –	2 / 0	6 / 0	0 / 4	4 / 4
Category A laboratories [7]	28 %	47 %	52 %	53 %	47 %
CV^* (average) [8] Compulsory / Optional	27 % / –	26 % / 26 %	20 % / 19 %	24 % / 19 %	28 % [6] / 30 % [6]

1) One compound (fenbutatin oxide) was evaluated for information only due to insufficient number of participants.
2) Two compounds (ethephon and glyphosate) were evaluated for information only due to insufficient number of participants.
3) One compound (dithiocarbamates as CS_2) was evaluated for information only due to uncertain assigned value.
4) Three compounds (chlorothalonil, cyromazine and fenbutatin oxide) were evaluated for information only due to uncertain assigned value.
5) Two compounds (4-OH-chlorothalonil and trimesium) were evaluated for information only due to uncertain assigned value.
6) Three compounds (tolylfluanid, dithianon and pymethrozine) were evaluated for information only due to uncertain assigned value and excluded in the evaluation
7) The criteria applied to define Category A and B in EUPT-SRM4 and -SRM5 were different from those in EUPT-SRM6 – 10.
8) CV^* = robust relative standard dieviation, known as Qn-RSD in EUPT-SRM1 – 9 (calculated for informative purpose)

Table 4-24: Overview of selected pesticides tested in the EUPT-SRMs 1 – 11. ***n***: Number of laboratories having analysed selected pesticides present in the test items. The figures in brackets show the percentage of laboratories submitting numerical results for a compound out of the total number of laboratories submitting results (only EU and EFTA labs considered; CV^*, formerly known as Qn, was calculated for populations with at least 10 laboratories). Only CV^*s based on 15 or more labs were used to calculated the average CV^*s at the bottom.

				Acidic pesticides					Requiring individual methods		Polar pesticides				Other
EUPT	No. of laboratories	Commodity type[1]		2,4-D	MCPA	Bentazone	Haloxyfop	Fluazifop	Bromide	Dithio-carbamates	Chlormequat	Mepiquate	Ethephon	Glyphosate	Fenbutatin oxide
SRM1	24	FV	*n*		10 (42 %)						23 (96 %)				5 (21 %)
		HW	CV^*		27.1 %						**13.8 %**				–
SRM2	30	CF	*n*		13 (43 %)						25 (83 %)				
		D	CV^*		45.8 %						**29.1 %**				
SRM3	66	FV	*n*		38 (58 %)			35 (55 %)		59 (89 %)					
		HW	CV^*		**27.0 %**			**26.6 %**		**38.4 %**					
SRM4	48	CF	*n*	32 (66 %)							38 (83 %)		4 (8.3 %)	6 (13 %)	
		D	CV^*	**27.5 %**							**25.8 %**		–	–	
SRM5	81	FV	*n*					51 (64 %)		70 (86 %)			28 (35 %)		35 (43 %)
		HW	CV^*					**19.8 %**		**58.9 %**			**23.0 %**		**24.3 %**
SRM6	77	CF	*n*	57 (74 %)			49 (64 %)		34 (44 %)	64 (83 %)			28 (36 %)	34 (44 %)	
		D	CV^*	**22.1 %**			**17.7 %**		**8.6 %**	**24.2 %**			**29.7 %**	**40.6 %**	
SRM7	110	CF	*n*	70 (64 %)					44 (40 %)	83 (75 %)			32 (29 %)	39 (35 %)	
		D	CV^*	**27.9 %**					**18.0 %**	**23.1 %**			**25.2 %**	**34.5 %**	
SRM8	110	FV	*n*				81 (74 %)					71 (65 %)		45 (41 %)	59 (54 %)
		HW	CV^*				**20.2 %**					**22.2 %**		**24.5 %**	**31.4 %**
SRM9	62	AO	*n*	50 (81 %)				50 (81 %)			50 (81 %)	49 (79 %)			
		HW	CV^*	**18.7 %**				**26.0 %**			**29.8 %**	**19.6 %**			
SRM10	104	CF	*n*	82 (79 %)	79 (76 %)	69 (66 %)				85 (82 %)	75 (72 %)	76 (67 %)	61 (59 %)	62 (60 %)	
		D	CV^*	**18.2 %**	**18.9 %**	**18.5 %**				**36.9 %**	**18.2 %**	**18.5 %**	**30.8 %**	**22.8 %**	
SRM11	119	FV	*n*							95 (80 %)					
		HW	CV^*							**34.6 %**					
Average CV^* EUPT-SRMs 1 – 11				**22.9 %**	**29.7 %**	**18.5 %**	**19.0 %**	**24.1 %**	**13.3 %**	**36.0 %**	**23.3 %**	**20.1 %**	**27.2 %**	**30.6 %**	**27.9 %**

Average CV^* of Group EUPT-SRMs 1 – 11	Acidic pesticides	Br⁻	Dithiocarbamates	Chlormequat + Mepiquat	Ethephon + Glyphosate	FBO
	24.1 %	13.3 %	36.0 %	22.0 %	28.7 %	27.9 %

1) Commodity type:
HW: High water content; D: dry = high strach or high protein content and low water content

6 among the total 27 compounds in the Target Pesticides List were included for the first time in the EUPT-SRM with 5 of them being present in the test item: ***dodine***, ***tolyfluanid***, ***dithianon***, ***pymetrozine*** and ***triclopyr***. All these new compounds were analysed by a sufficient number of laboratories to allow proper statistical evaluation. In the case of ***dithianon*** and ***tolylfluanid*** , however, the statistical the assigned value was too uncertain. Therefore, these two compounds were excluded from evaluation of the overall proficiency of the participants.

Phosphonic acid, a compound of high actuality within the analytical community, was included in an EUPT-SRM for the second time. The number of laboratories having analysed for this compound increased from 24 in the EUPT-SRM10 to 38 in EUPT-SRM11 with comparable overall quality of the results (CV^* 27.3 % versus 29.5 %). The results generated using the ILIS provided by the organiser showed a narrower distribution (13.9 % for SRM10 and 26.6 % for SRM11).

The robust relative standard deviation (CV^*) reflects the width of the result-distribution and was calculated for each target analyte. The average CV^*s of compulsory analytes based on the entire population excluding tolylfluanid was 26.7 % and the average CV^*s of optional analytes based on the entire population excluding ***dithianon*** was 31.9 %. Both were slightly higher than the FFP-RSD of 25 %.

The individual CV^* values of the compulsory compounds were as follows: ***cyromazine*** 31.8 % (sub-population using ILIS 19.8 %), ***dithiocarbamates*** 34.6 %, ***dodine*** 26.2 %, ***TFNA*** 20.0 %, ***TFNG*** 20.7 %, and ***tolyfluanid*** 57.4 %. The CV^* values of the optional compounds were as follows: ***BAC-C14*** 25.8 %, ***chlorate*** 44.6 % (sub-population using ILIS 15.5 %), ***dithianon*** 94.3 %, ***phosphonic acid*** 29.5 % (sub-population using ILIS 26.6 %), ***perchlorate*** 35.9 % (sub-population using ILIS 23.5 %), ***pymetrozine*** 42.3 %, ***quizalofop*** 24.6 % and ***triclopyr*** 18.7 %. Considering the alternative assigned values for ***cyromazine***, ***chlorate*** and ***perchlorate***, the average CV^*s of compulsory compounds and optional (excluding ***tolyfluanid*** and ***dithianon***) analytes were 24.3 % and 25.3 %, respectively.

Looking at the long-term CV^*s of selected individual compounds or compound groups (**Table 4-24**) we can see for acidic pesticides (*2,4-D*, *MCPA*, bentazone, *haloxyfop*, *fluazifop*) an average CV^* of 24.1 %, for chlormequat and mepiquat an average CV^* of 22.0 %, for *glyphosate*, and *ethephon* an average CV^* of 28.7 %, for fenbutatin oxide an average CV^* of 27.9 % and for bromide an average CV^* of 13.3 %. Most critical is the CV^*s of ***dithiocarbamates*** with an average value of 36.0 %.

In accordance with the definition in the General EUPT Protocol, z-scores based on the FFP-RSD of 25 % were calculated and classified into "acceptable", "questionable", and "unacceptable" for each laboratory/target-analyte combination. Overall, the quality of the results was high. In the case of compulsory compounds 73 out of 88 laboratories (83 %) reported results within the acceptable z-score-range for ***cyromazine***, 78 out of 95 (82 %) for ***dithiocarbamates***, 73 out of 83 (88 %) for ***dodine***, 59 out of 63 (94 %) for ***TFNA*** and 58 out of 63 (92 %) for ***TFNA***. In the case of optional compounds 55 out of 58 laboratories (95 %) submitted results within the acceptable z-score-range for ***BAC-C14***, 33 out of 46 (72 %) for ***chlorate***, 35 out of 40 (88 %) for ***phosphonic acid***, 34 out of 45 (76 %) for ***perchlorate***, 47 out of 62 (76 %) for ***pymetrozine***, 49 out of 58 (84 %) for ***quizalofop***, and 59 out of 63 (94 %) for ***triclopyr***.

Considering results reported by all participating laboratories, among the compulsory compounds false negative results were reported in 9 cases for ***cyromazine*** and ***dithiocarbamates*** (each two cases), ***TFNA*** (1×), ***MCPA*** and ***tolyfluanid*** (4×). Among the optional compounds false negative results were reported in 20 cases for ***quizalofop*** (6×), ***phosphonic acid*** (4×), ***chlorate*** and ***dithianon*** (each 3 cases) as well as ***pymetrozine*** and ***triclopyr*** (each 2 cases). False positive results were reported in 3 cases: 2× *ethephon* and 1× *BAC-C12*.

All participating laboratories were classified according to the number of compulsory pesticides detected following the rules of the General EUPT Protocol. Laboratories analysing at least 10 of the eleven compulsory compounds on the Target Pesticides List and correctly detecting five or more of the six compulsory pesticides present in the test item without reporting any false positive result were classified into Category A. A total of 56 EU/EFTA-laboratories (47 %) were classified into Category A and the remaining 64 (47 %) into Category B. Both the participating laboratories from third countries were classified into Category B.

19 of the 119 EU laboratories in this EUPT participated in this EUPT on a voluntary basis. The other 100 laboratories represent 81 % of the 124 laboratories that were finally considered as being obliged to participate in this exercise based on their function (NRL-SRM) or scope (routinely analysing official samples for pesticide residues in fruit and vegetable). Several laboratories originally considered as obliged to take part in the current PT provided explanations for their non-participation. Most of them stated that the SRM11 target pesticides were out of their routine scope. Some laboratories indicated the lack of required instruments or technical problems as reasons.

Post-PT measures and assistance to the laboratories: Following the distribution of the preliminary results all laboratories achieving questionable or unacceptable z-scores as well as false positive results were asked to investigate the reasons and report them to the organizers, as far as possible. The organizers have also contacted several laboratories that have not reported certain information or reported inconsistent information that was vital for the evaluations. Participants having reported fragmentary or inconsistent methodology information were furthermore contacted in order to correct the information and close the gaps and to improve the evaluation of the results as regards the critical aspects in the analysis of various compounds. Where the methodology data submitted by the participants suggested other or additional sources of errors, or where the reasons provided where not conclusive, the organizers contacted the participants asking specific questions helping them to better localize the real sources of errors and to hopefully avoid such errors in the future.

In the case of ***dithiocarbamates*** a special survey was furthermore conducted to collect details on the sample preparation in order to localize aspects influencing the results.

Improving the overall performance of NRLs and OfLs in the area of pesticides and metabolites not amenable to multiresidue methods, and expanding their scope is one of the main aims of the EURL-SRM. The EURL-SRM is thus pleased to assist the laboratories via bilateral discussions, workshops and trainings and will continue developing, validating and distributing easy-to-use, fast and cost-efficient methodologies for such compounds. In future PTs, the selection of target analytes will continue to focus on those included in the scope of the EU coordinated control program as well those recommended wthin the SANTE working documen for inclusion in national monitoring programs. Specific requests by NRLs and OfLs will be also taken into account.

5. ACKNOWLEDGEMENTS

The organisers wish to thank the members of the EUPT Scientific Committee (Quality Control Group and Advisory Group) for their valuable advice. Special thanks also go to Jens-Ole Frimann for his support in establishing the online registration and result submission tool.

6. REFERENCES

[1] Regulation (EC) N° 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

[2] Regulation (EC) N° 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.

[3] http://www.crl-pesticides.eu/userfiles/file/EurlSRM/EurlSrm_Observations_AcidicPesticides.pdf

[4] Thompson M., Ellison S.L.R. and Wood R., The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories (IUPAC Technical Report). Pure Appl. Chem., Vol. 78, No. 1, pp. 145 – 196, 2006

[5] http://quppe.eu/

[6] ISO 13528:2015: Statistical methods for use in proficiency testing by interlaboratory comparisons.

7. APPENDICES

Appendix 1 List of Laboratories Registered to Participate in the EUPT-SRM11

(a): Participating Laboratories of EU and EFTA Member States

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Austria	AT	Austrian Agency for Health and Food Safety, Institute for Food Safety Innsbruck - Department for Pesticide and Food Analytics	Innsbruck	x	Yes
Austria	AT	LVA GmbH	Kloster-neuburg		Yes
Austria	AT	MA 38 - Lebensmitteluntersuchung Wien	Vienna		Yes
Belgium	BE/FR/LU	Primoris - Belgium, Gent (Zwijnaarde)	Gent - Zwijnaarde		Yes
Belgium	BE	LOVAP (Laboratorium voor Onderzoek Van levensmiddelen en Aanverwante Produkten) NV	Geel		Yes
Belgium	BE	Scientific Institute of Public Health	Brussels	x	Yes
Bulgaria	BG	Central Laboratory for Chemical Testing and Control, Sofia	Sofia	x	Yes
Croatia	HR	Croatian National Institute of Public Health	Zagreb		Yes
Croatia	HR	Euroinspekt - Croatiakontrola d.o.o.	Zagreb		Yes
Croatia	HR	Teaching Institute of Public Health, Dr. Andrija štampar	Zagreb		Yes
Cyprus	CY	Laboratory of Pesticide Residues Analysis, State General Laboratory	Nicosia	x	Yes
Czech Republic	CZ	Central Institute for Supervising and Testing in Agriculture1)	Brno		Yes
Czech Republic	CZ	Czech Agriculture and Food Inspection Authority	Praha	x	Yes
Czech Republic	CZ	University of Chemical Technology, Dept. of Food Chemistry and Analysis - Prague	Praha		Yes
Denmark	DK	Danish Veterinary and Food Administration, Department of Residues, Ringsted	Ringsted		Yes
Denmark	DK	National Food Institute, Technical University of Denmark	Søborg	x	Yes
Estonia	EE	Agricultural Research Centre, Saku, Lab for Residues and Contaminants	Saku		Yes
Estonia	EE	Health Board - Tartu Laboratory	Tartu	x	Yes
Finland	FI	Finnish Customs Laboratory	Espoo	x	Yes
Finland	FI	Finnish Food Safety Authority	Helsinki	x	Yes
France	FR	Analysis Center Mediterranean Pyrenees	perpignan		Yes
France	FR	ANSES Laboratoire de Maisons-Alfort (Pesticides)	MAISONS-ALFORT	x	Yes
France	FR	Capinov	Landerneau		Yes
France	FR	CERECO SUD	GARONS		Yes
France	FR	GIRPA - Groupement Interrégional Recherche Produits Agropharma	BEAUCOUZE		Yes
France	FR	INOVALYS Le Mans	Le Mans		Yes
France	FR	Service Commun des Laboratoires / Laboratoire de Montpellier	Montpellier		Yes
France	FR	Service Commun des Laboratoires / Laboratoire Ile de France - Massy	Massy Cedex		Yes
France	BE	PHYTOCONTROL	NIMES		Yes
Germany	DE	Amt für Verbraucherschutz Düsseldorf - 39/2 Chemische und Lebensmitteluntersuchung	Dûesseldorf		Yes
Germany	DE	Bavarian Health and Food Safety Authority Office Erlangen	Erlangen		Yes
Germany	DE	Berlin-Brandenburg State Laboratory, Frankfurt (Oder)	Frankfurt (Oder)		Yes
Germany	DE	Chemical and Veterinary Analytical Institute Muensterland-Emscher Lippe	Münster		Yes
Germany	DE	Chemical and Veterinary Analytical Institute Rhine-Ruhr-Wupper	Krefeld		Yes
Germany	DE	Chemisches Labor Dr. Mang	Frankfurt am Main		Yes

* only for EU-Member States; 1) no reason reported to the organisers; 2) Technical or personall problem

Appendix 1-a (cont.): Participating Laboratories of EU and EFTA Member States

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Germany	DE	Federal Office of Consumer Protection and Food Safety, NRL for Pesticide Residues	Berlin	x	Yes
Germany	DE	Food and Veterinary Institute Oldenburg	Oldenburg		Yes
Germany	DE	Institut für Hygiene und Umwelt Hamburg	Hamburg		Yes
Germany	DE	Intertek Food Services GmbH Bremen	Bremen		Yes
Germany	DE	Kwalis Qualitätsforschung GmbH	Dipperz		Yes
Germany	DE	Labor Friedle GmbH	Tegernheim		Yes
Germany	DE	Landesamt für Landwirtschaft, Lebensmittelsicherheit und Fischerei Mecklenburg-Vorpommern	Rostock		Yes
Germany	DE	Landesamt für Verbraucherschutz - Sachsen-Anhalt	Halle/Saale		Yes
Germany	DE	Landesanstalt für Landwirtschaft und Gartenbau, Halle	Halle/Saale		Yes
Germany	DE	Landesuntersuchungsamt Institut für Lebensmittelchemie Speyer	Speyer		Yes
Germany	DE	Landwirtschaftliche Untersuchungs- und Forschungsanstalt Speyer	Speyer		Yes
Germany	DE	Landwirtschaftliches Technologiezentrum Augustenberg, Karlsruhe	Karlsruhe		Yes
Germany	DE	State Department of Environmental and Agricultural Operations in Saxony	Nossen		Yes
Germany	DE	State Laboratory Schleswig-Holstein	Neumünster		Yes
Germany	LT	GALAB Laboratories GmbH - Germany	Hamburg		Yes
Germany	MT	Eurofins - Dr. Specht Laboratorien GmbH	Hamburg		Yes
Germany	BE	LUFA-ITL GmbH	Kiel		Yes
Greece	GR	Agrolab rds SA	Thessaloniki		Yes
Greece	GR	Benaki Phytopathological Institute, Pesticide Residues Laboratory	Kifissia	x	Yes
Greece	GR	General Chemical State Laboratory, D Division, Pesticide Residues Laboratory	Athens	x	Yes
Greece	GR	Regional Center of Plant Protection and Quality Control of Achaia, Pesticide Residues Laboratory	Patra		Yes
Greece	GR	Regional Center of Plant Protection and Quality Control of Iraklion, Pesticide Residues Laboratory	Iraklion Crete		Yes
Hungary	HU	Agricultural Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Hódmezovásárhely	Hódmezovásárhely		Yes
Hungary	HU	National Food Chain Safety Office Directorate of Plant Protection, Soil Conservation and Agri-environment, Pesticide Residue Analytical Laboratory, Szolnok	Szolnok		Yes
Hungary	HU	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-environment - Pesticide Analytical Laboratory, Velence	Velence		Yes
Hungary	HU	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Miskolc	Miskolc	x	Yes
Ireland	IE	Pesticide Control Laboratory, Department of Agriculture, Fisheries and Food	Co. Kildare	x	Yes
Italy	IT	ARPA Puglia - Dipartimento di Bari	Bari		Yes
Italy	IT	ARPA VENETO DIP.REG.LAB. S.L. VERONA	Verona		Yes
Italy	IT	ARPAE Ferrara Laboratorio Tematico Fitofarmaci	Ferrara		Yes
Italy	IT	ARPALAZIO SEZIONE P.LE DI LATINA SERVIZIO LABORATORIO AMBIENTE E SALUTE UNITA' DI CHIMICA INORGANICA	latina		Yes
Italy	IT	Istituto Superiore di Sanità, Pesticide Section	Roma	x	Yes
Italy	IT	Istituto Zooprofilattico Sperimentale Abruzzo e Molise	Teramo		Yes
Italy	IT	Istituto Zooprofilattico Sperimentale Lombardia ed Emilia Romagna	Brescia		Yes
Italy	IT	Istituto Zooprofilattico Sperimentale Sicilia	Palermo		No [1)]
Italy	IT	Istituto Zooprofilattico Sperimentale Umbria e Marche, PERUGIA	Perugia		Yes
Italy	IT	Laboratorio Agroalimentare di Verona SRL	Verona		No [2)]
Italy	IT	Laboratorio analisi acque e cromatografia	Bolzano		Yes

* only for EU-Member States; [1)] no reason reported to the organisers; [2)] Technical or personall problem

Appendix 1-a (cont.): Participating Laboratories of EU and EFTA Member States

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Italy	IT	Public Health Laboratory - Florence	Firenze		Yes
Italy	IT	SAMER - Azienda Speciale della Camera di Commercio di Bari	Bari		Yes
Latvia	LV	Institute of Food Safety, Animal Health and Environment (BIOR) - Riga	Riga	x	Yes
Lithuania	LT	National Food and Veterinary Risk Assessment Institute (Lithuania, Vilnius)	Vilnius	x	Yes
Luxem-bourg	LU	National Health Laboratory Luxembourg (Food Laboratory)	Dudelange	x	Yes
Netherlands, The	NL	NVWA - Netherlands Food and Consumer Product Safety Authority	Wageningen	x	Yes
Netherlands, The	BE	Eurofins Lab Zeeuws-Vlaanderen (LZV) B.V.	Graauw		Yes
Netherlands, The	BE	Groen Agro Control	Delfgauw		Yes
Netherlands, The	BE	Handelslaboratorium Dr. Verwey	Rotterdam		No [2)]
Norway	NO	Norwegian Institute of Bioeconomi Research, Division of Biotech-nology and Plant Health, Department of Pesticides and Natural Bioactive Products	Aas		Yes
Poland	PL	Institute of Plant Protection - National Research Institute, Regional Experimental Station in Rzeszow	Rzeszow		Yes
Poland	PL	Institute of Plant Protection Pesticide Residue Laboratory, Bialystok	Bialystok		Yes
Poland	PL	Institute of Plant Protection, Department of Pesticide Residue Research - Poznan	Poznan		Yes
Poland	PL	Main Inspectorate of Plant Health And Seed Inspection, Central Laboratory	Torun		Yes
Poland	PL	Research Institute of Horticulture, Food Safety Laboratory (Skierniewice)	Skierniewice		Yes
Poland	PL	Voievodship Sanitary - Epidemiological Station in Warszaw	Warszaw	x	Yes
Poland	PL	Voievodship Sanitary - Epidemiological Station in Wroclaw	Wroclaw		Yes
Poland	PL	Wojewódzka Stacja Sanitarno-Epidemiologiczna w Opolu, Oddzial Laboratoryjny w Kluczborku	Kluczbork		Yes
Portugal	PT	INIAV- Pesticide Residues Laboratory	Oeiras		Yes
Portugal	PT	Regional Laboratory of Veterinary and Food Safety - Madeira Island	Funchal - Madeira Island	x	Yes
Portugal	PT	Vairão -Contaminant and Pesticides Laboratory Contol (Plant Origin Products)	Vairão - Vila do Conde		Yes
Romania	RO	Central Laboratory for Pesticides Residues Control in Plants and Vegetable Products - Bucharest	Bucharest		Yes
Romania	RO	Institute for Hygiene and Veterinary Public Health - Bucharest	Bucharest	x	Yes
Slovakia	SK	State Veterinary and Food Institute - Veterinary and Food Institute in Bratislava	Bratislava	x	Yes
Slovenia	SI	Agricultural Institute of Slovenia, Central Laboratories	Ljubljana		Yes
Slovenia	SI	National Laboratory of Health, Environment and Foodstuffs - Maribor	Maribor	x	Yes
Slovenia	SI	National Laboratory of Health, Environment and Foodstuffs - Maribor (Location Ljubljana)	Ljubljana	x	Yes
Spain	ES	Analytica Alimentaria GmbH Sucursal España	Almeria		Yes
Spain	ES	Instituto Tecnologico de Canarias, División de Investigación y Desarrollo Tecnológico - Laboratorio de Residuos	Agüimes, Gran Canaria		Yes
Spain	ES	Laboratorio Agrario Regional - Junta de Castilla y Leon	Burgos		Yes
Spain	ES	Laboratorio Agroalimentario de Extremadura (Cáceres)	Cáceres		Yes
Spain	ES	Laboratorio Agroalimentario de Zaragoza	Zaragoza		Yes
Spain	ES	Laboratorio Agroalimentario y de Sanidad Animal de Murcia	El Palmar-Murcia		Yes

* only for EU-Member States; [1)] no reason reported to the organisers; [2)] Technical or personall problem

Appendix 1-a (cont.): participating labs of EU and EFTA member states

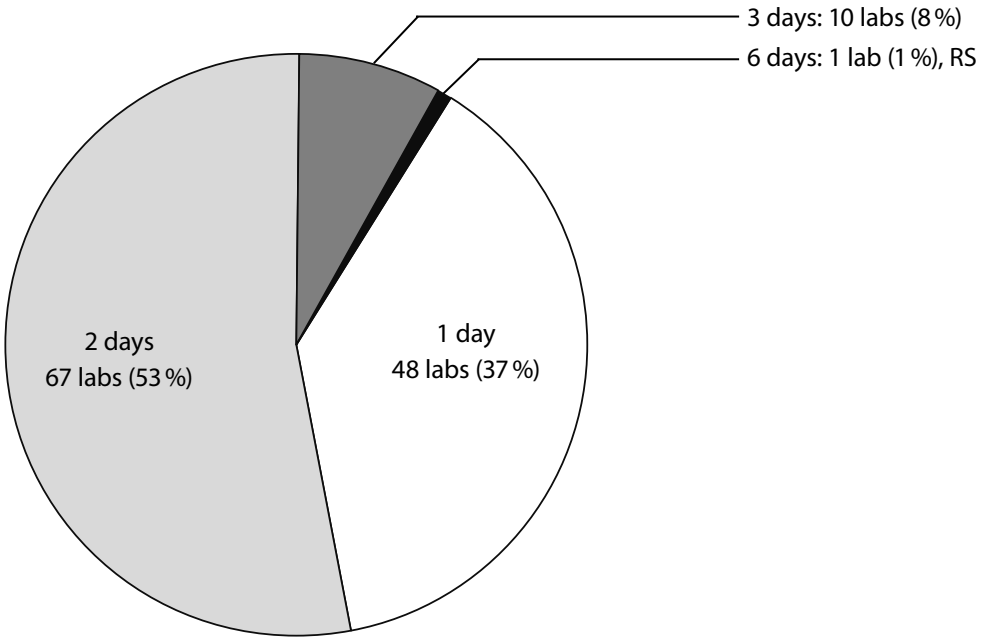
Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Spain	ES	Laboratorio Arbitral Agroalimentario, Madrid	Madrid	x	Yes
Spain	ES	Laboratorio de Producción y Sanidad Vegetal de Almería, Ministry of Agriculture	La Mojonera (Almería)		Yes
Spain	ES	Laboratorio de Producción y Sanidad Vegetal de Jaén	Mengibar (Jaén)		Yes
Spain	ES	Laboratorio KUDAM S.L.	Pilar de la Horadada		Yes
Spain	ES	Laboratorios Ecosur, S.A.L.	Lorquí (Murcia)		Yes
Spain	ES	Laboratory of Barcelona Public Health Agency	Barcelona		Yes
Spain	ES	Labs & Technological Services AGQ, S.L.	Burguillos (Sevilla)		Yes
Spain	ES	National Centre for Food - Spain, Majadahonda	Majada-honda	x	Yes
Spain	ES	National Centre for Technology and Food Safety - Laborytory of Ebro	San Adrián (Navarra)		Yes
Spain	ES	SiCA AGRIQ, SL	VÍCAR (ALMERIA)		Yes
Spain	ES MT	Agrofood Laboratory of the Comunidad Valenciana	Burjassot-Valencia		Yes
Sweden	SE	Eurofins Food&Feed Testing Sweden AB	Lidköping		Yes
Sweden	SE	National Food Agency, Science Department, Chemistry Division 1	Uppsala	x	Yes
United Kingdom	UK	Eurofins Food Testing UK Limited - UK, Wolverhampton	Wolver-hampton		Yes
United Kingdom	UK	Science and Advice for Scottish Agriculture	Edinburgh		Yes
United Kingdom	UK	Scientific Analysis Laboratories Ltd	Bar Hill		Yes
United Kingdom	UK MT	Fera Science Ltd	York	x	Yes
United Kingdom	UK MT	Laboratory of the Government Chemist - Teddington	Teddington		No [2)]

* only for EU-Member States; [1)] no reason reported to the organisers; [2)] Technical or personall problem

Appendix 1-b: Participating Laboratories from EU Candidate Countries and Third Countries

Country	Institution	City	Reported results
Egypt	Central Lab of Residue Analysis of Pesticides and Heavy Metals in Foods	Giza	Yes
Serbia	SP LABORATORIJA A.D.	BECEJ	Yes

Appendix 2 Shipment Evaluation: Compilation of Duration of Shipment



Appendix 3 Data of Homogeneity Test

COMPULSORY COMPOUNDS								
	Cyromazine		Dithiocarbamates		Dodine		TFNA	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
No. 010	1.447	1.656	1.304	1.045	1.286	1.298	0.841	0.821
No. 024	1.385	1.564	1.347	1.213	1.295	1.265	0.841	0.795
No. 053	1.551	1.611	1.229	1.423	1.338	1.329	0.838	0.896
No. 062	1.527	1.424	1.508	1.586	1.273	1.272	0.853	0.846
No. 081	1.517	1.593	1.432	1.479	1.309	1.327	0.761	0.865
No. 109	1.564	1.651	1.431	1.431	1.368	1.321	0.806	0.838
No. 115	1.465	1.534	1.492	1.464	1.247	1.239	0.815	0.828
No. 128	1.562	1.671	1.675	1.497	1.301	1.292	0.830	0.808
No. 166	1.590	1.722	1.561	1.608	1.275	1.196	0.776	0.833
No. 185	1.679	1.503	1.411	1.336	1.271	1.382	0.915	0.812
mean / AV*	1.561 / 1.512		1.424 / 1.297		1.294 / 1.243		0.831 / 0.756	

	TFNG		Tolylfluanid	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
No. 010	0.519	0.468	0.881	0.792
No. 024	0.496	0.519	1.333	0.815
No. 053	0.467	0.488	0.935	1.053
No. 062	0.487	0.490	0.939	0.835
No. 081	0.492	0.475	1.104	1.084
No. 109	0.457	0.490	1.086	0.936
No. 115	0.505	0.481	0.842	0.941
No. 128	0.482	0.480	0.803	0.744
No. 166	0.468	0.489	1.111	0.827
No. 185	0.473	0.504	0.976	0.793
mean / AV*	0.486 / 0.448		0.942 / 0.598 #	

* mean / AV = Average value of the homogeneity test data [mg/kg] / Assigned value of PT [mg/kg] derived from the entire population

Assigned value was with high uncertainty and for informative purpose only. Z-scores based on this assigned value were calculated for informative purpose only.

OPTIONAL COMPOUNDS								
	BAC-C14		Chlorate		Dithianon		Phosphonic acid	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
No. 010	0.307	0.289	2.232	2.374	4.449	4.340	9.386	9.140
No. 024	0.437	0.332	2.422	2.265	3.186	3.666	9.464	9.818
No. 053	0.280	0.371	2.338	2.254	3.274	3.951	9.258	9.217
No. 062	0.336	0.284	2.181	2.283	4.305	4.381	9.315	9.158
No. 081	0.420	0.415	2.340	2.294	3.310	3.236	10.026	9.932
No. 109	0.361	0.335	2.394	2.312	4.894	3.810	9.756	10.448
No. 115	0.327	0.335	2.329	2.353	3.766	2.959	8.909	9.140
No. 128	0.278	0.272	2.264	2.259	3.272	4.173	9.073	8.726
No. 166	0.342	0.281	2.408	2.322	3.787	3.755	9.360	9.702
No. 185	0.336	0.281	0.125	0.127	3.550	3.650	9.485	10.494
mean / AV*	0.331 / 0.285		2.316 / 2.033		3.786 / – ‡		9.490 / 9.831	

	Perchlorate		Pymetrozine		Quizalofop		Triclopyr	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
No. 010	0.264	0.255	0.529	0.543	0.162	0.147	0.188	0.180
No. 024	0.275	0.269	0.473	0.504	0.220	0.167	0.240	0.211
No. 053	0.260	0.248	0.507	0.536	0.157	0.172	0.194	0.194
No. 062	0.260	0.254	0.522	0.442	0.162	0.154	0.191	0.190
No. 081	0.270	0.265	0.560	0.477	0.231	0.201	0.238	0.244
No. 109	0.259	0.251	0.521	0.489	0.174	0.174	0.192	0.211
No. 115	0.268	0.263	0.495	0.469	0.162	0.166	0.198	0.199
No. 128	0.261	0.262	0.501	0.518	0.145	0.140	0.194	0.174
No. 166	0.251	0.264	0.474	0.518	0.185	0.165	0.213	0.192
No. 185	0.279	0.275	0.531	0.511	0.184	0.154	0.211	0.186
mean / AV*	0.263 / 0.260		0.506 / 0.432		0.171 / 0.171		0.202 / 0.177	

* mean / AV = Average value of the homogeneity test data [mg/kg] / Assigned value of PT [mg/kg] derived from the entire population

‡ The distribuation of participants results was very wide. The assigned value derived from the population was with high uncertainty and therefore not calculated.

Appendix 4 Data of Stability Test

COMPULSORY COMPOUNDS												
	Cyromazine			Dodine			TFNA			TFNG		
	25.04.2016	12.05.2016	22.06.2016	06.04.2016	12.05.2016	25.05.2016	06.04.2016	12.05.2016	25.05.2016	06.04.2016	12.05.2016	25.05.2016
Sample	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
No. 024	1.669	1.773	1.689	1.145	1.155	1.135	0.818	0.815	0.800	0.507	0.495	0.475
No. 081	1.655	1.678	1.692	1.255	1.195	1.210	0.813	0.800	0.775	0.484	0.470	0.445
No. 166	1.762	1.712	1.812	1.170	1.180	1.180	0.805	0.815	0.780	0.479	0.495	0.455
Mean [mg/kg]	**1.695**	**1.721**	**1.731**	**1.190**	**1.177**	**1.175**	**0.812**	**0.810**	**0.785**	**0.490**	**0.487**	**0.458**
RSD* [%]	**3.44 %**	**2.81 %**	**4.05 %**	**4.85 %**	**1.72 %**	**3.21 %**	**0.84 %**	**1.07 %**	**1.69 %**	**3.13 %**	**2.97 %**	**3.33 %**
Diviation [%] (ref. 1st Anaylsis)	**—**	**1.49 %**	**2.08 %**	**—**	**-1.12 %**	**-1.26 %**	**—**	**-0.23 %**	**-3.31 %**	**—**	**-0.67 %**	**-6.45 %**

	Tolylfluanid				Dithiocarbamates		
	06.04.2016	12.05.2016	25.05.2016		08.04.2016	13.05.2016	25.05.2016
Sample	[mg/kg]	[mg/kg]	[mg/kg]	Sample	[mg/kg]	[mg/kg]	[mg/kg]
No. 024	1.100	1.070	1.110	No. 053	1.326	1.371	1.224
No. 081	1.120	1.070	1.020	No. 109	1.431	1.234	1.394
No. 166	1.020	0.990	1.145	No. 185	1.374	1.362	1.265
Mean [mg/kg]	**1.080**	**1.043**	**1.092**	**Mean** [mg/kg]	**1.377**	**1.322**	**1.294**
RSD* [%]	**4.90 %**	**4.43 %**	**5.91 %**	**RSD*** [%]	**3.81 %**	**5.81 %**	**6.88 %**
Diviation [%] (ref. 1st Anaylsis)	**—**	**-3.40 %**	**1.08 %**	**Diviation** [%] (ref. 1st Anaylsis)	**—**	**-3.96 %**	**-6.00 %**

OPTIONAL COMPOUNDS												
	BAC-C14			Chlorate			Dithianon			Phosphonic Acid		
	06.04.2016	12.05.2016	25.05.2016	05.04.2016	12.05.2016	25.05.2016	06.04.2016	12.05.2016	25.05.2016	05.04.2016	12.05.2016	25.05.2016
Sample	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
No. 024	0.384	0.346	0.369	2.343	2.637	2.535	3.820	3.300	2.815	10.151	9.838	10.624
No. 081	0.418	0.362	0.328	2.317	2.432	2.487	3.470	3.805	3.185	10.116	9.579	10.504
No. 166	0.311	0.328	0.341	2.365	2.435	2.421	3.090	3.540	3.260	10.125	9.567	9.737
Mean [mg/kg]	**0.371**	**0.346**	**0.346**	**2.342**	**2.501**	**2.481**	**3.460**	**3.548**	**3.087**	**10.131**	**9.661**	**10.288**
RSD* [%]	**14.68 %**	**4.92 %**	**6.07 %**	**1.03 %**	**4.72 %**	**2.30 %**	**10.55 %**	**7.12 %**	**7.72 %**	**0.18 %**	**1.58 %**	**4.67 %**
Diviation [%] (ref. 1st Anaylsis)	**—**	**-6.82 %**	**-6.68 %**	**—**	**6.80 %**	**5.93 %**	**—**	**2.55 %**	**-10.79 %**	**—**	**-4.63 %**	**1.56 %**

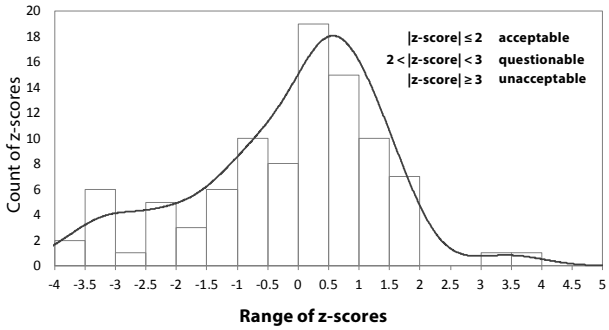
	Perchlorate			Pymetrozine			Quizalofop			Triclopyr		
	05.04.2016	12.05.2016	25.05.2016	25.04.2016	12.05.2016	22.06.2016	06.04.2016	12.05.2016	25.05.2016	06.04.2016	12.05.2016	25.05.2016
Sample	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
No. 024	0.247	0.239	0.250	0.454	0.469	0.433	0.194	0.174	0.205	0.226	0.210	0.215
No. 081	0.251	0.223	0.250	0.475	0.489	0.473	0.216	0.192	0.184	0.241	0.215	0.210
No. 166	0.243	0.229	0.238	0.506	0.459	0.470	0.175	0.181	0.177	0.202	0.215	0.200
Mean [mg/kg]	**0.247**	**0.230**	**0.246**	**0.478**	**0.472**	**0.459**	**0.195**	**0.182**	**0.189**	**0.223**	**0.213**	**0.208**
RSD* [%]	**1.65 %**	**3.31 %**	**2.66 %**	**5.41 %**	**3.22 %**	**4.93 %**	**10.43 %**	**4.81 %**	**7.73 %**	**8.74 %**	**1.35 %**	**3.67 %**
Diviation [%] (ref. 1st Anaylsis)	**—**	**-6.74 %**	**-0.38 %**	**—**	**-1.29 %**	**-4.11 %**	**—**	**-6.54 %**	**-3.14 %**	**—**	**-4.35 %**	**-6.59 %**

***** RSD = relative standard diviation

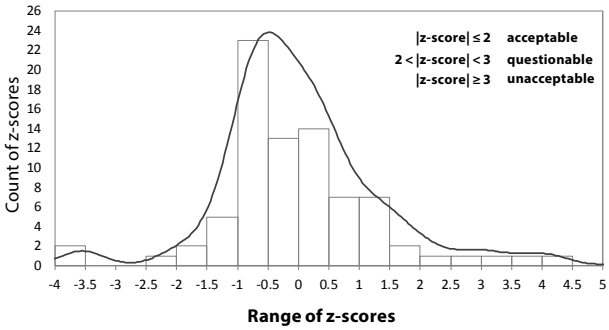
Appendix 5 Histograms and Kernel Density Estimates of z-Scores* Distributions

Compulsory compounds

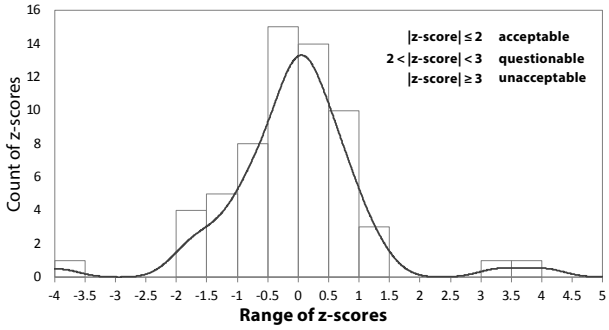
Dithiocarbamates
(AV derived from entire population)



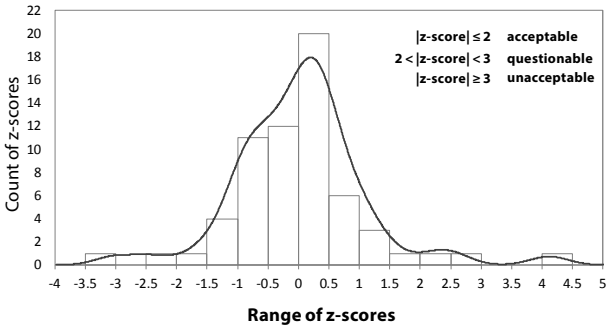
Dodine
(AV derived from entire population)



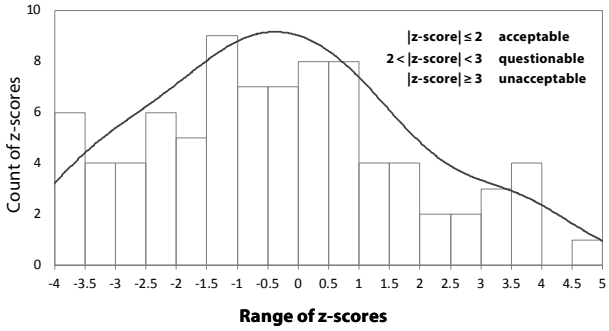
TFNA
(AV derived from entire population)



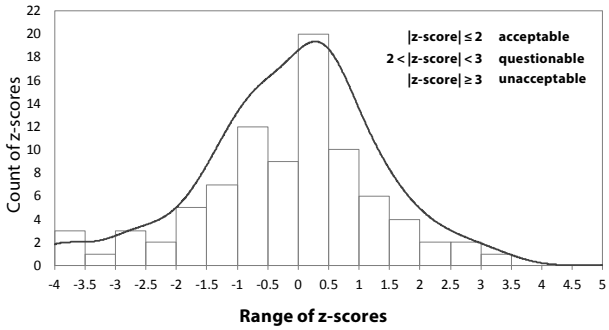
TFNG
(AV derived from entire population)



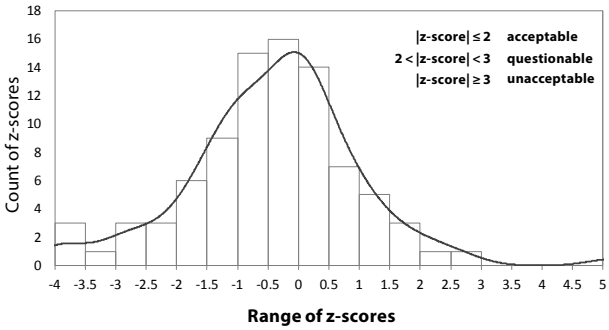
Tolylfluanid
(AV# derived from entire population)



Cyromazine
(AV derived from entire population)



Cyromazine
(AV derived from population using ILIS)



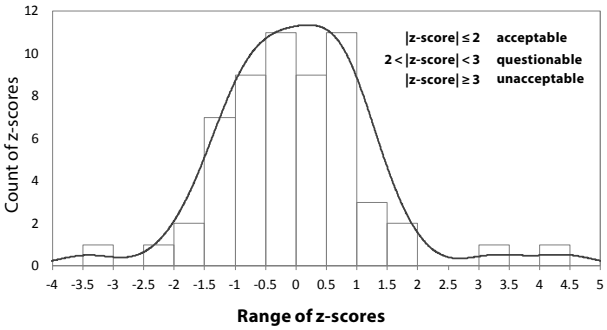
* Cut-off at z-score = 5;

Assigned value was with high uncertainty and z-scores derived from this assigned value were calculated for informative purpose only.

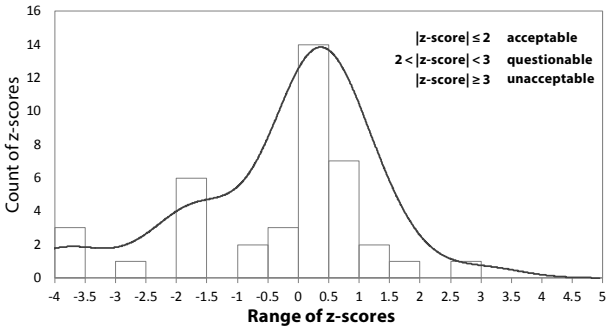
Appendix 5 (cont.) Histograms and Kernel Density Estimates of z-Scores* Distributions

Optional compounds

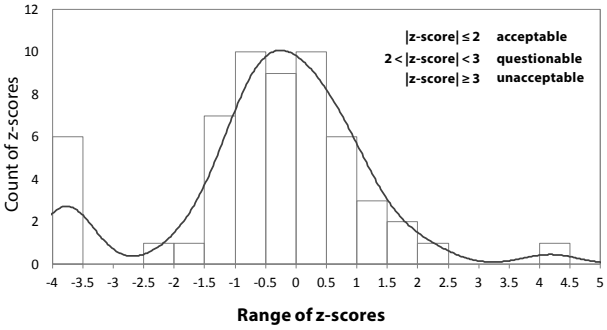
BAC-C14
(AV derived from entire population)



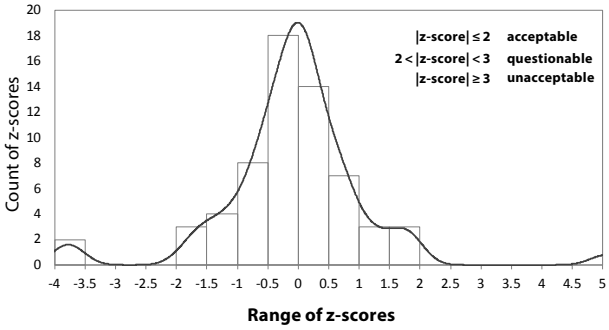
Phosphonic Acid
(AV derived from entire population)



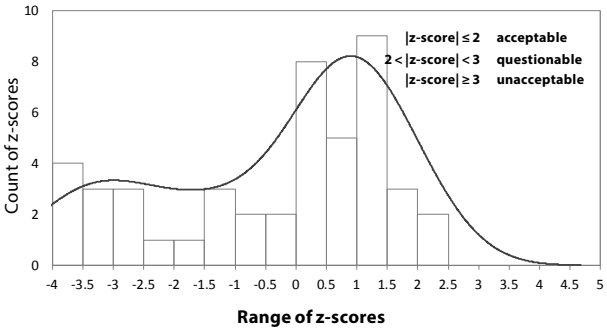
Quizalofop
(AV derived from entire population)



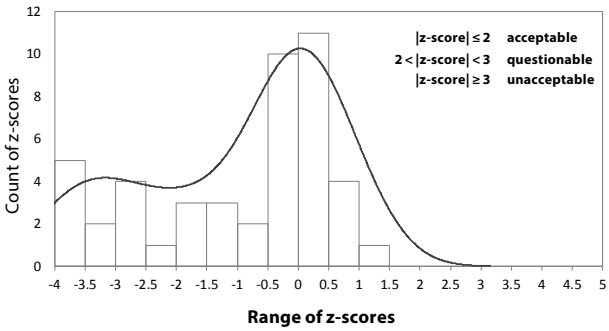
Triclopyr
(AV derived from entire population)



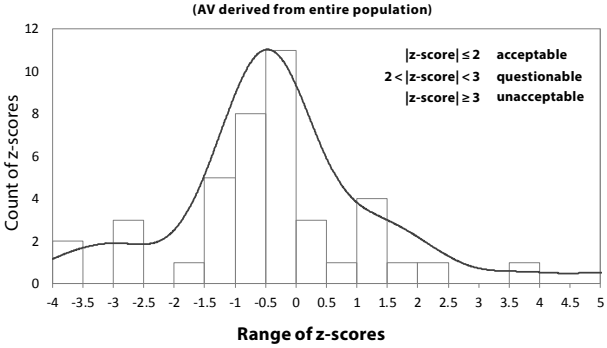
Chlorate
(AV derived from entire population)



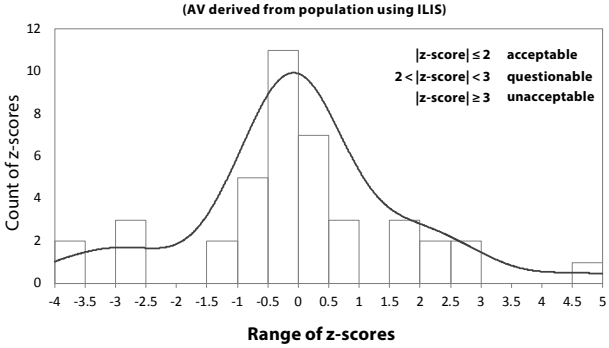
Chlorate
(AV derived from population using ILIS)



Perchlorate
(AV derived from entire population)



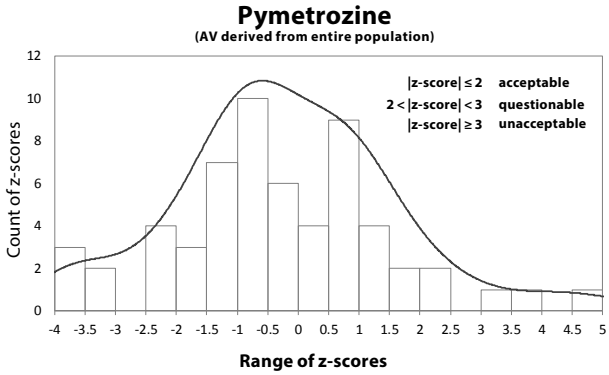
Perchlorate
(AV derived from population using ILIS)

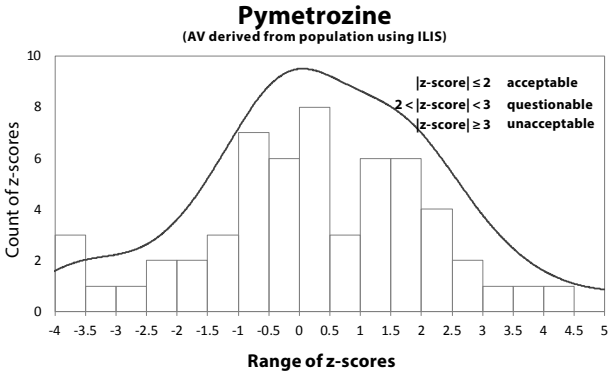


***** Cut-off at z-score = 5; # excluding dithianon due to high uncertainty of its assigned value

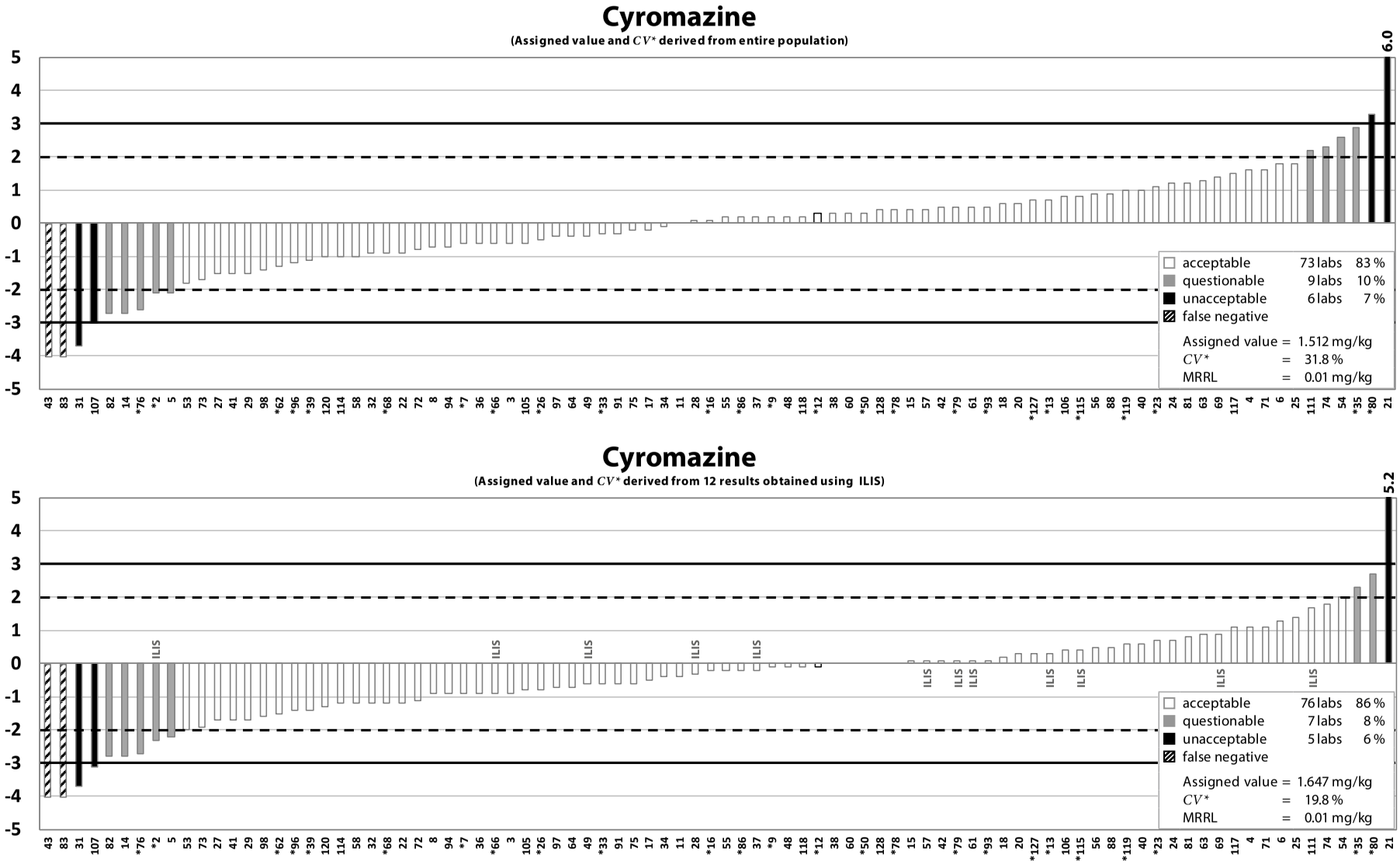
Appendix 5 (cont.) Histograms and Kernel Density Estimates of z-Scores* Distributions

Optional compounds

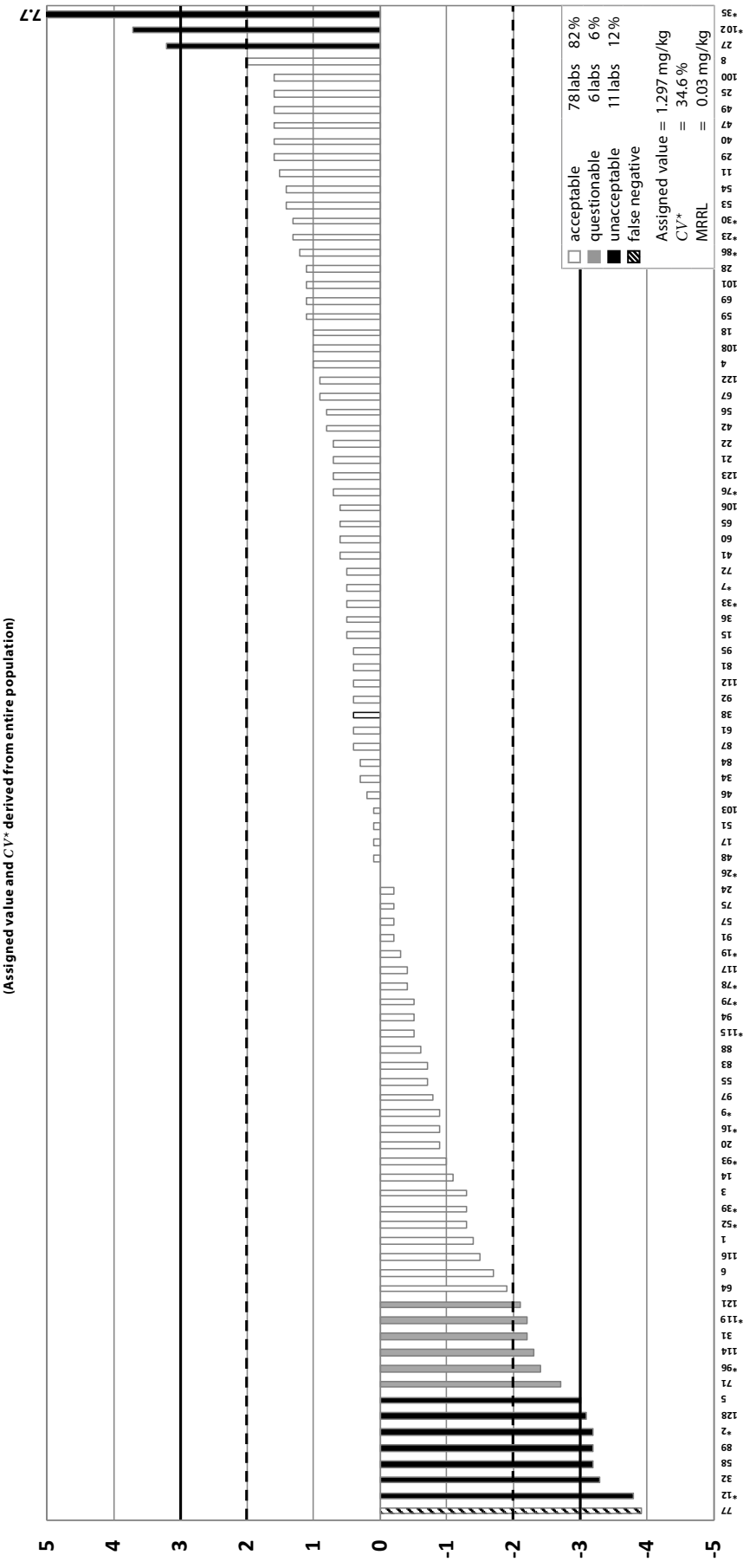




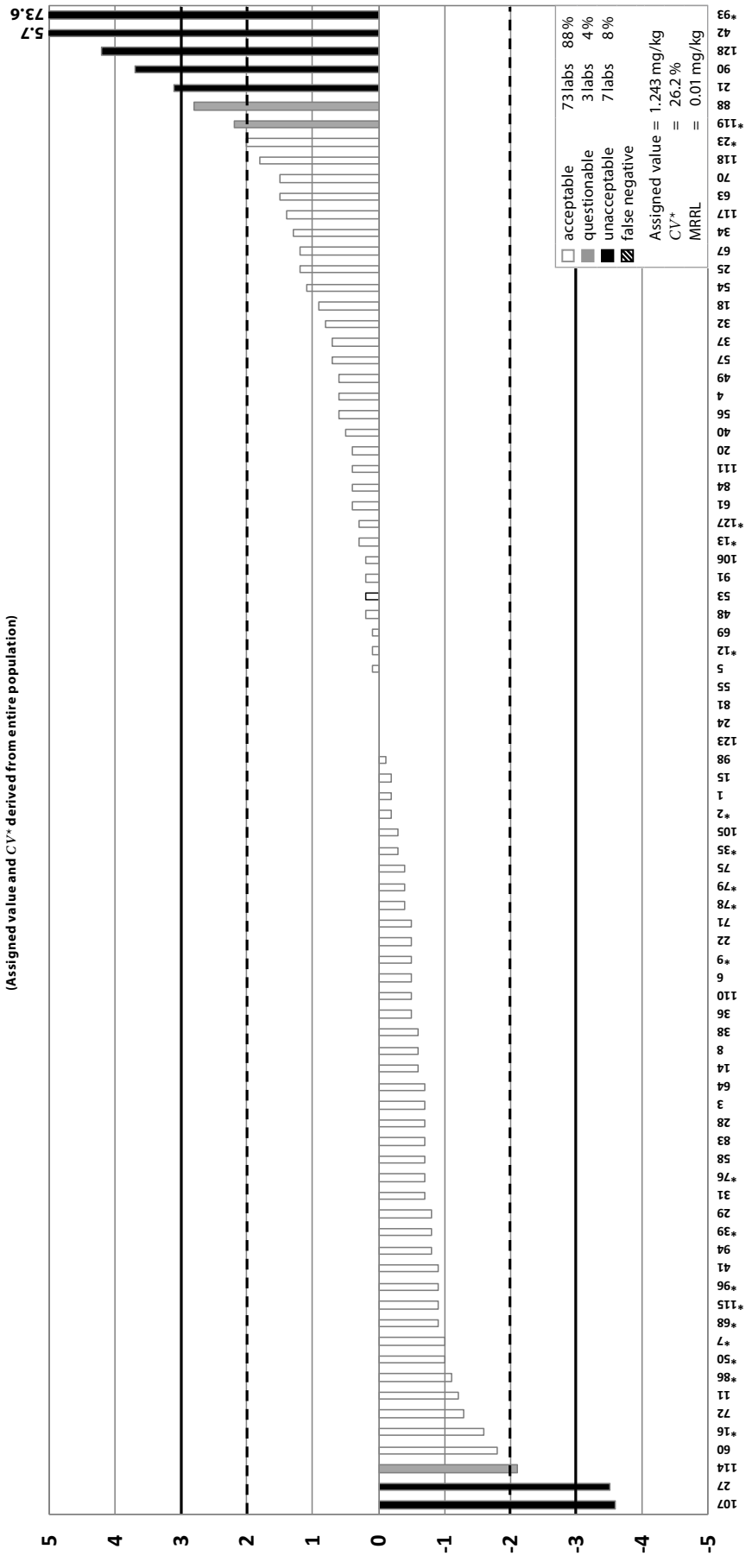
Appendix 6 Graphic Presentation of z-scores: Compulsory Compounds



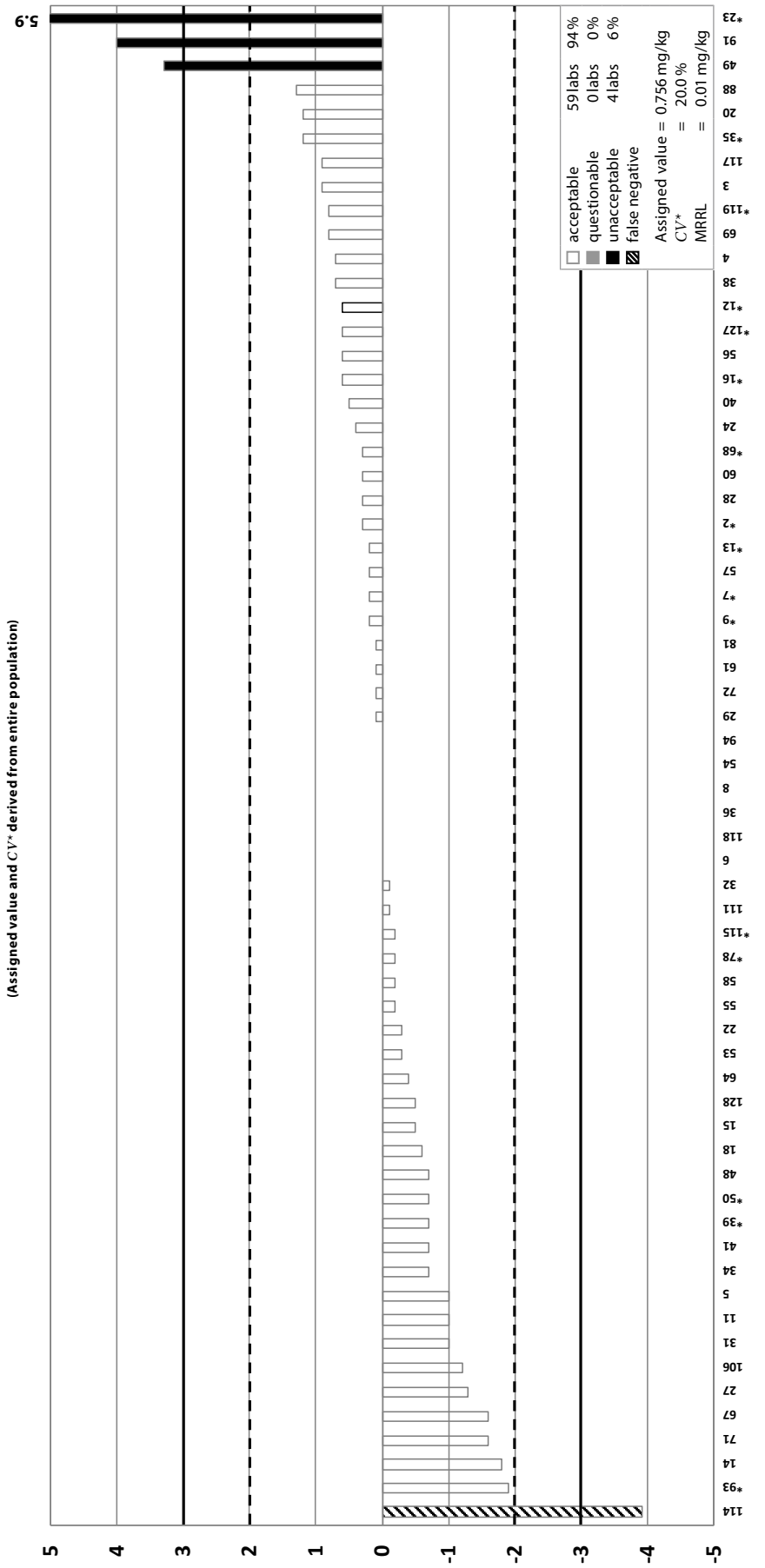
Appendix 6 (cont.) Graphic Presentation of z-scores: Compulsory Compounds



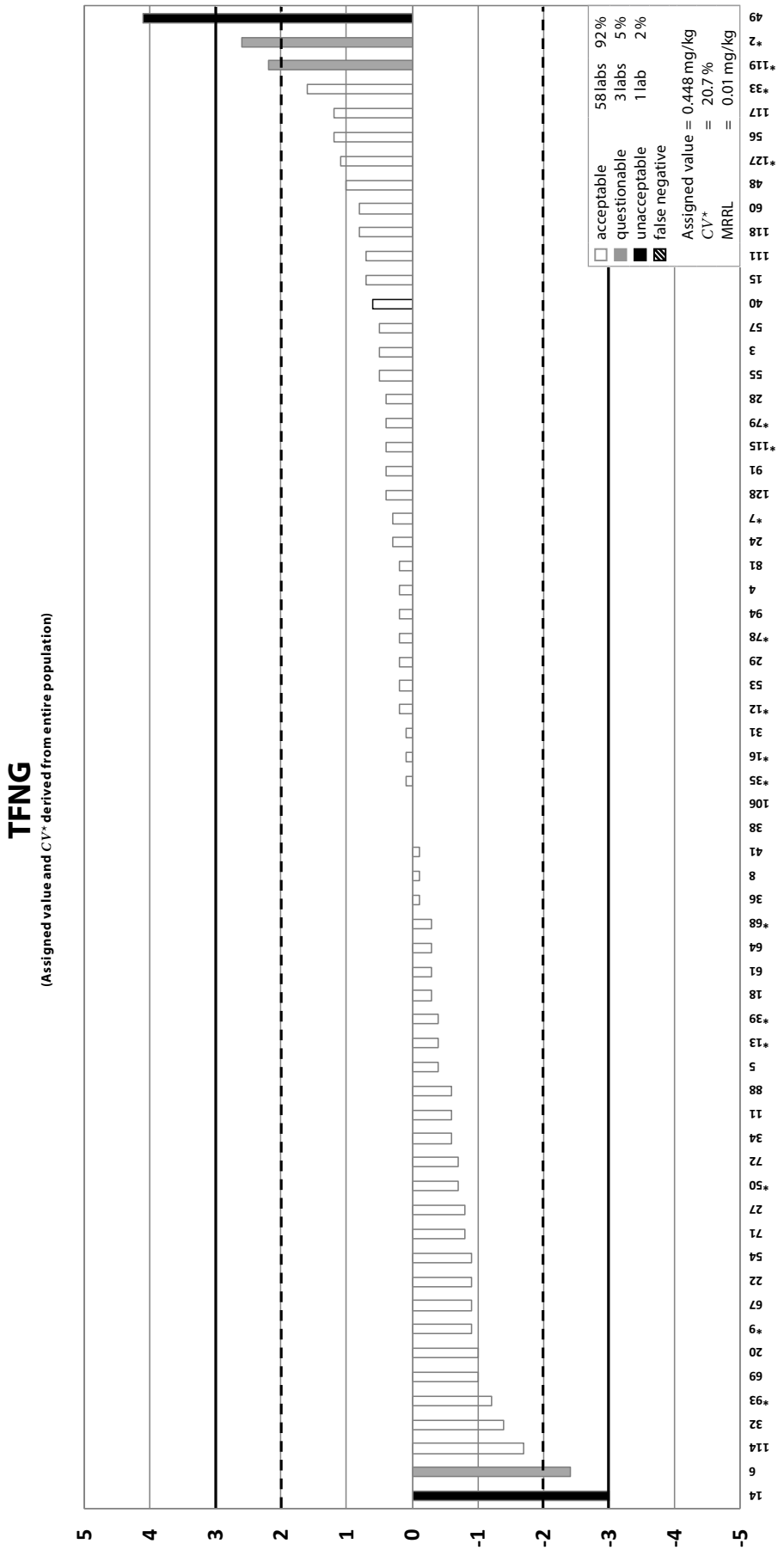
Appendix 6 (cont.) Graphic Presentation of z-scores: Compulsory Compounds



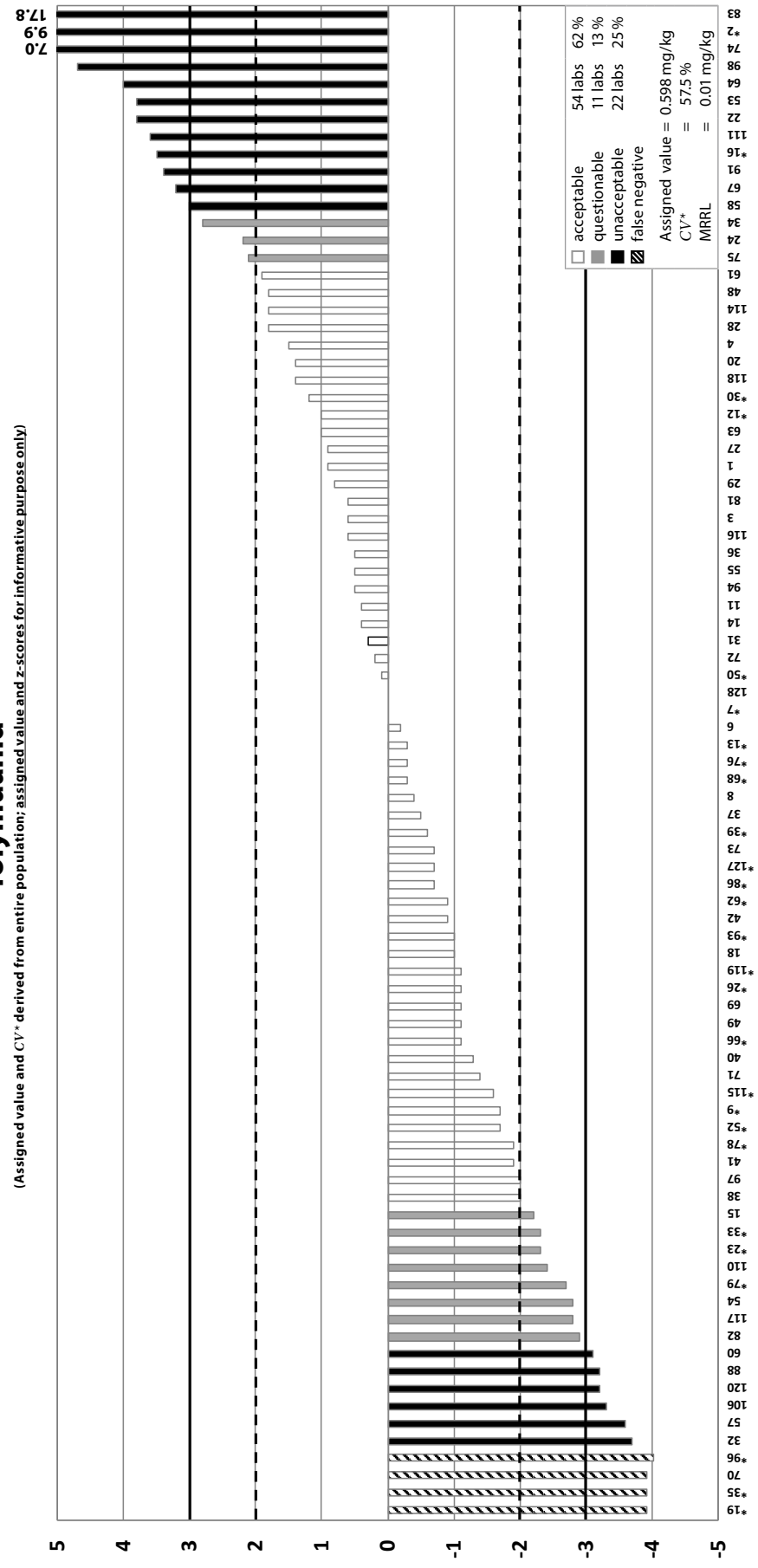
Appendix 6 (cont.) Graphic Presentation of z-scores: Compulsory Compounds



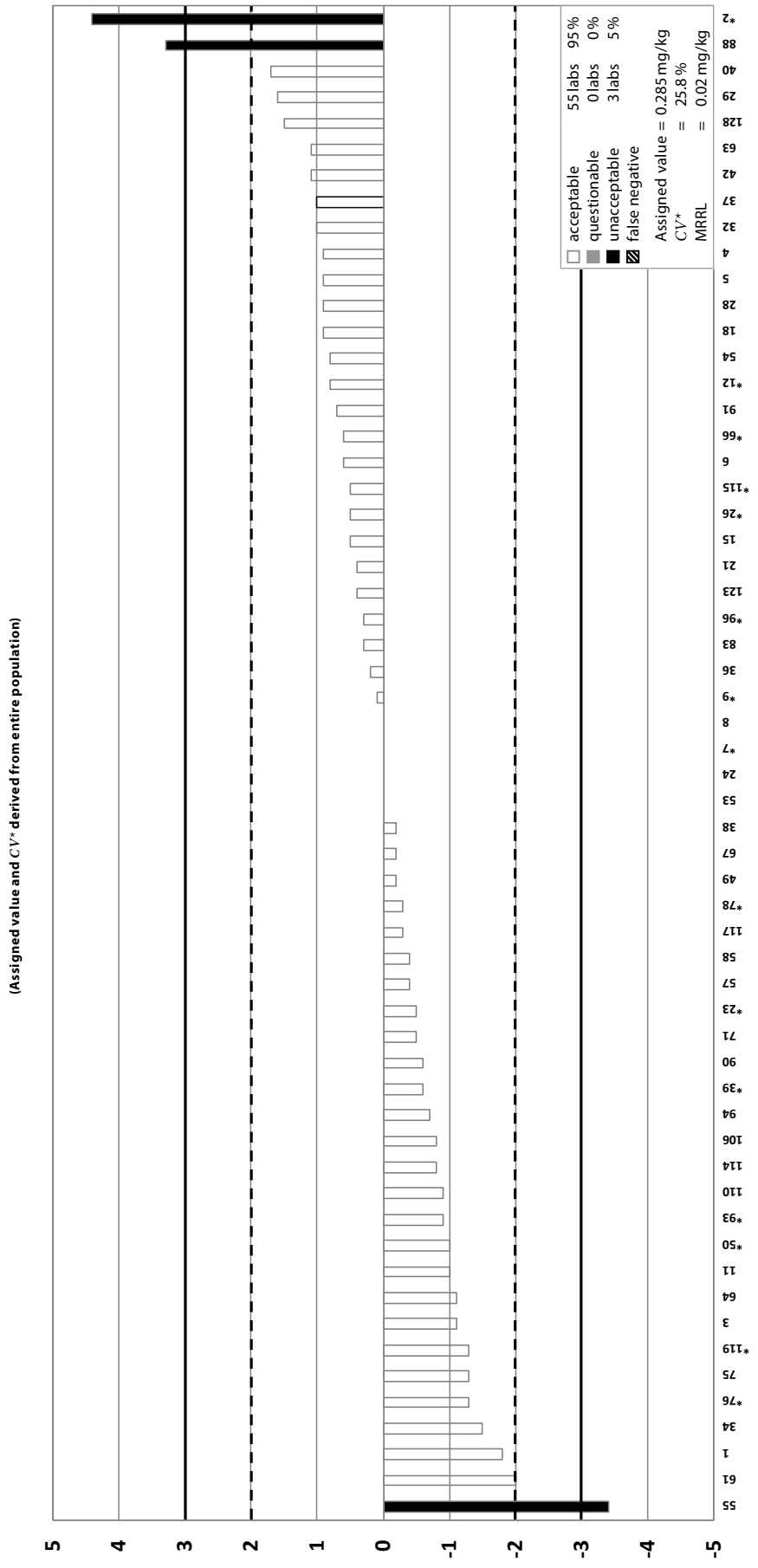
Appendix 6 (cont.) Graphic Presentation of z-scores: Compulsory Compounds



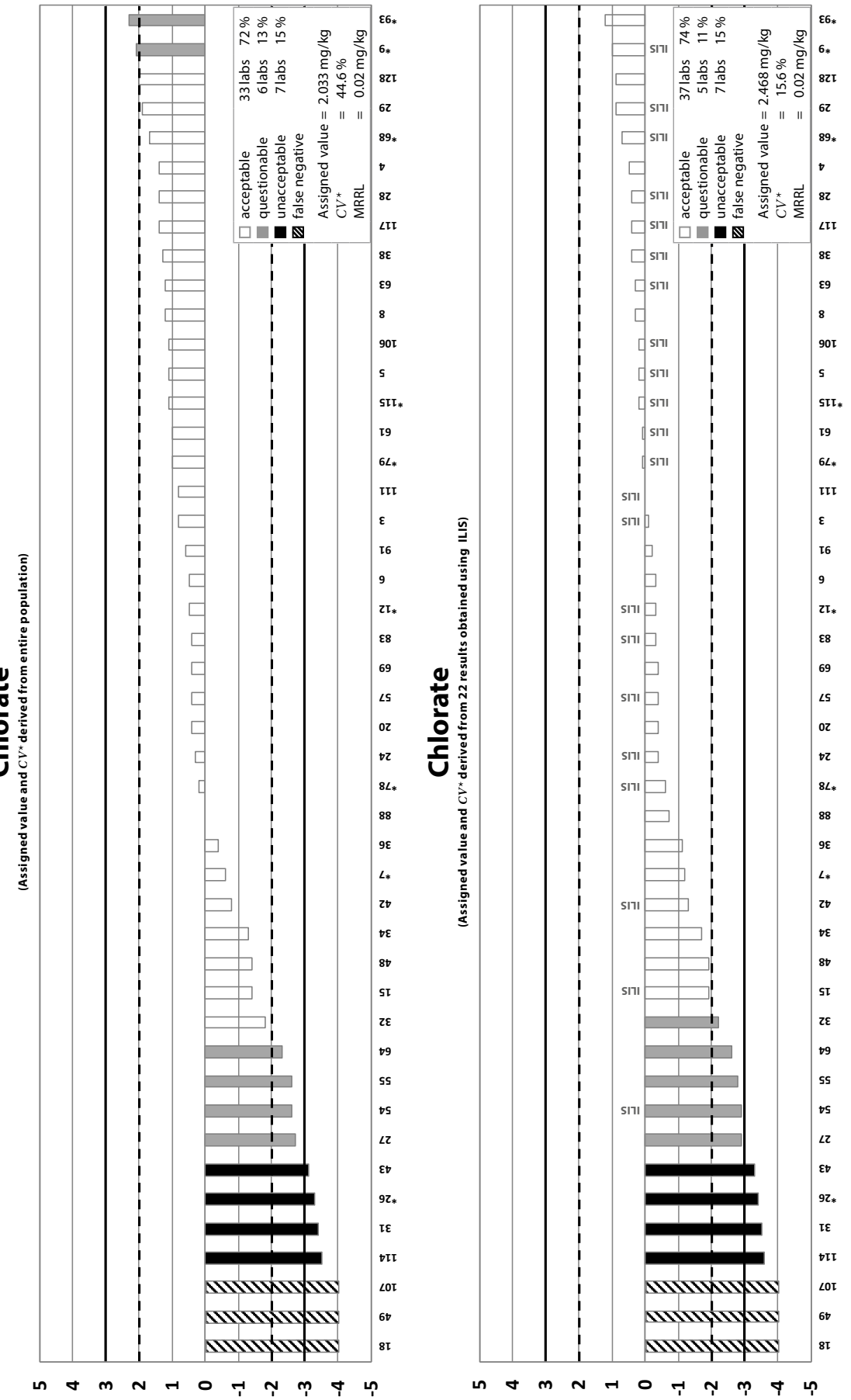
Appendix 6 (cont.) Graphic Presentation of z-scores: Compulsory Compounds



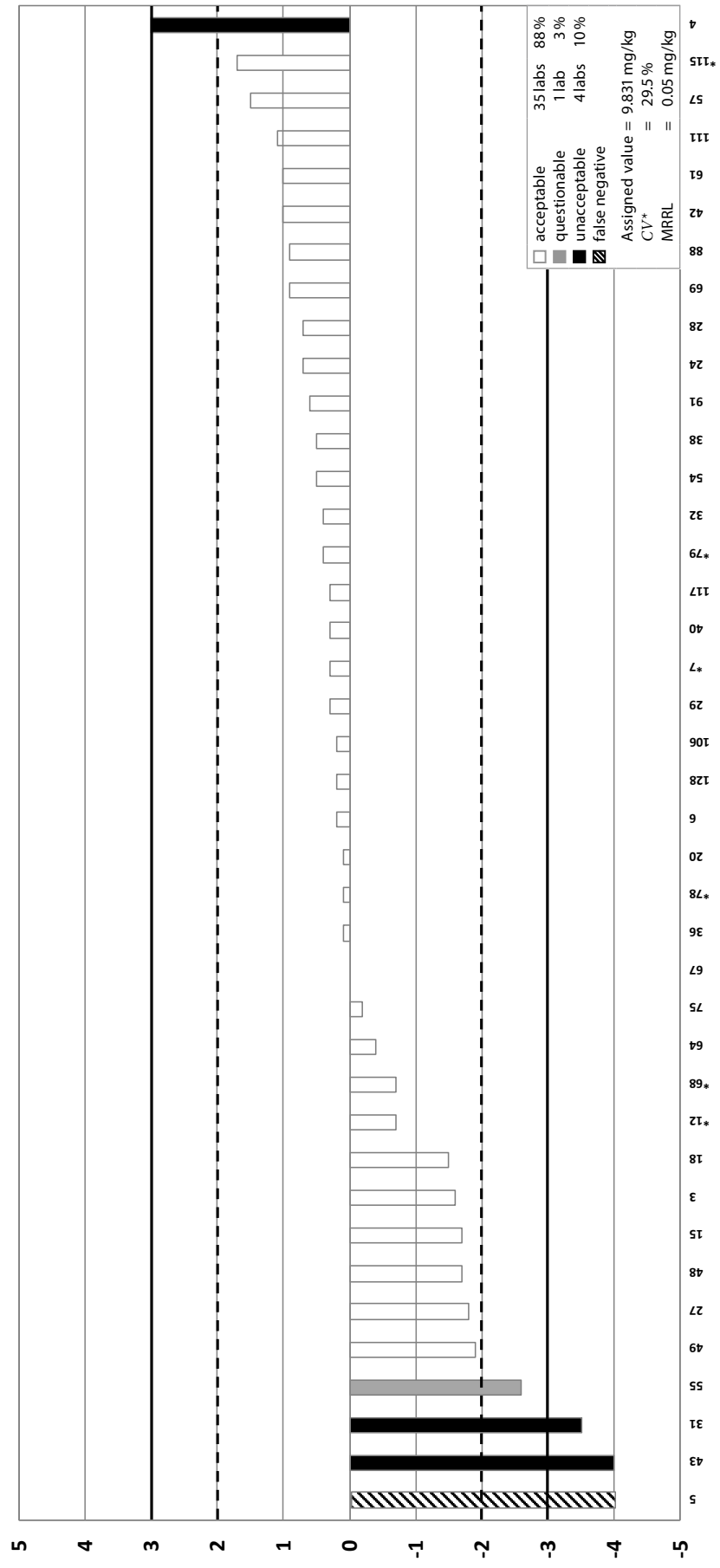
Appendix 6 (cont.) Graphic Presentation of z-scores: Optional Compounds



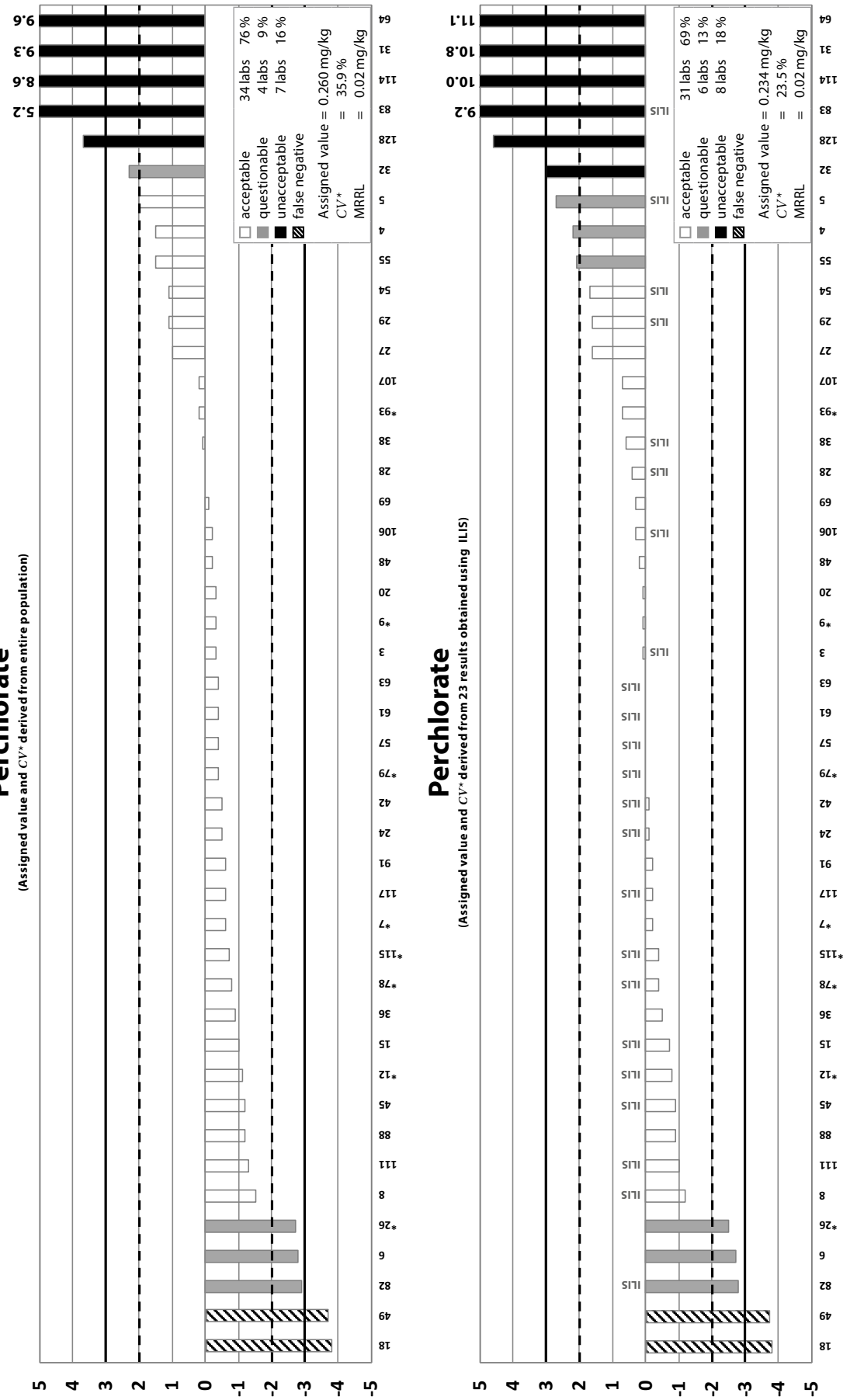
Appendix 6 (cont.) Graphic Presentation of z-scores: Optional Compounds



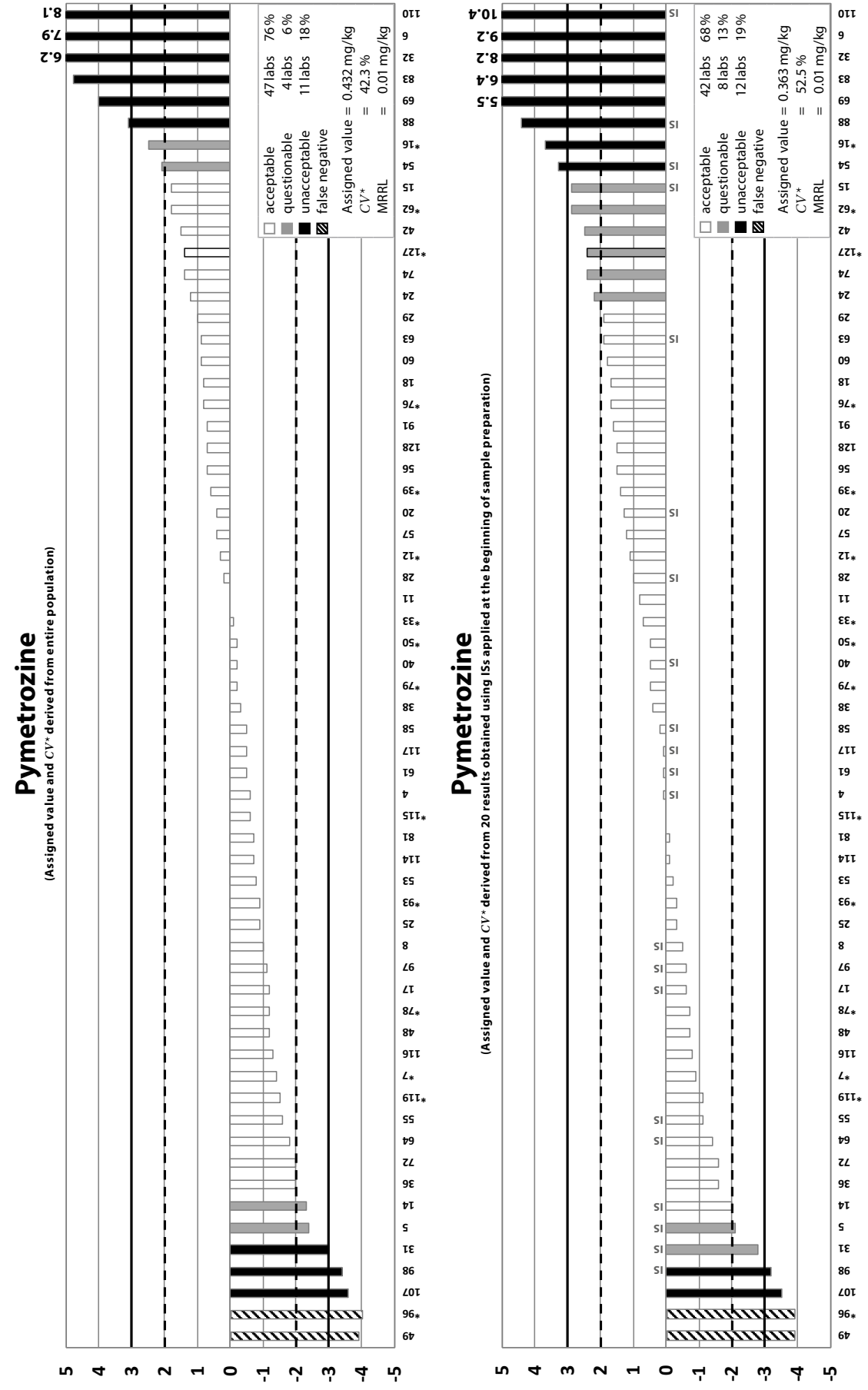
Appendix 6 (cont.) Graphic Presentation of z-scores: Optional Compounds



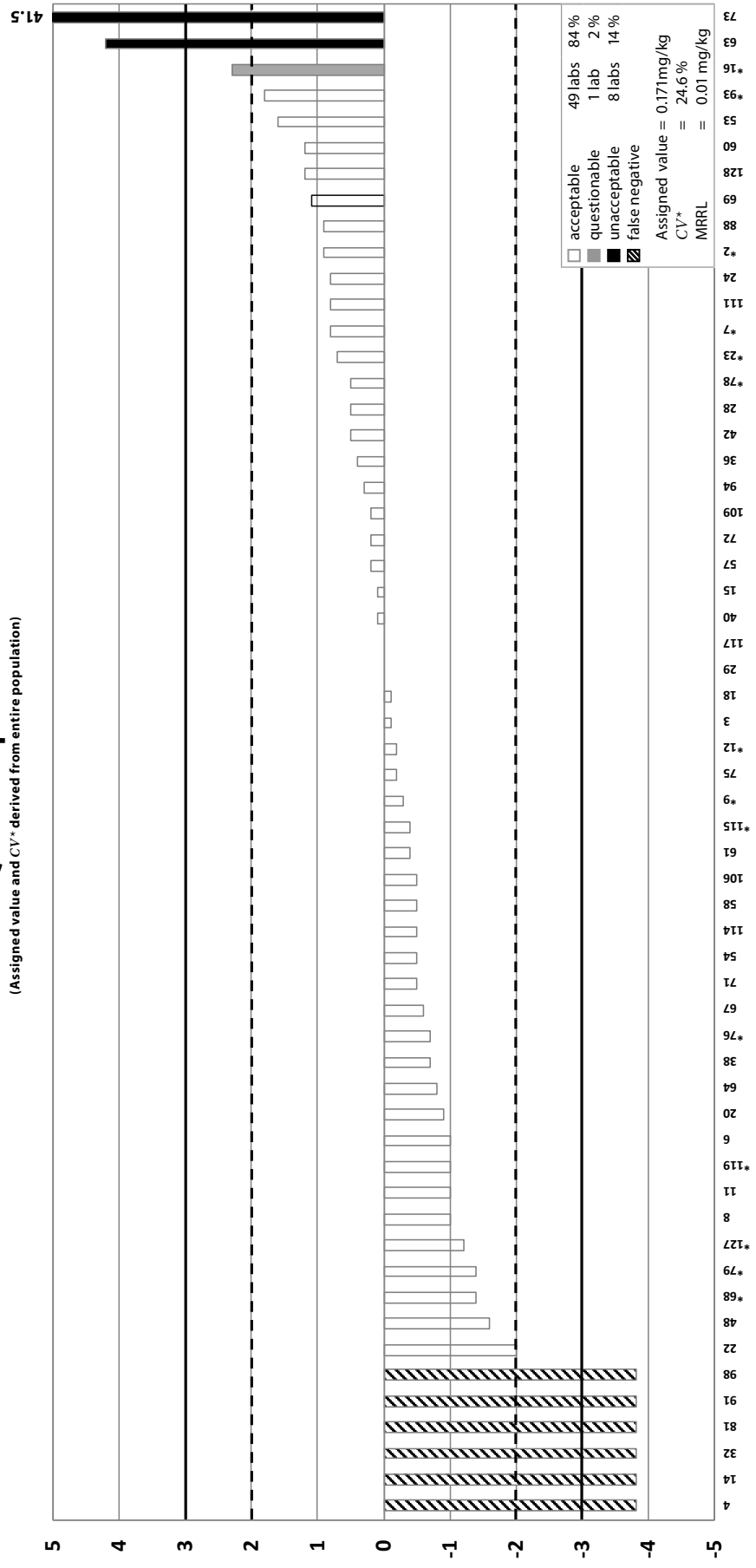
Appendix 6 (cont.) Graphic Presentation of z-scores: Optional Compounds



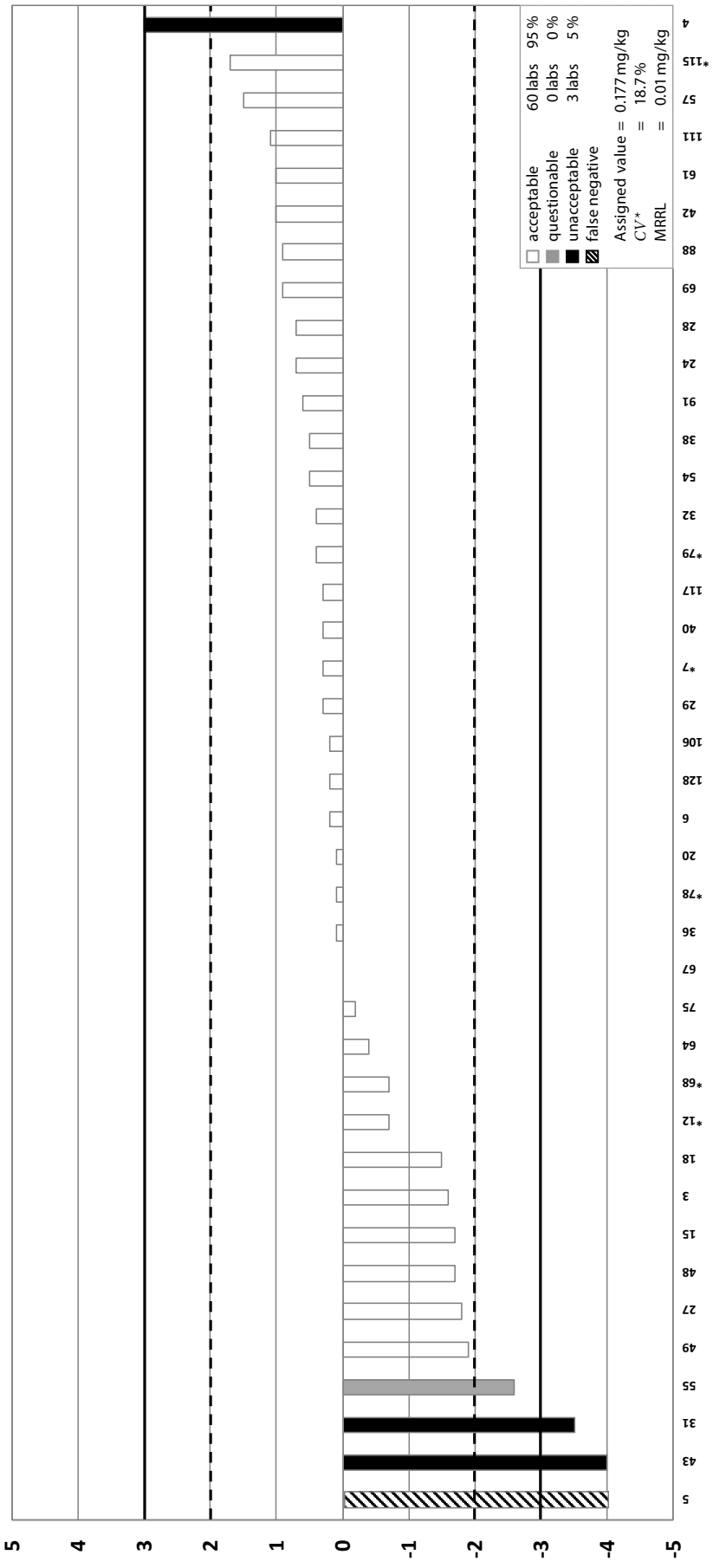
Appendix 6 (cont.) Graphic Presentation of z-scores: Optional Compounds



Appendix 6 (cont.) Graphic Presentation of z-scores: Optional Compounds



Appendix 6 (cont.) Graphic Presentation of z-scores: Optional Compounds



Appendix 7 Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)
I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

False Positive Results

Lab-Code	Analytes	Error Source localized?	Reason / Remarks	
88	Ethephon	–	Possible reason of the error: Interference due to the method used. Follow-up measures: Change of method to that indicated by EURL. ***Comment by the organizers:*** Consider the use of a good separation column to reduce matrix interferences. Consider the introduction of quality control measures to reduce the risk of false positives, such as recovery experiments, calibration standards on the same matrix and standard additions. The use of ILIS would additionally help you to reduce the risk of false positives, by showing you the expected retention time and peak shape of the native analyte (if it is present).	F, L, O
102	Ethephon	Yes	We analyze animal origin, cereals and feed samples for SRM analytes and don't have previous experience of spinach. SRM methods are not validated for fruits and vegetables. This is main reason for false positive in case of ethephon. Matrix background was very intensive in LC-MS/MS. In both samples, EUPT blank and EUPT sample, peaks at the same retention time than ethephon were detected for all four monitored mass spectrometric reactions (m/z 144.5–>81, m/z 144.5–>63, 147.0–>81, 147.0–>109). Two reactions (m/z 144.5–>81, m/z 144.5–>63) resulted in bigger peak in PT sample than blank sample and that was reason why we reported result for ethephon. I as a corresponding researcher, evaluated results incorrectly on the based on insufficient data and without experience of spinach matrix. I made mistake and gave result even identification was not clear at all. It is not possible to separate matrix peaks from ethephon with our method and thus it is not suitable method for analysis of ethephon residues in spinach. ***Suggestions/Comments by the organizers:*** If you use a hypercarb column try to prime it well to improve the peakshape of ethephon and other compounds	D, E, F, L, O
88	Glyphosate	–	Possible reason for error: Interference due to the method used. The actual quantification limit is 0.05 mg/kg. Our reported result was below this limit (0.03 mg/kg) propably due to interference due to lack of conditioning of the chromatographic column (Hypercarb). Follow-up measures: We are currently working with isotope pattern and calibrating with the same matrix. ***Comment by the organizers:*** The use of ILIS would additionally help you to reduce the risk of false positives by showing the expected retention time and peak shape of the native analyte (if it is present). Consider improving conditioning of the hypercarb column to improve peak-shape and chromatographic separation of glyphosate, as this would reduce the risk of interferences by matrix components. Also consider the introduction of additional quality control measures to ensure that the risk of false positive results is minimized (e.g. recovery experiments, calibration standards on the same matrix and standard additions).	F, L, O

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Cyromazine Assigned value: 1.51 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
2	-2.1	Vague initial suspicions	Usually we bought Cyromazine in liquid form at 10ng/ml, but this time we bought Cyromazine in powder, and we experienced some difficulties to dissolve it in solvent. We analyzed the sample twice, the first time as usual (QuPPe method) and the second time by standard addition to sample portion(Quppe). Results were very different and we chose result founded by standard addition to sample portion. ***Comments by the organizers:*** Normally a problem with incomplete dissolvation or with precipitation of the standard would lead to to an overestimated result. Still, please check your standard solution against a new one prepared in a different solvent (see proposed solvent composition in the QuPPe-protocol). As you have calibrated via standard addition to sample portions and additionally used ILIS it is surprizing that your result is within the questionable range. Please recheck your standard additions calculation and the ratio between the ILIS added to the test portion versus the ILIS added to the calibration standards.	(E), Adv1
5	-2.1	Yes	We analyse it with the multirresidue method. Perhaps we must analyse it with QuPPE method. ***Comments by the organizers:*** As cyromazine is very polar the recovery rate by MRMs is usually low (using QuEChERS typically in the range of 30 to 50 %). Individual recoveries may fall outside this range. By achieving a recovery rate of 72 % you obviously decided that no measures are needed to correct the result for recovery. If you had corrected your result for recovery by a recovery factor your it would have been within the acceptable range. Other means of recovery correction such as procedural calibration, standard additions to sample portions and ILIS would have also been an option. You can still use QuEChERS (or other MRMs) for cyromazine if you make sure that your final result is corrected for recovery, e.g. via ILIS, procedural calibration or standard addition to sample portions. If you apply QuPPe the use of ILIS is also indicated to match for matrix effects. Another possible source of error may be related to the use of blank tomato to prepare calibrationsolution.	(E), (G), (J), (L)
14	-2.7	Yes	Application of standard Quechers procedure. Proposed corrective action: Testing QuPPe method 4.1 ***Comments by the organizers:*** Agree with proposed measures. Another option would be to keep the method and correct for recovery e.g. by standard addition to sample portions, procedural calibration or the use of ILIS. The recovery rate of 71 % you have reported for TFNG is unusually high for CEN-QuEChERS (the typical range is between 30 and 40 %), and this may have made you believe that the negative bias is tollerable. Consider correcting for recovery even within the range of 70-80 % recovery.	E, G, J, L
21	6	No	Cyromazin is not validated and therefore not part of our scope, as reported. Further feedback provided following questions by the organizers: We have diluted the cyromazine extract 100-fold using cucumber commodity in order to fall within the range of our procedural calibration. The pocedural calibration standards were, however, not diluted. The extracts of the recovery experiments were also not diluted. Comments by Organizers: You reported the dilution of the test-Item extracts with blank-cucumber extract. For the matrix-effects to be properly compensated the procedural calibration extracts should have been diluted in a simmilar way. Using this approach recovery losses were largely compensated (via the procedural approach) but the matrix effects were not. Following 100-fold dilution with cucumber extract the test-item extract became comparable to cucumber in terms of matrix effects, whereas the calibration standards consisted purely of spinach extracts (undiluted). The recovery reported for cyromazine (103 %) is higher than what is typically expected by QuEChERS as it was corrected via the procedural calibration and as the recovery experiment extracts were not diluted as in the case of the test item. This is the reason why they do not not show the same overestimation-trend as the reported Test-Item results.	C, D, E, L, O
31	-3.7	Yes	Error calculation, not multiplied by the dilution factor (10) ***Comments by the organizers:*** matrix effects could have also played a role, since you have employed a calibration based on pure solvent	E, I

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Cyromazine Assigned value: 1.51 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
35	2.9	Vague initial suspicions	Unfortunately, we are not able to find precise reasons for questionable and unacceptable z-scores. Possible reasons could be decomposition of standard or contamination of the system. With Cyromazine we had problems during analysis. As I remember expert tried different sample preparation procedures (we do not perform cyromazine for routine samples) and finally she had some reliable results with acidified extraction without clean up with PSA which we have reported. ***Comments by the organizers:*** in theory acidification leads to reduced QuEChERS recoveries of cyromazine due to a drop of the logP value. The procedural calibration that you conducted should in theory correct for this increased bias. However, if recoveries become very low and peak areas too small accuracy may be compromised.Consider the use of ILIS to correct for recovery.	D, (E), G, (J), (L)
43	-4	–	In the case of cyromazine, our laboratory has NOT tested this active substance. ***Comments by the organizers:*** According to the rules such explanations are not accepted if they are received a posteriori. The result is thus treated as a false negative.	E, I
44	-3.4	No	We couldn't find the problem, concentration of standard solution is ok (checked with a new standard) and calculation of results is ok, too. For sample preparation and determination used EN 15662 (dSPE by Agilent, 5982-5356CH, column Hypersil GOLD aQ 1.9µm 2.1x50mm, Thermo and eluens 5mmol HCOONH4 in H2O with 0,1 % HCOOH and 5mmol HCOONH4 in MeOH with 0,1 % HCOOH). In the same method with the same conditions, we prepared the sample for determination of cyromazine, 2,4-D, haloxyfop and tolyfluanid. We didn't use for cyromazine the QuPPe-PO Method because, in validation procedure, we determined cyromazine in multiresidual analysis. ***Suggestions/Comments by the organizers:*** According to the methodology information you have applied the matrix matched calibration approach. This approach corrects for matrix effects but not for losses during extraction/partitioning. For analytes with lower than acceptable recovery rates consider introducing approaches that correct for recovery such as the use of ILIS, standard addition to sample portions and procedural caloibration. As your submitted concentration is very low (lower than the recovery via QuEChERS would suggest) please check if the concentration of the standard was wrong (e.g. by a factor 10). Please recheck the recovery figure using QuEChERS. The submitted recovery figure seems to be quite high for the QuEChERS approach.	J, L
54	2.6	(Yes)	After this result, we prepared a new standard of cyromazine and we observed a deviation of approx. 15 %. So we checked the test material and obtained an acceptable value. Comments by the organizers: It would be worthwhile checking whether the overestimated result is due to a duplicate correction for recovery (via procedural calibration and via recovery factor).	(E)
74	2.3	Initial suspicions	We assume it is because we did corrected results for recovery which were rather low (35 %). If we had not corrected results for recovery, all z-scores would be <2. We would like to know whether all other labs used recovery correction, and what to do next time with recovery <70 %? ***Comments by the organizers:*** Typically correction of results for recovery reduces the bias. The use of recovery factors is more tricky than other approaches of recovery correction and should optimally involve multiple analyses of the sample and multiple recovery experiments (judging on your methodology information the recovery factor was based on 4 replicate recoveries). Taking average figures of replicate analyses reduces the uncertainty assosiated with analytical variability. Please consider the use of ILIS in future.The robust mean of the results submitted by laboratories having corrected for recovery was 1.67 mg/kg. Taking this figure as assigned value the z-score recalculates to 1.78 which is within the acceptable range.	E, J

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Cyromazine Assigned value: 1.51 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
76	-2.6	Yes	Cyromazine failed our validation criteria. During the PT we got a recovery of 50.9 % . When the result was corrected for recovery the value we got was 1.53 ppm which would have given us a z-score of 0.05. Comments by Organizers: When recovery deviates considerably from 100 % (e.g. <70 %) results should not be reported unless corrected for recovery to reduce bias (e.g. via ILIS, standard addition to sample portions or procedural calibration).	E, J, L, O
80	3.3	?	The laboratory has little experience with cyromazine -An isotope labeled internal standard was not used -the lab applied a recovery factor (80 %) to the results for PT although normally use matrix calibration. ***Comments by the organizers:*** Please consider that the polarity (LogKow) of your internal standard (2,6 diamino 4 chloro pyrimidine) is highly influenced by the pH. As your method does not involve any buffering step the recovery of the IS is expected to be variable depending on the pH of the commodity analyzed. Cyromazine also shows a pH dependency on polarity that, however, follows a different pattern than that of the IS. We thus consider this IS unsuitable to correct for the recovery of cyromazine. Please consider introducing other approaches of recovery correction such as standard addition to sample portions or ILISs.	C, D, E, J, L
82	-2.7	Yes	The analytes had a value of Z score of about -3 due to a calculation error. An incorrect volume was used during the calculation. ***Comments by the organizers:*** Please consider that using QuPPe method matrix effects are strong. Using solvent based calibration these matrix effects may cause considerable errors unless compensated, e.g. via ILIS.	E, I
83	-4	Yes	Exterme matrix effects: We repeated the sample but with greater dilution of the extract and found closest to the target values results. Due to the limited experience in handling this type of column we saw that the peak shape and retention times varied greatly. As the matrix greatly influences proceeded to 1:10 and 1:20 dilutions and the new value was : 1.342 mg/kg ***Comments by the organizers:*** The result after dilution is very close to the AV (we assume that you have employed recovery correction as QuEChERS recoveries of cyromazine are typically low - in the rande between 30 and 50 %). Consider introducing procedures that will improve identification certainty to avoid false negative results, such the use of ILIS, standard addition approaches and recovery experiments on blank matrix of the same type. Dilution indeed reduces matrix effects and in some cases helps to avoid false negatives if it goes along with a better chromatographic separation of the target compound and matrix components. Also consider improving chromatographic separation using softer gradients or a different column.	C, D, E, L, O
107	-3	(Yes)	we used multiresidue method (the same method for analysis of pesticides in fruit and vegetables with ethyl acetate extraction). We didn't use internal standard and no recovery was performed. Just recently we started with SRM and so far we haven't accredited nothing but perchlorates itself. That was our primary goal due to the monitoring of perchlorates in fruit and vegetables. We only had 25 samples last year and another 25 samples in 2016. ***Comments by the organizers:*** a recovery experiment and a validation in general would have helped to assess the bias and trigger recovery correction measures (e.g. use of ILISs, standard addition to sample portions, procedural calibration).	(C), D, E, (G), (L)
111	2.2	No	We used an ILIS (Cyromazine-d4) for analysis and so our result is higher than results of other laboratories which use no ILIS ***Suggestions/Comments by the organizers:*** The robust mean of the population using ILIS was found being 9 % higher (1.647 mg/kg; n = 12) than that of total population that was used to calculate the assigned value (1.512 mg/kg; N = 86). Using the robust mean of the ILIS population as assigned value the z-score recalculates to 1.78 which is within the acceptable range. Please also consider the following: You have employed 2 g for analysis. In general using very small sample portions increases the risk of portion-to.portion variability.	E, (L), M, (N)

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Dithiocarbamates Assigned value: 1.30 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
2	-3.2	?	Recovery found is around 50 %; We gave results without correction of recovery as we always did. Chromatographically, the interpretation of the peak was very difficult, We will try to perform our condition. Moreover we wished to analyze the matrix again but unfortunately we didn't have enough samples. We used an external calibration, pure solvent, multiple level. ***Comments by the organizers:*** try to improve chromatographic and/or detection selectivity. Increase the temperature of the reaction step as the reaction is very slow at 50°C. Consider increasing the $SnCl_2$ concentration. The recovery rate (50 %) was determined based on a single experiment and it could be belonging to a normal statistical distribution with a mean recovery within the acceptable range. Still determining a recovery rate of 50 % in a recovery check should preferably trigger further actions to check if there is a systematic bias and, if indicated, an alternative procedure that corrects for recovery should be envisaged.	A, E, J, L, G
5	-3	Yes	When we noticed that we have a not satisfactory result, we investigated why because until this EUPT we always had had good results in others PT. Finally we realized that in that time we had made an error with the calculations. The standars were x3.3 concentrated so the our result was 3.3 lower ***Comments by the organizers:*** Please also keep in mind that employing very small sample portions (3g) increases the risk of errors due to portion-to-portion variability. Analysis of several replicates will minimize this risk.	E
12	-3.8	Yes	Hydrolysis conditions (concentration of $SnCl_2$/HCl solution) were inadequate to ensure quantitative release of CS_2 (in fact especially attributed to the presence of incurred propineb instead of e.g. thiram). ***Comments by the organizers:*** we agree with laboratory's conclusions. Indeed propineb needs more harsh conditions than thiram. Consider increasing both HCl and $SnCl_2$ concentartion. The procedural calibration standards prepared by fortifying blank portions with CS_2 matched for matrix effects and for partitioning losses of CS_2 but didn'tr match for the obviously reduced transformation of propineb and its intermediates to CS_2.	E, G, L
27	3.2	Yes	We used a standard of Thiram degraded for spike. We used the recovery obtained for correction of value in the sample. The value not correct for recovey is 1,257 mg/Kg ***Comments by the organizers:*** Normally the thiram recovery using the dithiocarmabate method involving LLP is in the range of 80-110 % on average. Individual recoveries may deviate. Applying a correction of a result based on a recovery figure of just one result is thus risky as it can introduce a very large bias. Please consider introducing suitable criteria for the correction of recovery by recovery factors. Another possibility for the correction of the result for recovery would be a procedural calibration with various portions of the blank being spiked with increasing amounts of CS_2 or thiram or another dithiocarbamate. Problematic with procedural calibrations in dithiocarbamate analysis is however that the different dithiocarbamates tranform to CS_2 with varying difficulty. The dithiocarbamate used was propineb that according to our experience is more difficult to convert to CS_2 than thiram. Please consider that thiram may decompose when spiked to defrosted sample homogenates, with not all decomposition products leading to the generation of CS_2 during analysis.	(E), (J), (L), (O)
31	-2.2	Yes	Procedure not properly conducted ***Comments by the organizers:*** Consider increasing the reaction time as 1 hour can be too short for some types of dithiocarbamates, such as propineb.	B, E, G, L
32	-3.3	No	Aufgrund eines vorangegangenen Ringversuches von FAPAS können wir uns diesen Messewert bisher nicht erklären. Weitere Tests werden durchgeführt Given our successful results in a FAPAS compatitive test we cannot explain this poor performance. Investigation is continuing. For calibration matrix was spiked with CS_2. Tests have shown that spiking with thiram gives better results. ***Comments by the organizers:*** Consider using stronger reagents. Experiments have shown that transformation of propineb to $CS_2$is more difficult than that of thiram.	G, L

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

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F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Dithiocarbamates Assigned value: 1.30 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
35	7.7	Vague initial suspi-cions	Unfortunately, we are not able to find precise reasons for questionable and unacceptable z-scores. Possible reasons could be decomposition of standard or contamination of the system. ***Comments by the organizers:*** CS_2 does not easily decompose. Evaporation could be a reason. If you have spiked with thiram a degradation in the sample portion prior to the start of the reaction procedure could also be a reason for underestimated calibration. Please also consider checking whether there is errors in the preparation of the calibration standard or the calculations. Although not related with your overestimated results please consider increasing the reaction temperature and time seeof your procedure as these seem to be not strong enough for the analysis of CS_2 propineb (which as contained in th e sample) as CS_2.	(A), (E)
58	-3.2	Strong assump-tions	After receiving the sample, it was first thawed, homogenized and frozen again, before the analyses. We think that this thawing and freezing has caused the poor performance. In the same sequence, another proficiency test sample was also analysed with a good result (z-score = -1.23). This sample was not thawed and frozen. For the moment, the stability of samples in the freezer and the effect on the analysis of dithiocarbamates is being tested. We conducted several analyses of 5 g portions and the precision was very poor: 20/4 (0.29; 0.59; 0.16) and 4/5 (0.21, 0.14, 0.12). ***Suggestions/Comments by the organizers:*** to our experience no signifficant decline of total CS_2 occurs during storage in the freezer. Consider prolonging the reaction time. It is worthwhile testing whether the conditions of the digestion are strong enough for propineb.The impact of defrosting was tested by the organizers and was found not to play a significant role.	(E), G, (H), L
71	-2.7	No	The analytical procedure (as well as calibration and calculation) was checked step-by-step, including the recovery of CS_2 release from propineb. Results of all control analyses were complient. Reason for questionable result is unknown. Possibilities: (i) degradation of analyte before analysis or (ii) insufficient test sample homogenization, (iii) falling into 5 % probability to be outside given z-score interval in normal (Gaussian) distribution of results. We have also perform the procedure with lower amount of sample (instead of 1,1g, only 0,55 g was weighted into a vial) and using reduced amount of sample with the same volume of decomposition reagent (i.e. higher ratio of reagent to sample) the concentration of CS_2 close to 1,3 mg/kg was obtained. Afterwards, decomposition reagent was prepared freshly and with original ratio 1,1g of sample + 2ml of reagent the result was correct again. ***Comment by the organizers:*** A poor conversion of propineb and its intermediates to CS_2 is the most likely reason for your underestimated result. Your reaction conditions (2N HCl and 20 min reaction time) seem to be too weak for the transformation of propineb to CS_2. Your experiments with propineb might not properly resemble the state of incurred propineb residues. In this respect, please consider that if transformation of propineb is not quantitative applying standard addition to sample portions using CS_2, will only partly corrects results for recovery. We consider possibility (i) rather insignificant as a good stability of propineb (determined as CS_2) was shown. The impact of thawing on the stability of the residue (determined as CS_2) was also found to be negligible and this was also confirmed by participants. As you have only analyzed 1 g portions, possibility (ii) - insufficient test sample homogenization - is also a likely explanation, especially if the result was derived from only one or very few analytical portions (information by participant upon request, n = 2). During homogeneity test the smallest portion tested was 20 g for dithiocarbamates and 10 g for other compounds. We haven't checked whether 1 g portions would pass the homogeneity criteria. Possibility (iii) is an option that always applies.	(B), (E), (H), (L), (N)

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Dithiocarbamates Assigned value: 1.30 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
77	-3.9	–	No recovery experiment was conducted Comment by the EURL: Based on the methodology data you have submitted it seems that the HCl concentration within the reaction mixture considerably very low. Also the $SnCl_2$ concentrationwas tentatively low. These conditions may have resulted in an insufficient generation of CS_2 from propineb. Propineb has been proven to be more difficult to transform to CS_2 compared to thiram. Other reasons for the false negative result are also conceivable. In any case consider introducing quality control practices that would allow detecting false negative results.	E, (G), (L), O
89	-3.2	–	–	–
96	-2.4	–	The calibration was wrong but as spiking was made with same solutions the recovery was OK. ***Comments by the organizers:*** Indeed, absolute errors in the concentration of the standard (e.g. due to degradation, wrong dilution) cannot be detected via a recovery experiment if the same standard is used. In addition please also consider increasing the ratio between reagent amount ($SnCl_2$ and HCl) and sample weight. For propineb it was noticed that more strong conditions are needed than for thiram.	(E), (G), (L)
102	3.7	No	We haven't yet found reason for too high z value for dithiocarbamates. One suspicion is old reference standard (exp. 2014). We have ordered new one and will repeat analyses. I will confirm reason for poor performance of dithiocarbamates when resolved. Second communication: we checked out and degradation of the standard was not the reason. Some part of the method is too hard. We have added water to the sample prior cleavage/hydrolysis reaction. ***Comments by the organizers:*** CS_2 if stored properly (in absence of light) is quite stable, so degradation is rather unlikely to be a mojor source of the error. There is however always the possibility of errors in the preparation of the stock standard solution due to the liquid nature of CS_2 which makes handling difficult. Evaporation losses from the working solution may be another source of error to be investigated. The reagent concentration, even after water addition, was within the typical range. Please check for possible calculation errors and the correctness of the stock and working standard concentrations.	(E), (L)
114	-2.3	–	We had analyzed the sample 3 times and every time I took lower results (I defrost and frost every time the sample). The final result was the average of three results (not in the same day). The problem is how we had treated the sample. ***Comments by the organizers:*** According to the tests of the EURL-SRM as well as one participant thawing the sample even repetitively did not affect the DTC levels. Please consider increasing the reaction time during analysis as propineb requires stronger conditions for its conversion to CS_2.	(E), G, (H), L
119	-2.2	Yes	The obvious reason for the too low result is the degradation of the analyte. The result had not been corrected by using recovery (79 %) ***Suggestions/Comments by the organizers:*** Please consider that CS_2 is quite stable. Evaporation due to a leaking vessel could be a source of losses. Other reasons for low recoveries including errors in calibration and the non-quantitative conversion of the dithiocarbamate pesticide or its intermediate breakdown products to CS_2. Consider increasing the reaction time as propineb does not convert to CS_2 as easy as thiram, which typically used in recovery studies.	(E), I, (J), L
121	-2.1	–	No reason provided ***Comments by the organizers:*** Please consider increasing the strength of the reagent, in particular the concentration of HCl in the reaction mixture seems to be too low, and to extend the duration of the reaction time.	L, G

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors
A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Dithiocarbamates Assigned value: 1.30 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
128	-3.1	(Yes)	We did not find any errors for the calibration, calculation, weighing, pipetting or any other errors, the method itself works for all plant- and animal derived commodities, we succeded in all respective PTs so far! We repeated the experiment three times with freshly prepared calibration solutions obtaining similar results. We use thiophene as an internal standard. We assume, that the homogenization step of the whole PT sample prior to the analysis, prescribed by the PT organizer, may have had a substantial effect on the concentration of dithiocarbamates in our test sample. By this homogenization step by milling in a metal blender the dithiocarbamates may have been degraded thoroughly. ***Suggestions/Comments by the organizers:*** Please consider increasing the reaction time. The organizers have tested the influence of the homogenization step and concluded that it does not have any significant influence on the results.	(E), (G), (H), (L)

Dodine Assigned value: 1.24 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
21	3.1	(Yes)	Dodine is part of our routine scope for QuEChERS and generally quantified by external matrix-matched calibration. For compensating the lack of SRM in corresponding proficiency testings required for certain compounds (i.e. Chlormequat, Mepiquat) we calibrate via procedural calibration. This usually works fine for all of the compounds, considering the recovery. This was also the case for Dodine. After receiving the preliminary report we reanalyzed the spinach sample with standard QuEChERS and matrix-matched (cucumber) calibration as we do with all routine samples. Results: 1,137 mg/kg (n = 2), recovery: 95,5 %. Further comments following questions by the organizers: We have diluted the dodine extract by a factor of 25 using cucumber commodity in order to fall within the range of our procedural calibration. The pocedural calibration standards were not diluted. The recovery experiments were also quantified using the procedural calibration with no dilution involved. In the additional experiment after the receiving the preliminary report we have also diluted the test-item extract 25-fold with cucumber extract. Comments by Organizers: You reported the dilution of the test-Item extracts with blank-cucumber extract. For the matrix-effects to be properly compensated the procedural calibration extracts should have been diluted in a simmilar way. This was not the case. Using this approach recovery losses were properly compensated (via the procedural approach) but the matrix effects were not. Following 25-fold dilution with cucumber extract the test-item extract became comparable to cucumber in terms of matrix effects. In the supplementary experiment the 25-fold diluted extract was measured against a cucumber-based standard. Here the matrix effects were compensated well enough resulting in a concentration level close to the AV.	C, E, L
27	-3.5	No	We are still investigating. We bought dodine stock standard solution in methanol (100 ppm). Afterwards we dilute this solution with acetonitrile (10 ppm and 1 ppm) to prepare working solutions. We used matrix blank provided by EURL for matrix match calibration. ***Comments by the organizers:*** From the methodology data we could not recognize any obvious error sources	–

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

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K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Dodine Assigned value: 1.24 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
42	5.7	Vague initial suspi-cions	We retested the spinach sample SRM11 in case of Dodine several times with new weighed portions and as well, because Dodine has a poor solubility, with a new less concentrated stock solution, each time with the same results. The standard was dissolved in acetonitrile. During our validation of QAC's we've expierenced contamination of Dodine (same ions, similar structure), but at our standard addition using only BAC-C14 in the sample blank we could not find Dodine, nor were other residues of QAC's in the test sample present which could have an influence on Dodine. From the analytical point of view, there were no mistakes made. We have already ordered a new Dodine analytical standard to check losses, but we didn't receive it so far. ***Comments by the organizers:*** The organizers agree with the measures undertaken as well as the further measures proposed. According to the EURL-SRM experience acetonitril is problematic when preparing stock-solutions of dodine. As dodine, having a guanidine moiety tends to interact with polar surfaces, such as glass, the use of aprotic solvents (e.g. acetonitrile), without any protic modifier, can be problematic.	E, L
88	2.8	–	By reviewing primary records it is detected that no graphite carbon was added to the extraction. Possible cause due to a greater matrix effect. The standard is firstly prepared in a concentration of 500 ppm im methanol. Secondly from that solution we prepare a 5 ppm mix in acetonitrile. Calibration solutions are prepared in acetonitrile extract of blank spinach using the 5 ppm mix. A different blank spinach than the one delivered by the EURL was used for calibration. Complementary comment: We found many matrix effect differences between our matrix of spinach and the blank spinach provided by the EURL. Comment by the Organizer: The differences in the matrix effects between the EURL-blank spinach and your blank spinach may explain the bias. However, two matrices of the same type normally do not deviate so much in their matrix effects to explain such a strong deviation. Please also consider checking the correctness of the standard solutions as dodine tends to interact with glass surfaces. The use of a matrix-matched rather than solvent-based calibration has surely reduced the risk of dodine losses on the glass walls and in the injector which could also be a source for overestimated results.	(C), (E), (L)
90	3.7	not yet	We know problems related to this molecules, but in another PT (apple matrix) we had acceptable results.To quantify DODINE we diluted the sample and used a matrix calibration curve, but this was not sufficient. Now we are investigating other possible causes. When we have finished the experiments, we'll send you our information. The dodine standard was purchased as a custom solution in acetonitrile (prepared by CPAChem). For every analytical batch we prepared a calibration curve (five points - matrix matched) using suitable matrix; the calibration curve is in water:acetonitrile (80:20). During further investigation we highlighted an important matrix effect, very different from matrix to matrix (for example is high for spinach and low for grapefruit), and it is difficult to eliminate or to understand how to control it. Now we are improving our method, we are changing the instrument (from agilent 6410 to agilent 6470) and dodine response is lower and instable, so we have to study better this difficult molecule. For our laboratory is a problem because in some type of samples dodine is present (apple, grapefruit). ***Comments by the organizers:*** Please check the correctness of your standard against a new one prepared in a protic solvent such as methanol. Acetonitrile being an aprotic solvent, does not hinder interactions of dodine with glass surfaces. By using a matrix-matched calibration solutions containing a relatively high percentage of water, you have most propably avoided a common error source of dodine analysis, related to interactions and losses in the LC-injector, which can lead to overestimation in the case of solvent-based calibration standards.	C, (E), (L)

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Dodine Assigned value: 1.24 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
93	73.6	Yes	Reported result should be 2,41 instead 24,1 mg/kg, but even with the correct figure the result would be too high. The standard solution of dodine used on EUPT-SRM-11 was prepared in acetonitrile. After stored at 2 - 5ºC, the solution showed some turbidity/precipitation that was impossible to redissolve. Quantifying dodine of the test with a new fresh solution, prepared in methanol, the z-score would be, approximately, 1.5. Reasons of poor performance: Human error and stock solution prepared with wrong solvent. Comments by Organizers: the reasons delivered seem plausible. Dodine is better soluble in methanol rather than acetonitrile, where it precipitates. In the case of dodine there is sometimes also adsorption-phenomena in the LC-injector, that can cause significant overestimation of results if calibration standards in pure solvent are used (this, however, does not apply in your case as you have employed standard additions to extract aliquots).	E, I
107	-3.6	(Yes)	we used multiresidue method (the same method for analysis of pesticides in fruit and vegetables with ethyl acetate extraction). We didn't use internal standard and no recovery was performed. Just recently we started with SRM and so far we haven't accredited nothing but perchlorates itself. That was our primary goal due to the monitoring of perchlorates in fruit and vegetables. We only had 25 samples last year and another 25 samples in 2016. Comment by organizers: a recovery experiment and a validation in general would have helped to assess the bias and trigger recovery correction measures (e.g. use of ILISs, standard addition to sample portions, procedural calibration).	(C), D, E, (G), (L)
114	-2.1	–	Dodine is accreditate pesticide for us and I don't have any logical reason why this happened. Just a random error. ***Comments by the organizers:*** You have employed a solvent-based standard for calibration. Consider the use of approaches correcting for matrix effects such as matrix matching with a suitable blank (e.g. the blank provided by the organizers), procedural calibration and standard addition approaches.	C, L
119	2.2	Yes	The obvious reason might be a matrix effect in the injector. The sample extract was diluted (1:10) and the matrix effect in diluted sample was not equal with non-diluted matrix matched standards. ***Suggestions/Comments by the organizers:*** This explanations seems plausible although matrix effects (in form of matrix-induced signal enhancement) in the ion-source cannot be excluded per-se. It seems strange that this bias was not recognized in the recovery experiment conducted within the same batch.	C, E, L
128	4.2	Yes	Ja, der Pipettierfehler ist bei der Standardaddition passiert. Es wurde eine angepasste Standardaddition durchgeführt und versehentlich die doppelte Menge gespikt. In dem Berechnungsblatt wurde nicht die erhöhte Konzentration eingetragen. Man kann also sagen, dass es sich um einen Dokumentationsfehler handelte, alle Berechnungsformeln waren korrekt. Andere Substanzen waren nicht betroffen, da kein Mixstandard verwendet wurde, sondern Dodin singulär gespikt wurde. Pipetting error during standard addition. A fitted standard addition was conducted with a double amount of standard being spiked. This double amount was not documented in the calculation sheet. All calculation formulae are correct. No other compounds were affected as dodin was spiked with an individual working standard, not with a mixture.	E, I

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

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K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

TFNA Assigned value: 0.756 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
23	5.9	–	We observed a calculation error. The sample was analyzed twice at the time and the correct values were 0.71 and 0.85 mg/kg (average 0.78 mg/kg). Please find attached a doc file with the new calculations and the chromatograms (including data and time) that indicate this.	E, I, L
49	3.3	No	Die beiden Analyten wurden zunächst mittels der Standard-QuEChERS-Aufarbeitung bestimmt (TFNG 0,647 mg/kg, Wiederfindung für 0,05 mg/kg 68 % und TFNA 0,852 mg/kg, Wiederfindung 0,5 mg/kg 46 %). Insbesondere wurde für TFNA eine schlechte Peakform unter den Standardbedingungen beobachtet. Da die Routineanalytik positive Befunde für TFNG / TFNA lieferte, wurde das LVU-Material gemäß der Modifikation aufgearbeitet. Die so ermittelten Gehalte wurden gemeldet, da Wiederfindungsraten (0,05 mg/kg) deutlich besser waren (TFNA 90 %, TFNG 101 %). Zudem wurde insbesondere für TNFA unter sonst identischen Chromatographiebedingungen eine deutlich bessere Peakform beobachtet. Die Standardlösungen wurden mit frisch angesetzten Standards verglichen. Hierbei wurden keine Auffälligkeiten festgestellt. TFNA and TFNG were initially analyzed by CEN-QuEChERS (TFNG 0,647 mg/kg, recovery rate at 0,05 mg/kg 68 % and TFNA 0,852 mg/kg, recovery rate at 0,5 mg/kg 46 %). The TFNA peak-shape was not satisfactory. TFNA and TFNG were then re-analyzed by the modified method (FA-QuEChERS). The recovery rates at 0.05 mg/kg were much higher (TFNA 90 %, TFNG 101 %) and the peakshapes under the same chromatographic conditions improved considerably. The correctness of the standard solutions was confirmed by measuring against newly prepared standard solutions. Comment by Organizers: the methodology data submitted do not reveal any obvious error. Critical conditions were avoided by extracting at acidic conditions, not employing PSA cleanup and calibrating using a matrix-matched standard based on the delivered blank material. Checking the correctness of the standard solutions was the right thing to do. Please also check the possibility of calculation errors.	(I), (L)
91	4	(Yes)	After comparison of the used standard with a new standard there was a significant difference of 22 %. Taking into acount that the used standard is degraded the correct value will have a z-score of < 2,8. The solvent used for TFNA was tolene for both stock and working solution. ***Comments by the organizers:*** the use of toluene for TFNA is not indicated as it is an acidic and polar compound and toluene a non-protic solvent. Also consider the possibility that even the new standard was not correct due to insufficient solubility and interaction of TFNA with the walls of the vessel used to prepare the standard solutions.	E, L
114	-3.9	–	***Comments by the organizers:*** The conduction of a recovery experiment at 0.01 mg/kg should have normally excluded the possibility of a false negative.	L, O
125	2.2	–	No reason provided Comment by Organizers: By extracting using QuEChERS under acidic conditions partitioning of TFNA and TFNG to the acetonitrile phase was favourable. Procedural calibration, provided that it has been prepared using the same type of matrix, should have additionally contributed to compensating matrix effects. Stangely your results for both TFNA and TFNG show a strong positive bias. Please re-check whether there is some error in the the preparation of the calibration solutions and the calculation.	–

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors
A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

TFNG Assigned value: 0.448 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
2	2.6	(Yes)	Recovery at MRRL obtain was in the acceptable range, we analyzed SRM10 to check our protocol, and the amount founded for TFNG give a score of 1.5 (which is correct). So the problem is not from the std solution. TFNG is eluted at 1.5 min and coeluted with TFNA. Comments by Organizer:As you have submitted several strongly overestimated results out of the acceptable range, it would make sense, additionally checking if there is any systematic error in the way you conduct/calculate the standard addition approach. For example, recheck your standard additions calculation and the ratio between the ILIS added to the test portion versus the ILIS added to the calibration standards. Please also consider checking the correctness of your standard solution. Coelution with TNFA should not be a problem as mass-spectrometric differentiation is still possible. Through in-source fragmentation TFNG would potentially degrade to TFNA and not vice versa.	(A), (E), (L), Adv1
6	-2.4	Strong assumptions	We specially ordered the TFNG standard for the test. We received it at the end of April. There was one extraction : 9th May 2016. The sensitivity of the method for the first test was very low (LD estimated : 0.1-0.2 mg/kg). After several method optimization the sensitivity improved. There was no time to analyze the test sample with the optimized method. The poor sensitivity involved a very bad reproducibility. The quantification was based on 1 point calibration (0.2 mg/kg) in spinach matrix. ***Comments by the organizers:*** Indeed bad sensitivity can have a very negative impact on repeatability. 1 point calibration can still be accurate if the calibration level is sufficiently close to the level in the sample	A, D, E
14	-3	–	pb of method (the pb has been corrected using procedural calibration. With this method, the new value found was 0,464) ***Comment by the organizers:*** Using QuEChERS recovery of TFNG is typically low and this is also confirmed by the recovery rate you have reported (51 %). As your recovery was too low it should have been assumed that the result is assosiated with a strong negative bias and a reanalysis with an approach correcting for recovery should have been sought (e.g. procedural calibration or standard addition to sample portions). Correcting the result for recovery by a recovery figure would have also been an option although this can be tricky due to the risk of spurious errors on the recovery figure and preliminary (non-corrected) result. In your case the z-score rating would have shifted from (-3 = unacceptable) to (-2.1 = questionable) which is not enough. Consider employing an acidified QuEChERS approach as described in the EURL-SRM method for acidic pesticides.	E, J, L, O
49	4.1	No	Die beiden Analyten wurden zunächst mittels der Standard-QuEChERS-Aufarbeitung bestimmt (TFNG 0,647 mg/kg, Wiederfindung für 0,05 mg/kg 68 % und TFNA 0,852 mg/kg, Wiederfindung 0,5 mg/kg 46 %). Insbesondere wurde für TFNA eine schlechte Peakform unter den Standardbedingungen beobachtet. Da die Routineanalytik positive Befunde für TFNG / TFNA lieferte, wurde das LVU-Material gemäß der Modifikation aufgearbeitet. Die so ermittelten Gehalte wurden gemeldet, da Wiederfindungsraten (0,05 mg/kg) deutlich besser waren (TFNA 90 %, TFNG 101 %). Zudem wurde insbesondere für TNFA unter sonst identischen Chromatographiebedingungen eine deutlich bessere Peakform beobachtet. Die Standardlösungen wurden mit frisch angesetzten Standards verglichen. Hierbei wurden keine Auffälligkeiten festgestellt. TFNA and TFNG were initially analyzed by CEN-QuEChERS (TFNG 0,647 mg/kg, recovery rate at 0,05 mg/kg 68 % and TFNA 0,852 mg/kg, recovery rate at 0,5 mg/kg 46 %). The TFNA peak-shape was not satisfactory. TFNA and TFNG were then re-analyzed by the modified method (FA-QuEChERS). The recovery rates at 0.05 mg/kg were much higher (TFNA 90 %, TFNG 101 %) and the peakshapes under the same chromatographic conditions improved considerably. The correctness of the standard solutions was confirmed by measuring against newly prepared standard solutions. ***Comments by the organizers:*** the methodology data submitted do not reveal any obvious error. Critical conditions were avoided by extracting at acidic conditions, not employing PSA clenup and calibrating using a matrix-matched standard based on the delivered blank material. Checking the correctness of the standard solutions was the right thing to do. Please also check the possibility of calculation errors.	(I), (L)

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

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Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

TFNG Assigned value: 0.448 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
119	2.2	Yes	The compound was new for us and the validation procedure had just been started while the proficiency test came in the lab. ***Comment by the organizers:*** The reported recovery figure is within the typical range using QuEChERS acidified with formic acid.	D, E
124	4	–	No reason provided Comment by Organizers: By extracting using QuEChERS under acidic conditions partitioning of TFNG to the acetonitrile phase was favourable. Procedural calibration, provided that it has been prepared using the same type of matrix, should have additionally contributed to compensating matrix effects. Please re-check whether there is some error in the the preparation of the calibration solutions and the calculation.	–

Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
2	9.9	?	We analyzed this compound in GC and LC. Response GC were not stable, and the calibration curve brook down. Injection on LC seem more stable, control point were correct, but the result are far from the attend value. We also made our standard solution from powder. The tolylfluanid solution was prepared in acetonitrile. It was the first time we prepared a solution for this compound, that is why we could not check for stability by comparison with an older solution. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one but still most probably outside the acceptable range. Indeed LC-MS/MS is the preferred option for this analyte. Analysis by GC is more challenging due to the thermal instability of tolylfluanid. It seems reasonable to check the stability of your standard solution (stock and working) since your result was highly overestimated. Tolylfluanid often degrades in acetonitrile solutions if these are not acidified (although there is differences between lots and between manufacturers) . As you have submitted several strongly overestimated results out of the acceptable range, it would make sense, additionally checking if there is any systematic error in the way you conduct/calculate the standard addition approach. Please also consider checking the correctness of your standard solution.	A, E, L, Adv1
15	-2.2	Yes	Application of standard QuEChERS procedure. Proposed corrective action: Testing acidified QuEChERS method Comments by Organizers: As the preliminary robust mean was most likely underestimated your real z-score is most likely even lower than the preliminary one. The organizers agree that the use of acidified QuEChERS is better suited for tolylfluanid, as this compound is sensitive to high pH. CEN-QuEChERS also works well if some critical points are addressed. Letting the sample to reach room temperature has surely caused degradation of tolylfluanid. Initial sample temperature should be kept low (especially in the case of commodities with high pH (such as spinach). dSPE with PSA should be avoided, but if PSA is used (as in your case) re-acidification should be immediate to minimize exposure to high pH causing degradation. For measurement, you have employed GC-MSD. For tolylfluanid LC-MS/MS is to be preferred over GC-techniques, as tolylfluanid decomposes to DMST in the hot GC-inlet especially if the pH of the extract is high. This decomposition of tolylfluanid is more pronounced the more contaminated the liner-surface is.	(E), (G), H, (J), L

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors
A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
16	3.5	Yes	At first we obtained 340 ppb and 470 ppb for SRM11 sample with a matrix matched calibration but the CS recovery was 40 %. At the 2nd defreezing we obtained 240 ppb. We concluded that this molecule is not stable in the sample and we cannot used the sample anymore for other experiments. The reinjection of our previous final extracts didn't show degradation. This molecule looks like stable in the final extract. Finally we decided to reinject our 1st extracts with a procedural calibration (to avoid low CS recovery) and we obtained 965 and 1280 ppb. We send this result. These values agreed with our first experiment if we considered the recovery. Following a 3rd defrosting an additional experiment was conducted employing standard addition to sample portiions, the result was too low. ***Comment by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. Taking the first result was of advantage as tolylfluanid is base-sensitive and known to degrade in homogenates of high-pH matrices especially if these are defrosted. The stability in QuEChERS extract following cleanup and reacidification is good. The low recovery of 35 % despite using an acidified method (with phosphoric acid) is surprizing. In any case, conducting procedural calibration, as in your case corrects for recovery. Still degradation of the stock- or working-solutions cannot be ruled out completely as a reason for the overestimated result and should be also checked.	L, M
19	-3.9	Yes	The reason: have been chosen not right determination technique (GC-MSD). The sample homogenate thawed several times, because to weigh the sample homogenate (exactly 10 g). 2 or 3 times x 24 h. ***Comment by the organizers:*** Indeed, measurement of tolylfluanid via GC is troublesome due to the tendency of this compound to degrade under thermal stress. Taking proper measures (e.g. matrix-matched calibration, use of analyte protectants, good condition of the GC-inlet) accurate GC-analysis is, however, still possible. For this compound LC-MS/MS is less prone to run-to-run variability and its use for the analysis of this compound is worthwhile considering. Repetitive thawing of the homogenate has most probably contributed to degradation. It is always indicated to reduce exposure of the homogenate to high temperatures especially if the case of a high natural pH (which applies to spinach). Furthermore, if cleanup with PSA is conducted (as in your case) re-acidification should be rapid to shorten analyte exposure to high pH.	(E), (G), H, L
22	3.8	Yes	The concentration of the old standard used for the SMR11 is only 54 % compared to the new one. Tolylfluanid stock solution was dissolved in acetonitrile and the working solution for spiking into the samples in ethanol (for calibration in the matrix). Comments by the organizers: As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. Considering the bias of the standard used your result would have been 0.598 mg/kg which translates in a z-score of 0.23 based on the preliminary assigned value. Please note however that the real assigned value (which is not known) is rather expected to be much higher that your correcetd result. Tolylfluanid is indeed known to degrade in some solvents including acetonitrile if not acidified. It is typically not only important to acidify the stock solution, but to also make sure that working solutions are also acidic enough. You have employed dSPE with PSA, which known to affect base-sensitive compounds such as tolylfluanid if re-acidification is not immediate. Alternatively consider to avoid cleanup with PSA to minimize this risk. In any case, as you have calibrated via a standard addition to sample portions, this error-source was most propably largely compenasated. The same remarks related to the use of PSA also apply to the following acidic pesticides with a tendency to interact with PSA, and for which you have still achieved good z-scores (propably as a result of following a calibration approach that corrects for recovery): Quizalofop (your z-score -2) and Triclopyr (your z-score: -0.4).	E, (L), (M)

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
23	-2.3	–	Sample was analyzed at room temperature. We cleaned-up with PSA. The recovery reported was 67.3 %. If we had corrected for recovery the value reported would had been 0.37 mg/kg. ***Comment by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. You have employed your Test Item homogenate at room temperature. This may have caused some degradation of tolylfluanid. It is important to avoid that the homogenate is exposed to high temperatures especially if the sample has a high natural pH (which is also the case in spinach). Furthermore you have cleaned-up with PSA, which is sensitive to PSA. This is also reflected by your low recovery figure.	(C), E, H, (J), (L)
24	2.2	–	We considered that the deviation between our result and the robust mean is related to the fact that we did not employ PSA-cleanup. Tolylfluanid and other base-labile compounds degrade during PSA cleanup and reproducibility is poor. All quantification standards were freshly prepared and measured agains old ones. The stock standard was dissolved in acetone and the working standard in acetonitrile. Die Abweichung (Ergebnis > preliminary robust mean) haben wir darauf zurückgeführt, dass wir keine PSA-Aufreinigung durchführen. Tolylfluanid und auch weitere basenempfindliche Wirkstoffe werden bei der PSA-Aufreinigung zum Teil abgebaut und können somit nicht reproduzierbar bestimmt werden.Alle Quantifizierlösungen werden für jeden Ringversuch frisch aus den Reinsubstanzen angesetzt und gegen die alten Quantifizierlösungen vermessen. Die Stammlösung von Tolylfluanid ist in Aceton gelöst. Die Quantifizierlösung in Acetonitril. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is most likely lower than the preliminary one and most probably within the acceptable range. Still, please consider the following comments. The procedure you have followed seems appropriate. The homogenate was employed in deep frozen condition, so tolylfluanid was protected. By applying standard additions to sample portions for calibration any recovery losses during extraction should have been compensated. Cleanup with PSA, which is a critical step as tolylfluanid is base-sensitive, was avoided (although even if PSA had been used recoveries would have been more or less compensated by the standard additions to sample portions calibration approach). Degradation of the stock- or workig-solutions cannot be ruled out and should be checked, especially since it is known that tolylfluanid degrades in acetonitrile if not acidified.	E, M
32	-3.7	No	Bei Pymethrozine/Tolylfluanid wurden die Messwerte der Std. Addition abgegeben. Es liegen ebenfalls Messungen mit einem matrix matched Std.(3 Punktkal.) vor, deren Werte einen z-score innerhalb der Tolleranz ergeben hätten. Bei 70 % der Wirkstoffe erzeugten die Matrix matched Std. deutlich bessere Werte, im Vergleich mit den erhaltenen Ergebnissen. For tolylfluanid we submitted results derived by standard addition. We also generated results using matrix-matched calibration (at 3 levels) the z-scores of which were within the acceptable z-score range. For 70 % of the compounds matrix-matched standards generated clearly better results than those submited. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. Please check whether there is a principal problem with the way standard addition is designed or calculated. Cleanup with PSA can be problematic for tolylfluanid if the extract is not re-aciified quickly, but this error-source is eliminated when standard addition to sample portions is used	I, L

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors
A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
33	-2.3	?	Recoveries were low (5 %-50 %) and not rerepetitive. As recoveries were not stable they were not used for correction of the result. The material was thawed but wasn't exposed to high temperatures prior to analysis. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. Correction of results via recovery factors is tricky especially if variability is high. As you knew from the recovery experiments that recoveries using this method are inconsistent it would have been indicated to employ a procedure that corrects for recovery (e.g. standard addition to sample portions) or to use a different method (e.g. an acidified version of SweEt). As tolylfluanid is sensitive to high pH, degradation in the thawed spinach homogenate may have taken place even though temperatures were kept between 4-10°C. Exposition time is an important aspect here. Degradation of tolylfluanid also occurs during GC analysis within the hot injector, especially if the inlet is very dirty. This can lead to errors if matrix effects are not properly compensated. By using standard addition to extract aliquots, matrix effects during measurement should have normally been compensated (please check if the calibration curve was good enough to allow extrapolation of the result). In any case LC-MS/MS is preferable for this compound.	(G), (H), J, (L)
34	2.8	Yes	Standard for calibration was degradated. nach eingehender Untersuchung habe ich keine wirklich schlüssige Erklärung für den Überbefund gefunden. Den einzigen Hinweis habe ich darin gefunden, dass die zur Herstellung des Kalibrierstandards verwendete Stammlösung bereist das Abbauprodukt DMST enthalten hat. Das heißt, die Kalibrationslösung hatte in Wirklichkeit einen geringeren Gehalt als angenommen, wodurch die Befund ein der Probe erhöht errechnet wurden. Ich muss dazu sagen, dass wir in unserem Stoffspektrum in der Routine nur das DMST enthalten haben und bei DMST- Befunden eine Einzeluntersuchung für Tolyfluanid machen würden. Ich bin natürlich sehr daran interessiert, ob die Fehlersuche über alle Teilnehmer eine Antwort auf die insgesamt recht große Streuung erklären kann. Following thorough investigations we were not able to find the reason behind this overestimated z-score. The only hint was that the stock solution used to prepare calibration standards was already containing DMST (the degradation product of tolylfluanid). This means that the calibration solution already conained less tolylfluanid than expected leading to an overestimated result. I must say that tolylfluanid is not within our scope. In case we have a positive DMST finding we repeat analysis with a proper single residue method. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. Still, please consider the following comments. As you have employed the sample in frozen condition (and assuming that it was not thawed before) there were no significant tolylfluanid losses prior to extraction. The preliminary assigned value was most likely lower than the real value. DMST detection when analyzing the csalibration standards can be an indication of degradation but this cannot be easily judged based on GC-MSD measurement as tolylfluanid degrades to DMST in the hot GC-injector. Use LC-MS/MS to check the stability of the standard solution. Also consider to acidifying stock and working standard solutions (e.g. with 0.5 % acetic acid if in acetonitrile). The low recovery rate of your recovery experiment suggests possible losses during sample preparation. Cleanup with PSA is critical for this compound if re-acidification is not done quickly after isolating the cleaned-up extract.	E, L, M

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
35	-3.9	?	False negative result for tolyfluanid might be due degradation of tolyfluanid during sample preparation to its metabolite DMST which was not analyzed for SST samples. We did extraction with acidified ACN and no clean-up with PSA. So maybe it was GC fault. Expert has found tolylfluanid but in concentration less than 0.010 mg/kg. Thats why we didn't report it and we didn't repeat analysis because there were not enough PT samples. ***Comments by the organizers:*** Degradation of tolylfluanid occurs during GC analysis within the hot injector, especially if the inlet is very dirty. This may lead to false negative results or biased quantifications. LC-MS/MS is preferable for this compound. A recovery experiment within the same badge and under the same conditions will normally help to identify false negatives but if degradation already took place in the homogenate before the start of the extraction (this is likely as you have allowed the sample to thaw) there is no way to recover the analyte afterwards, even when using procedures correcting for recovery.	(A), (E), (H), (J), (L), O
53	3.8	No	AV and z-score for informative purpose only, no further investigation. We used acidified QuEChERS (with 100 µl of H2SO4) without adding citrate salts and with no cleanup ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. The procedure you have followed seems appropriate. As the homogenate was employed in frozen condition tolylfluanid was protected. The use of an acidified version of the QuEChERS procedure minimized the losses during extraction. Cleanup with PSA , which is a critical step as tolylfluanid is base-sensitive, was avoided. Degradation of the stock- or workig-solutions cannot be ruled out any should, normally, be also checked as a potential source of errors.	E, L, M
54	-2.8	(Yes)	There was a great presence of metabolite DMST in the sample but we report only the Tolylfluanid as defined by you. We had a later proficiency test using the same standard (Fapas 19199 of peach) and with z-score of 0.4, so maybe the problem was degradation to metabolite in the test sample. ***Comment by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one.You indicate that you have employed your sample at room temperature for analysis. This has surely resulted in considerable losses of tolylfluanid that could not be compensated by applying a procedure correcting for recovery (procedural calibration). Surely, considerable degradation of Tolylfluanid to DMST already took place prior to shipment but this equally applied to all test portions (homogeneity test passed). Furthermore the stability of tolylfluanid during shipment and storage of the test Item was tested and found to be acceptable as long as the sample was kept frozen. Please consider switching tolylfluanid analysis to LC-MS/MS as GC-analysis is error-prone due to the thermal instability of tolylfluanid and the occurence of severe matrix effects. Conducting extraction at acidic conditions (rather than original QuEChERS) would have also helped to further minimize losses during extraction. Avoiding cleanup with PSA contributed in minimizing further losses during sample preparation.	E, H, L
57	-3.6	–	Our sample was not exposed to high temperatures before the analysis. After the reception it was kept in the freezer and the day before analysis it was defrosted under refrigeration over 14 hours. The high pH of the homogenate (we did not measured it) has clearly been the reason of our low recoveries, as you comment. It explains the huge differences obtained when we calibrated with basil an spinach. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is most likely even lower than the preliminary one. Leaving the test Item to defrost in the refrigerator over 14 h has surely caused considerable losses of tolylfluanid in the homogenate. Losses before extraction cannot be corrected afterwards, neither by protection measures nor by recovery correction measures during extraction (e.g. procedural calibration as in your case). Cleanup with PSA may have caused additional losses especially if reacidification was not immediate, however as you have conducted procedural calibration such losses should normally be compensated.	(E), H, (J), L

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

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C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
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Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
58	3	Yes	No clear cause for the poor performance could be found. All first line controls were OK. The stock solution was dissolved in acetone and the working solution in acetonitrile. Tolylfluanid belongs to the group of base-sensitive pesticides which are sometimes difficult to quantify. This might also explain the very high variation between the laboratories (CV% = 57.5 %). ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. Not allowing the test-item to defrost and skipping cleanup, helped to keep degradation losses during extraction low. As the entire test-item homogenate was thawed and mixed some tolylfluanid losses may have occured prior to extraction which would contradict the high result. It is therefore still worthwhile checking the stability of your tolylfluanid standard solutions and especially the working standard which was dissolved in acetonitrile as this solvent is known to cause degradation of tolylfluanid (unless acidified, e.g. with 0.5 % acetic acid).	(E), (L), M
60	-3.1	(Yes)	We have got a z-score of -3.2 for tolylfluanid in this EUPT. However, the result was not corrected for recovery, which in this case was low; 46.5 %. If I correct for recovery, the result would be higher and correspond to a z-score of -2.2. This is still questionable, but the z-scores given in the preliminary report are for information only, due to great variability in the results. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one.When recovery deviates considerably from 100 % (e.g. <70 %) results should not be reported ubless the results are corrected for recovery (e.g. via ILIS, standard addition to sample portions or procedural calibration). There are many reasons for the poor recovery in the spiking experiment and the low result in the Test Item. If estraction is delayed hydrolysis can take place in the thawed sample portion prior to extraction. Being sensitive to high pH tolylfluanid also experiences losses during the cleanup with PSA as well as in the cleaned-up extract if re-acidification is not done or delayed. Degradation of tolylfluanid also occurs during GC analysis within the hot injector, especially if the inlet is dirty. This effect can be compensated when conducting matrix-matched calibration and if signal drift is not significant. By preparing your calibration standards in cucumber matrix effects were not exactly compensated and this might have contributed to the bias. If cucumber-based calibration constitutes your routine approach, using to generate PT results was appropriate. In general LC-MS/MS is preferable for this compound. Degradation of the compound might have talken place prior to extraction (in the homogenate if this was exposed to high temperatures for a long time). This kind of losses are, however, not compensated by recovery correction approaches.	E, (H), (J), (L)
64	4	Yes	The standard of tolylfluanid in methanol , was degraded. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one, possibly even within the acceptable range. Skipping the cleanup with PSA has surely reduced the risk of losses during the procedure. On the other hand leaving the test item to reach room temperaturehas surely cause some degradation of tolylfluanid. It is thus important checking the degradation of the standards as a possible reason. Tolylfluanid is for example known to degrade in acetonitrile stock and working solutions if these are not acidified (e.g. with 0.4 % acetic acid).	E, L, M

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

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L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
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Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
67	3.2	Yes	The reasons for the deviating result of tolylfluanid are still unclear. The tolylfluanid standard was stored in pure acetone. Second feedback: We have tested the old tolylfluanid standard and it showed losses of 35 % ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. The degradation of your standards would be a possible reason for the overestimated result. Please also consider the following comments. Avoiding PSA in the cleanup step has reduced the risk of losses during sample preparation. Recovery correction by a factor of 2 has largely compensated the losses during sample preparation. An acidified version of QuEChERS would have minimized losses further. On the other hand, leaving the homogenate to reach room temperature prior to extraction has most likely led to losses depending on the time it was exposed before the actual analysis of tolylfluanid.	(E), (L), (M)
70	-3.9	Yes	In this case we did several repetitions, at least five, the results were not good and not repetitive. Our method has to be checked for the Tolyfluanid, We did not submit result of this analyte, the false negative assigned is correct. According to the above-mentioned errors, we remove Dodine and Tolyfluanid from our scope until all the issues raised –methods, false negative result or anything else– have been resolved. ***Comments by the organizers:*** Based on your statements it seems that you have generated some results but not submitted them. If this is the case the false negative is only formal (following the rules of the EUPT-General Protocol). In any case by employing the sample in thawed condition tolylfluanid degradation has surely occured. Exposure time to high temperatures is an important facto here. Same applies to the use of PSA in dSPE cleanup, especially if re-acidification was not immediate	H, (J), (L)
74	7	?	We assume it is because we did corrected results for recovery which were rather low (51 %) If we had not corrected results for recovery, all z-scores would be <2. A certifiet mixture in acetone was bought. This solution is ilute in methanol. We did not conduct stability tests. We would like to know whether all other labs used recovery correction, and what to do next time with recovery <70 %? ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one but still not within the acceptable range. Still, please consider the following comments. Avoiding PSA in the cleanup step has reduced the risk of losses. On the other hand, leaving the homogenate to reach room temperature prior to extraction has most likely led to losses depending on the time it was exposed. As your z-score was very high, checking the stability of the stock- or workig-solutions is indicated.	E, J, (L), (M)
75	2.1	No	Following extensive follow-up actions the source of error could not be localized. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. Still, please consider the following comments: As tolylfluanid is sensitive to degradation during GC-analysis attention is needed to equalize matrix effects. Analyzing the sample in frozen condition minimized losses prior to extraction. The use of PSA in the cleanup step increased the risk of losses. Rapid re-acidification is indicated here.	L, M
79	-2.7	Yes	The standard of Tolylfluanid used for the quantification was checked and it was correct (in line with SANTE requirements). The standard of Tolylfluanid used did not give signal for the degradation product DMST, The QC samples spiked with Tolylfluanid also did not give signal for the degradation product DMST and the recovery was >80 %. . The PT Samples contained DMST in amount almost equal (even higher) to that of Tolylfluanid. The DMST was not included in the final result as it was required to give only result for the parent compound Comment by the Organizer: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. The non-reporting of DMST was not requested within this PT. The acidification during the extraction step minimized degradation. Allowing the sample to thaw surely had some negative influence on tolylfluanid depending on the exposure time.	H, L

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

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C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
82	-2.9	Yes	The analytes had a value of Z score of about -3 due to a calculation error. An incorrect volume was used during the calculation. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. Allowing the sample to reach ambient temperature surely has negatively impacted tolylfluanid, depending on the time the homogenate was exposed to these conditions. Please consider that using QuPPe method matrix effects are strong. Using solvent based calibration these matrix effects may cause considerable errors unless compensated, e.g. via ILIS.	C, E, H, I, L
83	17.8	Yes	Tolylfluanid's standard supplied in ACN likely degraded. ***Suggestions/Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one. But even then, your result is so high that it would not fall within the acceptable range. We agree that standard degradation (stock or working) is the most likely reason for your overestimation. Tolylfluanid is particularly sensitive to degradation in acetonitril solutions if these are not acidified.	E, (L), (M)
88	-3.2	–	Possible cause due to a greater matrix effect. From the review of intercomparative data, a high variability of results is observed, which could indicate a possible degradation of tolylfluanide in the sample. In our procedure the sample is defrosted and re-frozen. Aliquots that are defrosted are not frozen again. We cannot say for sure for how long the sample was in a defrosted state before beginning extraction. Possibly the deviation in some results has been caused by excessive defrosting time before extraction. ***Comment by the organizers:*** We agree that degradation in the test item homogenate was propably the main source of your highly understimated result. As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. Tolylfluanid is sensitive to high pH and measures (such as keeping low temperatures) are needed to minimize degradation in homogenates of high pH commodities such as spinach. The use of PSA in dSPE cleanup may have caused additional losses if re-acidification was not immediate.	(H), (J), (L)
91	3.4	Yes	For the determination of tolyfluanide there has been spiked with a standaard of tolyfluanid where the concentration used for the calculation whas 10 % lower that the real concentration. This due to a human mistake. For the measured the some of DMST and tolyfluanide is rapported. The standard was prepared in acetonitrile. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. According the Pesticide Target List you shouldn't have reported the sum of Tolylfluanid and DMST. Please also check the stability of your standard as tolylfluanid tends to degrade in acetonitrile solutions if not acidified..	E, I, K, L, M

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
96	-4	–	Actually the case is quite unclear despite of my follow-up investingations in this field. During PT I made two batches of analyses on different days (using an ethylacetate-based method) and the results were strange: at first batch there was OK with tolylfluanid. On second batch there was no peaks anywhere, not in blank and sample as well. But recovery sample and calibration was OK! As I had no time to make a third batch, we decided not to give out any findings (not to report false positive result). Actually, after recieving preliminary results I made one more batch from the sample (frozen up to that time) and get quite satisfactory results for both compounds. But during reporting we made a wrong conclusion that the first batch was contaminated somehow. Most probably a wrong GPC clean-up method was applied during preparation of second batch. We have several methods for different compounds based on their retention in column and most probably a method with too late collecting time was chosen. Comments by the Organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. Irrespective on whether GPC was the main reason for the error, please consider measuring tolylfluanid via LC-MS/MS. Tolylfluanid is prone to decomposition in the hot GC-inlet with this effect increasing as the GC-inlet surface becomes more contaminated and decreasing in presence of protective matrix components. This results in severe matrix-effects that are difficult to handle. When analyzing via GC avoid using calibration standards in pure solvent to reduce the impact of matrix effects. The use of LC-MS/MS will further allow you to use simple methods are less prone to errors. Consider introducing better QC-standards to avoid false negatives.	(B), (E), F, L, O
98	4.7	Yes	We quantified this pesticide with a straight line of strengthened obtained from the blank of the intercomparative that we spiked several volumes of a pesticide working solution and processed in the same way as the sample with the method Quechers. We diluted the sample approximately 100 and 200 times in order to quantify the pesticide tolilfluanida. We had problems at the moment of achieving that there was coinciding the response of the dilution of the level estimated with the response of the dilution of the sample. We think there is a lot of matrix effect and it influences in the results of the sample. It's different to quantify with standards prepared as the samples that those are obtained evaporating aliquots of the blank extract and added the same volume with solvent standards. Ethylacetate/Cyclohexane 1:9 was used for the reconstitution of the QuEChERS extract after evaporation. Stock standards were in acetone and stability was tested. Working standards were those spiked on matrix (procedural calibration). ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. Still consider the following remarks: Diluting will reduce the protective effect of the matrix in GC analysis. For equalizing matrix effects it is important to treat the blank that will be used to prepare the calibration standards in the same way as the sample, e.g. If you dilute your sample extract 100 fold the same should be done with the matrix-matched standard solution. Keep in mind that by diluting too extensively your internal standard peak may become to small and affected by signal fluctuation. Alternatives for mantaining a protective effect in GC is the dilution with blank extract or the addition of analyte protectants to sample extracts and calibration standards. Following evaporation, not all matrix components will redissolve especially if the solvent used for reconstitution is different. Thus matrix effects may shift. Please also consider checking the stability of your standard solution as degradation of the standard can also lead to overestimated results. Consider introducing measurement with LC-MS/MS as tolylfluanid is sensitive to degradation in the hot GC-inlet especially if the liner surface is dirty. This may lead to severe matrix-effects and quantification errors. As tolylfluanid is base-sensitive, cleanup with PSA should be either avoided or conducted with care by ensuring immediate re-acidification after the separation of the cleaned up extract. Despite the use of PSA the submitted recovery figure was very high (142 %). Please check the design/calculation of the recovery experiments as recovery figures were also too high for cyromazine (133 %), dodine (132 %) and triclopyr (117 % despite the use of PSA in dSPE cleanup).	(C), (E), (L), (M)

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors
A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
106	-3.3	(Yes)	We confirm you the obtaining of low recoveries (ie = 28 %) which could explain the insufficient performance Comments by the Organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. Correction of results for recovery is indicated if recovery is lower than 70 %.	E, J, L, O
110	-2.4	No	We analyzed the sample on April 13th and we obtained a indicative value of about 0,7 mg/kg. Then we analyzed the sample twice in two different days (after 6 and after 10 days). The sample was stored at -20°C and we obtained very different results: 0,260 and 0,242 mg/kg. After the first the first defrosting several sample portion were weightet, which were used for the second and third analysis. Finally the problem about the modality of PT samples defrosting. Our procedure should provide a single defrosting phase at refrigerator temperature. Then we homogenize the sample and we put into falcon vials in 10 g rates. The falcon vials are then stored at -20°C and we process the sample starting direct from a new falcon every time we need. Unfortunately sometimes the defrost samples are refrozen without division in falcon tube. I can't tell you if we encountered this situation or not when we analyzed the EUPT SRM 11 sample. Comments by the Organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. Leaving the sample to defrost in the refrigerator as you have indicated by e-mail and to finally reach room temperature as you have indicated in your methodology data has surely affected tolylfluanid, which is very sensitive to degradation in homogenates of high pH such as spinach. Please note that each defrosting of the homogenate before analysis leads to additional degradation, even if the homogenate is stored in the freezer inbetween the analyses.	(H), (L)
111	3.6	No	The assigned value is only given for information. So we think at this point of report it is not necessary to give any feedback. Stock and working standard solutions of tolylfluanid were dissolved in acetonitrile. ***Suggestions/Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. Employing the sample in frozen state has surely minimized losses in the homogenate prior to analysis. The use of PSA in dSPE can be critical if the extract is not re-acidified quickly as tolylfluanid is very sensitive to high pH. Still, please consider the following aspects: You have employed 2 g for analysis. In general using very small sample portions increases the risk of portion-to.portion variability. A possible degradation of the standard should also be considered as tolylfluanid degrades in acetonitrile if this is not acidified	(E), (L), M, (N)
117	-2.8	(Yes)	We have only submitted the values for Tolylfluanid, and not for its metabolite DMST. We found additional amounts of DMST (nearly 80µg/kg). That could partially explain the bad recovery. Comments by Organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. You indicate that you have employed your sample at room temperature for analysis. This has propably resulted in considerable losses of tolylfluanid which could not be compensated by applying a procedure correcting for recovery (standard additions to sample portions). Surely, considerable degradation of tolylfluanid to DMST already took place in the preparation of the test item but these losses concern all laboratories. The stability of tolylfluanid during shipment and storage of the test Item was tested and found to be acceptable as long as the sample was kept frozen. Conducting extraction at acidic conditions rather than using the original QuEChERS would have also helped to reduce losses.	H, (J), (L)

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Tolyfluanid *Assigned value: 0.598 mg/kg and z-scores for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
120	-3.2	–	No reason provided Comment by Organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. You indicate that the initial temperature of the sample was ambient. As spinach has a high natural pH and tolylfluanid is base-sensitive it is very likely that the degradation occured in the homogenate prior to extraction. All efforts to minimize or compensate losses during or after the exttraction (standard addition to sample portions, skipping cleanup with PSA, use of LC-MS/MS) cannot compensate for losses in the homogenate.	H, L
124	-3.1	–	No reason provided Comment by Organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. As you have left your sample to thaw prior to analysis, considerable losses of dithianon have surely occured. Exposition time is an important factor here. Acidification during extraction and the skipping of the cleanup step with PSA has surely helped to minimize losses during extraction but it could not match for losses which have occured before extraction.	H, L

BAC-C14 Assigned value: 0.285 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
2	4.4	(NO)	no experience for these compounds in this matrix ***Comments by the organizers:*** As you have submitted several strongly overestimated results out of the acceptable range, it would make sense, additionally checking if there is any systematic error in the way you conduct/calculate the standard addition approach. Please also consider checking the correctness of your standard solution.	D, E, Adv1
55	-3.4	?	the laboratory assumes a matrix effect on the 3 molecules (BAC-C14, chlorate et phosphonic acid) ***Comments by the organizers:*** The organizers agree with the conclusion of the laboratory. The use of solvent-based calibrations is risky in case of strong matrix effect unless matrix effects are corrected otherwise (e.g. via ILIS) .	C, E
88	3.3	–	Deviation due possibly to a matrix effect. Follow-up measures: Calibration in the same matrix. A different blank spinach than the one delivered by the EURL was used for calibration. Complementary comment: We found many matrix effect differences between our matrix of spinach and the blank spinach provided by the EURL. Comment by the Organizer: The differences in the matrix effects between the EURL-blank spinach and your blank spinach may explain the bias. Normally two matrices of the same type do not deviate so much in their matrix effects to explain such a strong deviation.	C, E, L
124	2.1	–	No reasons provided.	–

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

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B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Chlorate Assigned value: 2.03 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
9	2.1	Vague initial suspi-cions	We checked the results for chlorate and concluded that some possible error(s) could probably come from sample preparation during standard addition approach (e.g. dilution of sample extracts). ***Comment by the organizers:*** Dilution can be indeed critical in certain cases. If only the extract of the Test-Item is diluted but not the calibration standard, matrix effect compensation is compromized. However, since you have employed an ILIS, this effect was propably compensated. If, after extensive dilution, the signal of the Internal standard and/or analyte becomes very small this can also increase uncertainty of measurement.	E
18	-4	Yes	due to an administrative fault, no method problem After further thorough evaluation, Please ignore our previous feedback. To our opinion the PT blank is contaminated with chlorate, perchlorate and pymetrozine. We did perform a blank correction and therefore our results for chlorate and perchlorate are reported as <RL. Therefore we can not consider these results as false negative. ***Comment by the organizers:*** Taking all aspects into consideration and allthough it was acknowledged that there was some room for confusion, the EUPT-AdvG decided to still classify this result as a False Negative following the general protocoll rules.The fact that the blank spinach of the EUPT-SRM11 contained chlorate and perchlorate through irrigation, as well as pymetrozine through spraying was clearly communicated by the organizer and it was indicated that calibration should be preferably based on standards in pure solvent or on a different blank. Conducting blank correction where the blank contains the analyte of interrest at a similar level as the sample is inappropriate anyway (also in routine analysis situations). Reporting Not Detected combined with a Reporting Limit of 0.01 mg/kg was surely not appropriate in this case.	E, L
26	-3.3	–	We think that the mistake was that we forgot adding water (0.5 ml) to the sample before the extraction. Then we took part in a proficiency test (FAPAS 19215) in parsley, adding water with a z-score for chlorate of -0.6. ***Comments by the organizers:*** The impact of adding 0.5 mL water is rather low. Even if you have scaled down the QuPPe procedure 2-fold using 5g sample (as you have indicated) plus 5 g of solvent to reach a target volume of 10 mL in total, the error would correspond to maximally 10 %. Please also check the possibility of having employed 5 g of sample but made calculations on the basis of 10 g. The error might be also related to differences in the matrix effects between calibration standard and the test Item extract (despite using blank spinach). In any case, consider using isotope labelled chlorate to compensate both for matrix effects as well as volume deviations as the one explained.	(B), C, (E), (L)
27	-2.7	(Yes?)	We used the blank of EUPT SRM-11 to quantify the analyte but the presence of the analyte in the blank led us into a wrong quantification. For chlorate and perchlorate we used an own spinach blank. ***Comments by the organizers:*** By employing an own blank spinach for calibration matrix effects may have not been properly compensated. Consider the use of an ILIS to avoid such errors.	(C), E, (L)
31	-3.4	Yes	No experience with the analyte and method. Error in concentration of analitical standard ***Comments by the organizers:*** Phosphonic acid (z-score -3.5) and chlorate (z-score -3.4) show a different trend than perchlorate (z-score 9.3). If you have used those standards in mixture, please recheck the claimed source of error.You have indicated the use of the EUPT-blank for the calibration. As the EUPT-blank contained chlorate this could have been a source of error.Please consider the use of ILIS to compensate for matrix effects.	D, E

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

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K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Chlorate Assigned value: 2.03 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
43	-3.1	–	At the time of implementation of EUPT-SRM 11 we were in the initial phase of the development of the analytical technique for the measurement of Chlorate and Phosphonic Acid, the methodology was at a very early stage of its development, which led to negative results. We have fine-tuned the method ever since. Our method is able to measure Chlorate, Perchlorate, Fosetyl and Phosphonic Acid using caffeine as internal standard, to control the percentage of recovery. ***Comments by the organizers:*** Caffeine may correct for volumetric errors but will not correct for matrix effects, which is the main source of errors.Please consider introducing isotope labelled chlorate as internal standard, which will correct for matrix effects as well as volumetric errors. As you have used another matrix (not spinach) to prepare the calibration standard matrix effects on chlorate and your internal standard were most propably not compensated. Each type of matrix has different matrix effects depending on the elution times of analytes and matrix components.It should be noted, however, that the less accurate matrix-based rather than the matrix-matched calibration approach is preferable to be used in a PT if it reflects routine procedures. In any case, by introducing isotope labelled chlorate as IS (ILIS) you become independent of matrix effects and gain the flexibility of using calibration standards based on pure solvent or on another blank matrix	C, D, E, L
48	-1.4	–	Questio: For Chlorate you have indicated the use of fosetyl D15 as IS with addition at the beginning of procedure. Does this also apply to Perchlorate? Answer by participant: No correction was performed for perchlorate, only for chlorate. ***Comment by the organizers:*** Although your result for chlorate (z =-1.4) is within the acceptable range we believe that it is indicated to emphasize that the use of fosetyl D15 as IS for chlorate is risky as the two compounds normally experience a different matrix effect. This risk is reduced if you use matrix-matched calibration. In your case your own spinach blank was used which was surely not exactly correcting matrix effects. In QuPPe method matrix effects are the main source of errors as the recovery of such highly polar compounds is normally quantitative. A generic IS as fosetyl D15 in this case would mainly correct for volumetric errors, which are normally small. Consider implementing the use of chlorate ILIS.	(C), (L),
49	-4	Yes (formal reasons, non-consideration of EURL-communication)	Analyten wurden nicht gemeldet, da im Blank-Material zur LVU vorhanden. Hinweis, dass für die Bestimmung dieser Stoffe eine alternative Blank-Matrix verwendet werden muss, wurde vergessen zu berücksichtigen. Die erneute Auswertung für Chlorat aus der Messung für die LVU gegen eine Lösungsmittelkalibrierung liefert ähnliche Ergebnisse wie der ensprechende assigned value der LVU. Eine Auswertung von Chlorat gegen eine Lösungsmittelkalibrierung ergab einen Mittelwert von 2,28 mg/kg entspräche einem Z-score von 0,1. Analytes were not reported as they were present in the blank material provided. The advice to use an alternative blank matrix for these compounds was forgotten and thus not considered. Evaluation of chlorate against a solvent calibration resulted results simmilar to the assigned value with a mean value of 2.28 mg/kg, which corresponds to a z-score of 0.1	E, L
54	-2.6	(Yes)	We participate in august-2016 in the proficiency test 19215 in parsley, and we have a z-score of -0.2 using the same standard. But we have checked the SRM-test another time and we observed some deviations in the calibration curve prepared for it. We didn´t use the PT-blank for the analyis of Chlorat and we didn´t correct with recovery ?????? In the case of Chlorat we spiked three bio spinach with different amounts of analyte prior to extraction, and we used 18O Chlorat as internal standard. ***Comment by the organizers:*** As you have used ILIS this deviating result is rather unusual. Please check again the procedure, especially the way you prepare the calibration solutions and the calculations	(I), (L)

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors
A: Problems with measurement (e.g. chromatography, sensitivity)
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C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Chlorate Assigned value: 2.03 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
55	-2.6	?	the laboratory assumes a matrix effect on the 3 molecules (BAC-C14, chlorate et phosphonic acid) ***Comments by the organizers:*** The organizers agree with the conclusion of the laboratory. The use of solvent-based calibrations is risky in case of strong matrix effect unless matrix effects are corrected otherwise (e.g. via ILIS) .	C, E
64	-2.3	–	Chlorate and perchlorate were analyzed together ***Comments by the organizers:*** The IS used (diethylphosphate) is critical as it is of limited use when it comes to correcting for recovery and volumetric deviations and at the same time of high risk of introducing errors through matrix effects. As you have used lettuce instead of spinach blank matrix effects on chlorate and the internal standard were most propably not compensated. Each type of matrix has different matrix effects depending on the elution times of analytes and matrix components.It should be noted, however, that the less accurate matrix-based rather than the matrix-matched calibration approach is preferable to be used in a PT if it reflects routine procedures. In any case, by introducing isotope labelled chlorate as IS (ILIS) you become independent of matrix effects and gain the flexibility of using calibration standards based on pure solvent or on another blank matrix.	C, L
93	2.3	–	No comments Comments by Organizers: consider the use of ILIS to compensate for matrix effects	(C), (L)
107	-4	(Yes)	we used multiresidue method (the same method for analysis of pesticides in fruit and vegetables with ethyl acetate extraction). We didn't use internal standard and no recovery was performed. Just recently we started with SRM and so far we haven't accredited nothing but perchlorates itself. That was our primary goal due to the monitoring of perchlorates in fruit and vegetables. We only had 25 samples last year and another 25 samples in 2016. For chlorates we recently ordered another PT scheme from FAPAS (parsley) and our z-score was 0.2. Comment by organizers: A recovery experiment at the reporting limit would have helped to recognize the risk of false negatives.	D, E, L, O
114	-3.5	–	We had a technical problem with the instrument we used. I had suspected that the results was not good and after this I made a maintenance to this instrument. ***Comments by the organizers:*** Please consider the use of ILIS to compensate for matrix effects.	C, L

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

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L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Dithianon *Assigned value: 1.73 mg/kg for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
2		(NO)	no experience for these compounds in this matrix ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. As you have left your test sample to thaw prior to extraction several times extensive losses have surely occured in the homogenate. Extraction under acidic conditions surely helped to minimize further losses but could not match for the losses occured previously in the homogenate.	D, E, H, L, Adv1
7		–	We did not analysed this compound. It was a transcription error. Comments by the Organizers:	E, I
8		No	AV and Z-Score for informative purpose only, no further investigation ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is most likely lower than the preliminary one and possibly within the acceptable range. By extracting the sample in frozen condition and by a strongly acidified QuEChERS version the losses prior, during and after extraction were minimized.	E, L, M
11		Strong assumptions	In order to investigate our questionable z-score of 2.7 for dithianon, we prepared a fresh stock solution of dithianon and tested it against the stock solution used for the PT. The difference was < 5 %. We also repeated the extraction of the test material in duplicate using fresh dithianon standards. The new results were both 2.65 mg/kg which were comparable with our previously reported value of 2.90 mg/kg. I am not sure why our value was higher than the assigned value but it may be due to the fact that we always carry out dithianon analysis very quickly to minimize losses. ***Comments by the organizers:*** Agree with the above assumptions. As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range.	E, L, M
12		Yes	Our experience in previous PTs (although not too many over the last years for dithianon) we had quite nice results for this compound but in different matrices. We are aware of the fact that Dithianon is a very tricky compound, especially in vegetables - that´s also the reason why we do not analyze for dithianon in this type of matrix in routine. Our feeling is that the indicated assigned value for Dithianon is not very conclusive. This is also demonstrated by the fact that CV is much too high and there is not a unimodal distribution but rather 3 - 4 subpopulations within the small number of results. As already stated in the result submission we performed extraction with acidic MeCN, calibration has been done with classical matrix matched standards (result 2,3 mg/kg and recovery value of 58 %). Subsequently, we used again acidified MeCN, but instead performed procedural matrix calibration and got quite a reasonable increase (4,11 mg/kg, recovery 100 % by definition) which has been reported. So from our point of view this is the most practical approach (apart from using ILIS) which should give reasonable quantitative values though with higher z-scores due to recovery correction). Still, performing this approach we are among a significant number of labs reporting levels far beyond 3 ppm (most probably all of them performed recovery correction in one or the way). Checking standard solutions would be another option, however, stock solution has been renewed for this PT as well. As we know the fact (and this is first of all input from your side) that this compound is extremely unstable and taking into account our experience as well we think that levels reported below 1 ppm should be definitively categorized as huge underestimation of dithianon residues. Considering them (and 10 ppm) as outliers one should at least end up with a (more realistic) assigned value beeing somewhere around 3 ppm ... or even higher. Information provided during last EURL/NRL/OFL workshop in Almeria the homogeneity test gave a result of 3,79. Even though stability test failed there is a clear tendency which supports statements mentioned above. ***Comments by the organizers:*** The organizers fully agree with all above conclusions. As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and most probably within the acceptable range.	E, L, M

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Dithianon *Assigned value: 1.73 mg/kg for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
14		?	unknown. Pb of stability in the calibration mix? Comments by the Organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. A degradation of the analyte in the calibration standard would have resulted in an overestimation of the result and not in a strong underestimation as in your case. By leaving the test sample to thaw prior to analysis considerable losses may have occured as this compound is highly sensitive to degradation, especially in commodities of high pH. Extraction using the acidified QuEChERS method protected the analyte during extraction but could not match for losses occuring prior to extraction.	(E)
22		No	Dithianon is degraded rapidly at condition analysis; investigation of coelution with other compounds in process (Std in Toluene, Sample prep: acidified QuEChERS, no citrate buffer!) ***Comments by the organizers:*** Indeed dithianon degrades very rapidly if not protected. As many of the participants did not take the appropriate measures for protection, the preliminary robust mean of dithianon is most likely strongly underestimated. your real z-score is thus likely to be lower than the preliminary one, but still propably outside the acceptable range. Extracting the sample in deep frozen consition and the use of FA-QuEChERS has surely helped to reduce losses. Many of participants did not take care of these issues.	E, L, M
23		–	Sample was analyzed at room temperatur. The recovery reported was 68.3 %. Sample and QC was performed from the same analyst. However, QC samples from another analyst showed recovery values 43.6 and 26.5 % which were significantly different from the first. Additional QC was scheduled. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. By leaving the test sample to reach room temperature prior to analysis considerable losses have surely occured as this compound is highly sensitive to degradation, especially in commodities of high pH. Extraction using the acidified QuEChERS method protected the analyte during extraction but could not match for the losses occuring prior to extraction.	E, H, L
24		–	Dithianon bestimmen wir mittels QuEChERS ohne PSA-Aufreinigung (aus demselben Grund wie bei Tolylfluanid) und nicht mit einer sauren Variante. Die Reproduzierbarkeit ist gegeben, in diesem Fall hatten wir 8 Messungen mit einer Abweichung von 23 %. Die Messextrakte sind gekühlt in Acetonitril gut stabil. Nach 24 Stunden merkt man schon einen langsamen Abbau, aber wenn man über eine Standardaddition quantifiziert sollte man das gleiche Ergebnis erhalten. Wir sind stets bemüht diese Proben sofort zu vermessen. Des Weiteren achten wir darauf, dass bei der Homogenisierung und der ProbeNowaage das Probenmaterial gefroren bleibt. Beim Antauprozess haben wir einen signifikanten Abbau von Dithianon festgestellt. We analyze dithianon via QuEChERS without PSA-cleanup (for the same reason as tolylfluanid). We do not apply an acidic QuEChERS version. Reproducibility is good (23 % at n = 8). The compound remains stable in the extract if it is kept at low temperatures. After 24 hours a slow degradation is noticed, which is however, compensated via calibration through standard additions. Still we thrive mesuring such samples immediately. We also take care to keep the homogenate frozen at all stages including hogenization and weighing. During melting we have noticed signifficant degradation. ***Comments by the organizers:*** Your very high z-score can be explained by the fact that the robust mean, based on which the preliminary z-scores were calculated, is most propably highly underestimated. The compound is highly sensitive in spinach and many participants did not take proper ,measures for protection. Your sample was employed in frozen condition, so, assuming that it was not defrosted before, dithianon was protected. By applying the standard additions to sample portions approach any recovery losses during extraction should have been compensated. Cleanup with PSA , which is a critical step as dithianon is base-sensitive, was avoided (although even if PSA had been used recoveries would have been more or less compensated by applying standard additions to sample portions for calibration .	E, L, M

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

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J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Dithianon *Assigned value: 1.73 mg/kg for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
28		Yes	no experience with Dithianon, not in our scope, it was only for our information ***Comments by the organizers:*** The compound is highly prone to decomposition in spinach and many participants did not take proper ,measures for protection. As you have kept the sample frozen until analysis and extracted at acidic conditions you managed to minimize losses. As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range.	(D), (E), L, M
42		Strong assumptions	No reasons provided ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. By leaving the test sample to thaw prior to analysis certain losses have surely occured prior to extraction. Acidified QuEChERS helped to minimize further degradation during extraction and the additional procedural calibration approach helped to correct for recovery. These measures could, however, not match for any losses that occured before.	H, L
53		No	AV and z-score for informative purpose only, no further investigation. We used acidified QuEChERS (with 100 µl of H2SO4) without adding citrate salts and with no cleanup ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. The procedure you have followed seems appropriate. As the homogenate was employed in frozen condition dithianon was largely protected. The use of an acidified version of the QuEChERS procedure minimized the losses during extraction. Cleanup with PSA , which is a critical step as dithianon is base-sensitive, was avoided.	E, L, M
54		No	Dithianon is a low stability standard solution, so we think that it is necessary work with a new one in case of detection as we prepared for the test. Maybe a great quantity of labs did not perform it in this way. In spring of 2016 we have participated in the QS Spring test and we obtained a successful result with the same solid raw standard. ***Comments by the organizers:*** It is true that a degradation of the standard solution would lead to an overestimated concentration and, if this applies to many participants, also to an overestimated assigned value. However, dithianon is normally relatively stable in standards if these are kept in the dark. Stability in matrix standards can be problematic if these are not acidified, but normally such standards are prepared freshly within each batch and are typically stored under simmilar conditions as the extracts of the samples. We thus believe that this error-source, that would theoretically lead to overestimations has not affected many labs. In the contrary we believe that the assigned value is strongly underestimated. Your real z-score is thus most likely even lower than the preliminary one (-3.0). Leaving the sample to reach ambient temperature has surely resulted in considerable losses of dithianon in your test-item. These losses could not be compensated by applying a procedure correcting for recovery procedural calibration. Please also consider that extracting this compound by the original QuEhERS is not recommended. Acidification heps to minimize further losses.	(E), G, H, J, L, (M)
57		–	***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is mot likely even lower than the preliminary one. Leaving the test Item to defrost in the refrigerator over 14 h has surely caused extensive losses of dithianon in the homogenate. Extraction at acidic condition has minimized further losses. Losses that occured before extraction can, however, not be compensated afterwards, neither by protection measures during extraction nor by recovery correction measures (e.g. procedural calibration).	E, H, L

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors
A: Problems with measurement (e.g. chromatography, sensitivity)
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F: Misinterpretation of measurement data
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H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Dithianon *Assigned value: 1.73 mg/kg for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
61		No	All aspects of the dithianon extraction and analysis were reviewed, there were no noticeable errors with regards to the traceability, instrument performance was within specification and all method quality controls were fit for purpose. It was noted at the time that the residue seemed peculiarly high, The diluted results matched the original neat results within the expected range. It was concluded that, as our result was a (very) high bias, but our calibration and QCs were good, it was most likely the dithianon standard was not stable and had degraded in solution. As this is an infrequently used un-accredited method and the result was optional and subsequently for information only, no further investigation was carried out ***Comments by the organizers:*** Dithianon is highly sensitive in spinach and many participants did not take proper measures for its protection. As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one but still outside the acceptable range. You have taken all indicated measures to protect dithianon. As you have kept the sample deep frozen until analysis and extracted at acidic conditions you managed to minimize losses prior to extraction. By strongly acidifying during extraction you minimized losses during sample preparation. You have additionally corrected for recovery by using ILIS and at the same time conducting procedural calibration. Given the extremely high result we agree that it is indicated to check if the standard solution was affected by degradation or precipitation. Different degradation rates of ILIs and native compound in the calibration standard and the test item may also explain the strong overestimation (i.e. higher degradation rate of the ILIS in the test item and/or of the native compound in the procedural calibration portions). Such errors are normally compensated by the use of ILIS, but in the case of dithianon the use of ILIS is more tricky. The order of spiking ILIS and native standard plays an important role here, with the compound being spiked first experiencing higher degradation rates and at the same time protecting the compound spiked later. In this respect differenes in the oxidation potentials (e.g. presence of antioxidants or free radicals) of test item and blank material used for procedural calibration may also play a role. These may be due to a different pretreatment of the materials as regards, e.g. thawing, exposure to light.	(E), (L), (M)
64		Yes	The dithianon standard in methanol, was poorly prepared Comments by the Organizer:As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. Dithianon is highly sensitive in spinach homogenates (due to high pH) so the homogenate should be kept frozen to minimize degradation. As you have left the test sample to reach ambient temperature before extraction extensive losses surely occured at this stage. Extraction at acidic conditions surely minimized further losses but could not compensate for the losses that had already occured prior to extraction. A degradation or precipitation of the standard would have resulted in an overestimation of the result.	E, (H), (L)
67		–	In a PT by QS-GmbH in April 2016 with dithianon in apples there was also a broad distribution of the results with clear underestimations. With a spiking level of 0.4 mg/kg the results of the participants were in the range of 0.017-0.175 mg/kg with an average at ca. 0.09 mg/kg. There seems to be a degradation in frozen state or during thawing. Analysis under acidic conditions resulted in acceptable recovery rates on spiked blank of 86 %. We have thawed the EUPT-SRM11 several times and we assume that the low dithianon level determined is related to this. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is most likely even lower than the preliminary one. As the sample was thawed repetitively and employed at ambient temperature considerable losses of dithianon have surely occured even before starting the analysis. Extraction at acidic conditions surely minimized further losses but could not compensate for the losses that had already occured prior to extraction.	E, H, L

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

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K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
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Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Dithianon *Assigned value: 1.73 mg/kg for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
72		Yes	It was our first time attempt with this pesticide, no previous experience. The recovery was extremely low, we did not calculate with it (we should have done). ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. By leaving the test sample to reach ambient temperature before extraction extensive losses surely occured before extraction. Extraction at acidic conditions helped to minimize further losses but could not compensate for the losses that had already occured. Avoid thawing the samples before analysis. When recovery deviates considerably from 100 % (e.g. <70 %) results should not be reported unless corrected for recovery, e.g. by using procedure involving standard addition to sample portions, by using procedural calibration or by using ILIS.	(D), (E), (H), (J), (L)
75		No	Umfangreiche Untersuchung, keinen Fehler gefunden. Extensive investigations, no error localized ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range.	, L, M
88		–	Recoveries from laboratory internal controls on dithianon are correct. From the review of the intercomparative data, a high variability of results is observed, which could indicate a possible degradation of dithianon in the sample. In our procedure the sample is defrosted and re-frozen. Aliquots that are defrosted are not frozen again. We cannot say for sure for how long the sample was in a defrosted state before beginning extraction. Possibly the deviation in some results has been caused by excessive defrosting time before extraction. Comment by the Organizer: Dithianon is indeed very sensitive to degradation. Degradation is especially fast in homogenates of high-pH matrices if these are not kept frozen. Cleanup with PSA has surely also contributed to degradation. Keep the homogenate in frozen condition until analysis to minimize losses Also consider the use of acidified QuEChERS to minimize losses during and after extraction.	G, H, J, L, O
96		–	Standard solutions were couple of days old, not real fresh ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. You have employed a procedure that minimizes losses during extraction and cleanup. There is always the possibility that your calibration standard has degraded, but if it was based on a blank extract that was extracted using the acidified QuEChERS degradation should be slow.	(E), L, M
98		–	The first time that we analyzed the sample of the intercomparative, we didn't detect ditianona and neither on the control at LOQ. After realizing the search of modifications of the method Quechers to improve the extraction and of proving several of them, we decided on the results obtained on having added sulphuric concentrate initially of the extraction and without adding PSA. We think that our result doesn't coincide with the value assigned by several reasons. One of them is that in the preparation of the sample before the extraction, the acidificación was not realized as it is indicated in Analysis of Dithianon by the QuEChERS Method - Impact of pH on recovery rates. Version 2 . In addition the sample was received 5/04/2016 and though it was stored in freezing, the result that we sent was of the extraction we made on 17/05/2016. ***Comments by the organizers:*** As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. Dithianon is indeed very prone to losses in samples of high pH and with low antioxitative potential and should be protected at any stage of analysis. Low temperatures, protection from light exposure and strong acidification can help to reduce losses. Even in the freezer some losses can occur but degradation are faster at higher temperatures and especially when homogenates are thawed. So, conducting the analysis at a late stage of the PT period has surely contributed to some extend to the low z-score but cannot fully explain it. Please also check whether the sample was defrostedat some stage prior to the analysis.	D, E, (H), (L)

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

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H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Dithianon *Assigned value: 1.73 mg/kg for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
106		not yet, ongoing	Concerning the dithianon, we did not find explanation. However, our R&D works at present for the improvement of our monitoring. We ordered the internal standard (dithianon D4) and we are going to validate it. Comment by organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. The use of dithianon ILIS will surely help to match for the losses during extraction, cleanup and measurement. it will however not compensate for any losses that occured prior to extraction. Even if ILIS is used acidification during extraction is needed to avoid a complete degradation of the analyte and/or the ILIS. Protection measures prior to extraction include keeping the sample frozen at any time and homogenization under cryogenic conditions and optimally following acidification.	(H), (J), (L)
107		(Yes)	we used multiresidue method (the same method for analysis of pesticides in fruit and vegetables with ethyl acetate extraction). We didn't use internal standard and no recovery was performed. Just recently we started with SRM and so far we haven't accredited nothing but perchlorates itself. That was our primary goal due to the monitoring of perchlorates in fruit and vegetables. We only had 25 samples last year and another 25 samples in 2016. Comment by organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. A recovery experiment at the reporting limit would have helped to recognize the risk of false negatives. Please also consider other comments on points to be considered in the analysis of dithianon.	D, E, L, O
114		–	We have employed QuEChERS variant with sulfuric acid. We have defrosted the sample repetitively ***Comments by the organizers:*** The thawing of the sample has surely led to severe losses of this compound. The use of acidified QuEChERS for extraction may have reduced further losses but could not recover any previous losses.You have employed solvent-based calibration. his may have also introduced a bias due to matrix effects and should also be checked.	H, L
117		Yes	We haven't used the acidified Quechers-Method for the analysis of Dithianon, so maybe that will explain the bad recovery rate. Comments by Organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one.The non-acidification during extraction has surely caused a degradation. At least in theory these losses should have been compensated by the procedural calibration. However, in the methodology information you have also indicated that the sample was extracted at ambient conditions. This has most propably caused significant degradation that could not be compensated by the procedural calibration conducted.	E, G, H, J, L
123		–	For dithianon we acidified our extracts significantly more than recommended by the EURL method as we find that this helps further reduce degradation; I note that there is a good spread of results in the preliminary report for this analyte. ***Comments by the organizers:*** the preliminary assigned value (= robust mean) is most probably much lower than the real value as many labs experienced losses at various stages prior to or during the analysis. This also explains the spread of the results. Your real z-score is likely to be much lower than the preliminary one and probably within the acceptable range. The strong acidification during rextraction has surely protected the compound from degrading.	E, L, M
124		–	No reasons provided. Comment by organizers: As the preliminary robust mean was most likely underestimated your real z-score is likely to be even lower than the preliminary one. As you have left your sample to thaw prior to analysis, considerable losses of dithianon have surely occured. Exposition time is an important factor here. Acidification during extraction has surely helped to minimize losses during extraction but it could not match for losses which have occured before extraction.	H, L

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Dithianon *Assigned value: 1.73 mg/kg for informative purpose only*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
128		Yes	It is common sense, that dithianone is labile to pH conditions > 3. We therefore applied the extraction protocol using acidified QuEChERS with 1 % formic acid proposed by the EURL SRM for this active compound leading to a stabilization of dithianone during the extraction process. Prior to the extraction the sample was not thawed. A aliquot (aliquoted in frozen state) of the frozen sample was immediately extracted with the extraction solvent. In our opinion, this is the most appropriate way in sample preparation to determine the accurate value of this pH-labile pesticide parameter. Furthermore we did not find any errors for the calibration, calculation, weighing, pipetting or any other errors. We assume, that we obtained a good effective recovery rate for dithianone and reported an accurate value for dithianone for this sample material. The CV for this compound within the PT was calculated with 94,4 %. Other labs (labs 8, 12, 22, 24, 28, and 75) also reported higher (and probably more accurate) values in the range of 3.3 - 5.6 mg/kg. ***Suggestions/Comments by the organizers:*** Indeed, the way you have treated and analyzed the sample has minimized the possibility of losses. Many labs have not taken such measures to properly protect dithianon. As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range.	E, L, M

Dithianon *Assigned value for informative purpose only: 1,73 mg/kg*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
128		Yes	It is common sense, that dithianone is labile to pH conditions > 3. We therefore applied the extraction protocol using acidified QuEChERS with 1 % formic acid proposed by the EURL SRM for this active compound leading to a stabilization of dithianone during the extraction process. Prior to the extraction the sample was not thawed. A aliquot (aliquoted in frozen state) of the frozen sample was immediately extracted with the extraction solvent. In our opinion, this is the most appropriate way in sample preparation to determine the accurate value of this pH-labile pesticide parameter. Furthermore we did not find any errors for the calibration, calculation, weighing, pipetting or any other errors. We assume, that we obtained a good effective recovery rate for dithianone and reported an accurate value for dithianone for this sample material. The CV for this compound within the PT was calculated with 94,4 %. Other labs (labs 8, 12, 22, 24, 28, and 75) also reported higher (and probably more accurate) values in the range of 3.3 - 5.6 mg/kg. ***Suggestions/Comments by the organizers:*** Indeed, the way you have treated and analyzed the sample has minimized the possibility of losses. Many labs have not taken such measures to properly protect dithianon. As the preliminary robust mean was most likely underestimated, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range.	E, L, M

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

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G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Phosphonic acid *Assigned value for informative purpose only: 9.83 mg/kg*

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
4	3	Yes	As we had no experience with this analyte, we did misjudge the baseline of the chomatogramm and integrated wrong. ***Comments by the organizers:*** Indeed phosphonic acid analysis requires some experience as phosphorous acid elutes close to it and interferes with one of its mass-transitions.	D, E, F
5	-4	Yes	We saw in our instrument phosphonic acid of the fosetyl (when fosetyl degradated in the source), but not phosphonic as phosphonic, and we didn´t known it until this EUPT. We are working in it. ***Comments by the organizers:*** Indeed fosetyl decomposes to phosphonic acid both in solution as well as the ion-source. Calibrating with fosetyl will thus give a phosphonic acid signal at the retention time of fosetyl. If this fosetyl-based signal is erroneously considered as the one produced by free phosphonic acid there is a risk of false negatives results for phosphonic acid. At the same time, there is a risk of false positives if fosetyl-ILIS spiked to the sample has decomposed in solution or if the phosphonic acid generated as an in-source fragment of fosetyl-ILIS is considered as belonging to free phosphonic acid . The use of phosphonic acid ILIS would have helped to recognize that the retention time of free phosphonic acid is different from the one formed from fosetly through in-source fragmetation.	E, F, L, O
31	-3.5	Yes	No experience with the analyte and method. Error in concentration of analitical standard ***Comments by the organizers:*** Phosphonic acid (z-score -3.5) and chlorate (z-score -3.4) show a different trend than perchlorate (z-score 9.3). If you have used those standards in mixture, please recheck the claimed source of error. You have indicated the use of the EUPT-blank for the calibration. Please consider the use of ILIS to compensate for matrix effects.	D, E
43	-4	–	At the time of implementation of EUPT-SRM 11 we were in the initial phase of the development of the analytical technique for the measurement of Chlorate and Phosphonic Acid, the methodology was at a very early stage of its development, which led to negative results. We have fine-tuned the method ever since. Our method is able to measure Chlorate, Perchlorate, Fosetyl and Phosphonic Acid using as caffeine internal standard, to control the percentage of recovery. We introduce a matrix recovery test into all the analysis runs. For the case of phosphonic acid the fortification level was 0.050 mg / kg with a recovery percentage of 80 %. ***Comments by the organizers:*** Please consider introducing isotope labelled phosphonic acid as internal standard (ILIS). The ILIS will help you avoid false negative results as it will give you a hint on suppression and also show you the expected retention time and peak-shape.	D, E, L, O
55	-2.6	?	the laboratory assumes a matrix effect on the 3 molecules (BAC-C14, chlorate et phosphonic acid) ***Comments by the organizers:*** The organizers agree with the conclusion of the laboratory. The use of solvent-based calibrations is risky in case of strong matrix effect unless matrix effects are corrected otherwise (e.g. via ILIS) .	C, E

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Perchlorate Assigned value: 0.260 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
6	-2.8	tentative assump-tions	There were two extractions (6th April 2016 and 9th May 2016). The first extraction was injected twice on a column at the end of life. The values were 0.22 and 0.16 mg/kg. The second extraction was injected on a new column (passivated according to the QuPPe protocol). The value was 0.076 mg/kg. The peak shape was better and the retention time was higher for the second extraction. So the result of the second extraction was submitted. Unfortunately there was no time to analyze a third extract to confirm the first or the second extraction (the differences in values were lower for other test molecules). ***Comments by the organizers:*** when applying standard addition approach check if linearity is good and residuals small. Consider the use of perchlorate ILIS for additional certainty.	A, E
18	-3.8	Yes	due to an administrative fault, no method problem After further thorough evaluation, Please ignore our previous feedback. To our opinion the PT blank is contaminated with chlorate, perchlorate and pymetrozine. We did perform a blank correction and therefore our results for chlorate and perchlorate are reported as <RL. Therefore we can not consider these results as false negative. ***Comment by the organizers:*** Taking all aspects into consideration and allthough it was acknowledged that there was some room for confusion, the EUPT-AdvG decided to still classify this result as a False Negative following the general protocoll rules.The fact that the blank spinach of the EUPT-SRM11 contained chlorate and perchlorate through irrigation, as well as pymetrozine through spraying was clearly communicated by the organizer and it was indicated that calibration should be based on standards in pure solvent or on a differ-ent blank. Conducting blank correction where the blank contains the analyte of interrest at a similar level as the sample is inappropriate anyway. Your reporting of Not Detected with the LOQ being at 0.01 mg/kg was surely not appropriate in this case	E, F, L
26	-2.7	–	We think that the mistake was that we forgot adding water (0.5 ml) to the sample before the extraction. Then we took part in a proficiency test (FAPAS 19215) in parsley, adding water with a z-score for chlorate of -0.6. ***Comments by the organizers:*** The impact of adding 0.5 mL water is rather low. Even if you have scaled down the QuPPe procedure 2-fold using 5g sample (as you have indicated) plus 5 g of solvent to reach a target volume of 10 mL in total, the error would correspond to maximally 10 %. Please also check the possibility of having employed 5 g of sample but made calculations on the basis of 10 g. The error might be also related to differences in the matrix effects between calibration standard and the test Item extract (despite using blank spinach). In any case, consider using isotope labelled chlorate to compensate both for matrix effects as well as volume deviations as the one explained.	(B), C, (E), (L)
31	9.3	Yes	No experience with the analyte and method. Error in concentration of analitical standard ***Comments by the organizers:*** Phosphonic acid (z-score -3.5) and chlorate (z-score -3.4) show a different trend than perchlorate (z-score 9.3). If you have used those standards in mixture, please recheck the claimed source of error.You have indicated the use of the EUPT-blank for the calibration. As the EUPT-blank contained chlorate this could have been a source of error.Please consider the use of ILIS to compensate for matrix effects.	D, E
32	2.3	–	No comments provided Comments by the Organizers: consider employing an isotope labelled internal standard (ILIS) to compensate for matrix effects	(C), (L)

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Perchlorate Assigned value: 0.260 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
49	-3.7	Yes (formal reasons, non-consideration of EURL-communication)	Analyten wurden nicht gemeldet, da im Blank-Material zur LVU vorhanden. Hinweis, dass für die Bestimmung dieser Stoffe eine alternative Blank-Matrix verwendet werden muss, wurde vergessen zu berücksichtigen. Die erneute Auswertung für Chlorat aus der Messung für die LVU gegen eine Lösungsmittelkalibrierung liefert ähnliche Ergebnisse wie der ensprechende assigned value der LVU. Analytes were not reported as they were present in the blank material provided. The advice to use an alternative blank matrix for these compounds was forgotten and thus not considered. Comments by Organizers: The EUPT-AdvG decided to consider these results as False Negatives, following the rules of the General Protocol.	E, L
64	9.6	–	Chlorate and perchlorate were analyzed together ***Comments by the organizers:*** The IS used (diethylphosphate) is critical as it is of limited use when it comes to correcting for recovery and volumetric deviations and at the same time of high risk of introducing errors through matrix effects. As you have used lettuce instead of spinach blank matrix effects on perchlorate and the internal standard were most propably not compensated. Each type of matrix has different matrix effects depending on the elution times of analytes and matrix components.It should be noted, however, that the less accurate matrix-based rather than the matrix-matched calibration approach is preferable to be used in a PT if it reflects routine procedures. In any case, by introducing isotope labelled chlorate as IS (ILIS) you become independent of matrix effects and gain the flexibility of using calibration standards based on pure solvent or on another blank matrix.	C, L
82	-2.9	Yes	The analytes had a value of Z score of about -3 due to a calculation error. An incorrect volume was used during the calculation.	E, I
83	5.2	Yes	exterme matrix effect: We repeated the sample but with greater dilution of the extract and found closest to the target values results. Due to the limited experience in handling this type of column we saw that the peak shape and retention times varied greatly. As the matrix greatly influences proceeded to 1:10 and 1:20 dilutions and the new value was: -0.240 mg/kg. Chlorate and perchlorate were analyzed in parallel but at different dilutions for their sensitivity. Procedural calibration using blank spinach was employed. We do not use ILIS. ***Comments by the organizers:*** The new value after dilution is very close to the AV. The use of ILIS would have helped you to avoid errors. Dilution indeed reduces matrix effects and in certain cases also helps to avoid false negatives as it improved separation of analytes of interrest from coeluting matrix thus reducing signal supression. Also consider improving chromatographic separation using softer gradients or other column. Please additionally check the possibility of a calculation error.	C, D, E
114	8.6	–	We had a technical problem with the instrument we used. I had suspected that the results was not good and after this I made a maintenance to this instrument. ***Comments by the organizers:*** Please consider the use of ILIS to compensate for matrix effects.	C, L
128	3.7	Yes	Einwaagefehler . Es wurde versehentlich die doppelte Menge Probe eingewogen. Dieses wurde bei der Berechnung von Perchlorat nicht berücksichtigt, bei der Berechnung der Konzentrationen der anderen Analyten wurde die erhöhte Einwaage berücksichtigt. Es handelt sich auch in diesem Fall um einen Dokumentationsfehler. Weighing/documentation error. The weight of the test portion was double as high as the number used for calculations. The result should be 0.25 mg/kg	E, I

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Pymetrozine Assigned value: 0.260 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
5	-2.4	Yes	We analyse it with the multirresidue method. The recovery of our control was 100 %. Perhaps we must analyse it with QuPPE method. ***Comments by the organizers:*** You may try to use QuPPe but you should be aware that this will lead to larger matrix effects that would need to be compensated.Unfortunately there is no pymetrozine ILIS available at the moment.The recovery rate of 100 % achieved for the control seems very high. Normally using QuEChERS-CEN recovery rates are between 50 and 70 %. Due to the untypically high recovery rate in the control you have decided not to take measures to correct the result for recovery (e.g. procedural calibration or standard addition to sample portions). Please also consider using the method provided by the EURL for the analysis of pymetrozine in which the pH is higher to facilitate partitioning into the acetonitrile phase. Another possible source of error may be related to the use of blank tomato to prepare calibrationsolution.	(E), (G), (J), (L)
6	7.1	(Yes)	The range of calibration wasn't in spinach because Pymetrozine was detected in the Blank sample. The recovery of Pymetrozine is poor with quechers method. So the result was adjusted for recovery (25 %). Usually Pymetrozine has a recovery between 20 % and 45 %. The difference between the calibration matrix and the sample is certainly a reason of the unacceptable result. 25 % was based on ONE recovery experiment (on an own blank spinach) made as the same time as the assay. ***Comments by the organizers:*** Adjusting results for recovery based on recovery factors is tricky and much care is needed to account for the variability of recovery figures as well as the variability of test sample results. Repeitive analyses are necessary. A reliable alternative is the standard addition to sample portions approach, which corrects for recovery rates and matrix effects but also adresses variability issues. Consider the use of a modified QuEChERS version (see EURL-website) in case of positive pymetrozine findings. The preliminary robust mean was probably underestimated, thus, your real z-score is likely to be lower than the preliminary but most likely still not within the acceptable range.	(E), (J), (L)
14	-2.3	No	reason unknown ***Comments by the organizers:*** Employing CEN-QuEChERS you have reported a recovery rate of 70 %, which is within the typical range for this type of matrix (50-75 %) but rather on the upper side. If you had corrected your result for recovery you would have achieved an acceptable z-score. Rather than using a recovery factor (which is tricky) the use of other approached for the cofrrection of results for recovery would be preferred,standard addition. Please consider initiating correction of results for recovery even at recovery rates of 70 % to reduce the bias.	J, L, O
16	2.5	Strong assumptions	Unfortunately I have no clear answer for this problem. Indeed the molecule was for information only on the preliminary report and we didn't intensify our investigations. We checked at this moment only that there is no reporting error, no problem during experiment. I have no more matrix to repeat the experiment again. ***Comment by the organizers:*** The preliminary robust mean was probably underestimated, thus, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range.	E, L, M
31	-3	Yes	No experience with the analyte and method. Error in concentration of analitical standard ***Comments by the organizers:*** matrix effects could have also played a role, since you have employed a calibration based on pure solvent	D, E

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors
A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Pymetrozine Assigned value: 0.260 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
32	6.2	No	Bei Pymethrozine/Tolylfluanid wurden die Messwerte der Std. Addition abgegeben. Es liegen ebenfalls Messungen mit einem Matrix matched Std.(3 Punktkal.) vor, deren Werte einen z-score innerhalb der Tolleranz ergeben hätten. Bei 70 % der Wirkstoffe erzeugten die Matrix matched Std. deutlich bessere Werte, im Vergleich mit den erhaltenen Ergebnissen. For Pymetrozine we submitted results derived by standard addition. We also generated results using matrix-matched calibration (at 3 levels) the z-scores of which were within the acceptable z-score range. For 70 % of the compounds matrix-matched standards generated clearly better results than those submited. Pymetrozine standard was prepared freshly and dilution is assisted by ultrasound. From own experiments and a past PT we are aware of the poor recoveries of pymetrozine. The error can be explained by a combination of a non-fully dissolved standard and variable recovery rates. Comments by the Organizers: Normally standard addition to sample portions is more accurate than matrix matched calibration as it corrects for both matrix effects and recovery. Precondition is a linear relationship between analyte concentration/amount and the instrument response. It is recommended to also check the way you conduct the standard additions approach as well as the caluclations. Having obtained a highly overestimated result, checking the correctness of the pymetrozine standards (stock- and working-) would indeed make sense. The low recovery rates should not play a role as you have corrected for recovery by the standard addition to sample portions approach. Consider checking whether you have additionally applied a recovery factor to the alraedy recovery-corrected result. The preliminary robust mean was probably underestimated, thus, your real z-score is likely to be lower than the preliminary but most likely still not within the acceptable range.	(E), (J)
49	-3.9	Yes (formal reasons, non-consideration of EURL-communication)	Analyten wurden nicht gemeldet, da im Blank-Material zur LVU vorhanden. Hinweis, dass für die Bestimmung dieser Stoffe eine alternative Blank-Matrix verwendet werden muss, wurde vergessen zu berücksichtigen. Die erneute Auswertung für Chlorat aus der Messung für die LVU gegen eine Lösungsmittelkalibrierung liefert ähnliche Ergebnisse wie der ensprechende assigned value der LVU. Analytes were not reported as they were present in the blank material provided. The advice to use an alternative blank matrix for these compounds was forgotten and thus not considered. Comments by Organizers: The EUPT-AdvG decided to consider these results as False Negatives, following the rules of the General Protocol.	E, L
54	2.1	not yet, ongoing	One of the values that we have performing this test is 0.62 mg/kg that it is under z-score of 2, so we are waiting for a new proficiency test that include this substance. In case of no possibility of this, we are going to buy a new standard to check with this one. We spiked a series of blank test portions with different amounts of analyte, prior to extraction, and we think that our results are higher than the assigned value due to the standard, we are checking them. ***Comment by the organizers:*** The preliminary robust mean was probably underestimated, thus, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range. A degradation or precipitation of the analyte in the standard can indeed lead to overestimated results.It would be worthwhile checking whether the overestimated result is due to a duplicate correction for recovery (via procedural calibration and via recovery factor).	(E), L, M
69	4	No	I checked the standard – we used a new stock solution from the standard, before we started, we checked it with measure against the old stock solution – the comparison was oK. We worked at a pH of 7, the calculation was matrix-matched. I checked the calculation, I found no mistake (same procedure like dodine). Finally I didn't find the reason for the high z-Score. Comment by Organizers: The preliminary robust mean was probably slightly underestimated, thus, your real z-score is likely to be slightly lower than the preliminary one but probably still not within the acceptable range. Please check whether the strongly overestimated result was due to a stronger suppression of the pymetrozin signal by components contained in the ruccola-extract used to prepare the calibration standard.	C, L

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Pymetrozine Assigned value: 0.260 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
83	4.8	Yes	Exterme matrix effect: We repeated the sample but with greater dilution of the extract. and found closest to the target values results. As the matrix greatly influences proceeded to 1:10 and 1:20 dilutions and the new value was: 0.442 mg/kg ***Suggestions/Comments by the organizers:*** The new value after dilution is very close to the AV. Dilution indeed reduces matrix effects. By employing standard addition to sample portions normally the result is corrected for low recovery. The preliminary robust mean was probably underestimated, thus, your real z-score is likely to be lower than the preliminary but most likely still not within the acceptable range.Please check the possibility of a calculation error.	(C), (E)
88	3.1	–	From the review of the intercomparative data, a high variability of results is observed, which could indicate a possible degradation of pymetrocine in the sample. Follow-up measures: Calibration in the same matrix ***Comment by the organizers:*** Please note that a degradation of pymetrozine in the sample would lead to underestimated result rather than an overestimated as in your case.The preliminary robust mean was probably slightly underestimated, thus, your real z-score is likely to be a bit lower than the preliminary one, but probably still not within the acceptable range. Pymetrozine is not particularly sensitive to degradation. However as it is polar the recovery with QuEChERS is not very high due to unfavorable partitioning equilibrium. Recovery rates typically increase with pH. In high pH commodities, such as spinach, average pymetrozine recovery rates by the original (non-buffered) QuEChERS, the procedure you have used, typically exceed the 70 % threshold. For higher recovery rates consider using the variant of QuEChERS for pymetrozine published in the EURL- website. Due to the presence of pymetrozine in the blank material provided you have used an own blank spinach to prepare matrix-matched calibration. It cannot be excluded that this spinach showed considerably different matrix effects thus introducing a bias. A procedural calibration as you have suggested would avoid such errors.Please also consider checking the stability of your standard solution.	(C), (E), (J), (L)
96	-4	–	Actually the case is quite unclear despite of my follow-up investingations in this field. During PT I made two batches of analyses on different days and the results were strange: at first batch there was an identical size peak both in blank and sample so that I couln't make any calibration (matrix mached). On second batch there was no peaks anywhere, not in blank and sample as well. But recovery sample was OK! As I had no time to make a third batch, we decided not to give out any findings (not to report false positive result). Actually, after recieving preliminary results I made one more batch from the sample (frozen up to that time) and get quite satisfactory results for both compounds. Most probably a wrong GPC clean-up method was applied during preparation of the second batch. We have several methods for different compounds based on their retention in column and most probably a method with too late collecting time was chosen. Comments by the Organizers: Irrespective on whether GPC was the main reason for the error, please consider measuring pymetrozine via LC-MS/MS as it is prone to matrix effects in GC. When analyzing via GC avoid the use of calibration standards in pure solvent to reduce the impact of matrix effects. Even if the blank matrix provided was not suitable another matrix or analyte protectants could have been used to reduce the impact of matrix effects. Consider introducing better QC-standards to avoid false negatives. Please also check for any potential losses of pymetrozine during GPC cleanup due to interactions.	(B), (E), F, O
98	-3.4	?	Several volumes of a working solution of pimetrozina were added to aliquots of the extract obtained by the method Quechers, except to one of them. After revising all the calculations together with the EURL, we have realized that we failed to apply the correct factor for obtaining the concentration in the sample. Considering this factor the result would have bene 0.635 mg/kg. ***Comments by the organizers:*** In the standard additions approach first determine via extrapolation (or cross-multiplication) the absolute amount of analyte in the non-spiked sample portion (or extract aliquot) and then divide this analyte amount by the sample mass in the corresponding sample portion (or the sample mass represented in the extract aliquot).	E, I, L

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Pymetrozine Assigned value: 0.260 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
107	-3.6	(Yes)	we used multiresidue method (the same method for analysis of pesticides in fruit and vegetables with ethyl acetate extraction). We didn't use internal standard and no recovery was performed. Just recently we started with SRM and so far we haven't accredited nothing but perchlorates itself. That was our primary goal due to the monitoring of perchlorates in fruit and vegetables. We only had 25 samples last year and another 25 samples in 2016. Comment by organizers: a recovery experiment and a validation in general would have helped to assess the bias and trigger recovery correction measures (e.g. use of ILISs, standard addition to sample portions, procedural calibration).	D, E, L, O
110	8.1	(Yes)	We haven't this analyte in our scope and we were working to validate the method to extend our accreditation. We tryed to analyze Pymetrozine to collect data for our validation study that was just started durin April. Then we applied some method changes to minimize the matrix effect for some anaytes, like Pymetrozine, that shows a very short retention time. Now we are testing a second internal standard that seems useful in minimizing matrix effect. TPP was finally not used as IS. We do not calculate via IS when evaluating diluted extracts. Comments by the Organizers: As the QuEChERS-CEN method typically shows relatively low recoveries your z-score would have been expected to be towards the lower side. There is various resons for result overestimation. Please check the possibility of erroneous standard e.g. due to pipetting error, degradation or precipitation. As you have employed a solvent-based calibration, matrix-effects may have influenced your result. Introducing a second IS as you have suggested is usefull, but unless it is the pymetrozin ILIS (which currently does not exist), this second IS will not help you get rid of matrix effects. Consider introducing approaches that will control your matrix effects such as matrix matching and standard additions.The preliminary robust mean was probably underestimated, thus, your real z-score is likely to be lower than the preliminary one, but most likely still not within the acceptable range.	C, D, E
125	2.1	–	***Comment by the organizers:*** The preliminary robust mean was probably underestimated, thus, your real z-score is likely to be lower than the preliminary one and possibly within the acceptable range.	(L), (M)
4	-3.8	–	We searched for Quizalofop ethyl instead of Quizalofop free acid. ***Comments by the organizers:*** This happend to several labs. Please carefully read the Target Pesticide List (TPL) of each PT carefully as the residue definitions there may differ from the legal ones.	E, K, L
14	-3.8	Yes	Out of our scope. Confusion with quizalofop ethyl, also named as quizalofop ***Comments by the organizers:*** This happend to several labs. Please read the Targt Pesticide List (TPL) of each PT carefully as the residue definitions there may differ from the legal ones.	E, J, K
16	2.3	Vague initial suspicions	We didn't find the cause of our error (concentration of solutions ok, calculation and processing ok, QC ok, reporting ok. We did the experiment again and we found 172 ppb. This new experiment was realized with EURL-SRM blank and the previous one with EURL-FV blank. ***Comment by the organizers:*** The blank spinach of the EUPT-FV18 was different than that of the EUPT-SRM11. Although the spinach variety was the same the growing season was different as well as the harvesting stage. It is thus possible that the matrix effects were different.	C, E, L
32	-3.8	–	Auf diesen Wirkstoff wurde nicht geprüft We have not searched for this compound ***Comments by the organizers:*** According to the rules such explanations are not accepted if received a posteriori. The result is thus treated as a false negative.	E, I

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Pymetrozine Assigned value: 0.260 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
63	4.2	?	In sample preparation we did not use a single residue method for Quizalofop but QuEChERS. We applied the raw-extract (without PSA) for the determination although the peak of Quizalofop showed a negative impact of matrix and a low sensitivity. The qualifier ratios were not stable in all measured solutions and the concentration of 3 repetitions showed a high variation. But the recovery seemed to be good with 104%. We thought that with standard addition we could delete these effects. In a pre-experiment we measured the normal QuEChERS extract (with PSA) too and received a concentration of 0.147 mg/kg with decreasing recovery up to 60%. The internal standard nicarbazine also showed reduced recovery. For this reason we ignored this concentration although the peak shows no negative impact of matrix (but low sensitivity). The report of this result would have been better. But our validation data are for the raw-extract without PSA. So we decided to report this content (0.349 mg/kg). ***Comments by the organizers:*** Skipping PSA in the cleanup step is helpfull as quizalofop is an acidic pesticide with a tendency to interact with PSA. Please check if the losses of Nicarbazin in your pre-experiment were related to the use of carbon in dSPE. The low sensitivity of the peak that you mentioned has surely compromized precission, so that your final result might be a spurious outlier. Consider measuring quizalofop in the ESI-Neg. mode, where sensitivity is better.	E, G, L
73	41.5	–	The reason for our very high z-score was the analytical standard used. We buy custom standard mixtures in concentration of 100 µg/ml with approximately 30 pesticides in each. By mistake from the company the concentration of cyhalofop was wrong. We have bought a new standard of quizalofop and now the result is OK. ***Comments by the organizers:*** For an initial check of the pesticide concentration and stability of purchased mixtures the exchange of standards with other labs would be an option to consider.	E, L, O
81	-3.8	–	The initial data transmission (target pesticide list) is unintentional mistake. We analyse residues of Quizalafop-P-tefuryl and Quizalafop-ethyl as Partial legal residue definition analysed for Quizalafop. Our mistake was that we equate Quizalafop as Quizalafop (free acid). ***Comments by the organizers:*** This happend to several labs. Please carefully read the Targt Pesticide List (TPL) of each PT carefully as the residue definitions there may differ from the legal ones.	E, K
91	-3.8	–	This substance are not analysed because it is not included in our scope, and because using the GCMSMS the ester quizalfop ethyl are analyses and it is a mistake by us giving quizalofop free acid as analyzed ***Comments by the organizers:*** This happend to several labs. Please carefully read the Targt Pesticide List (TPL) of each PT, as the residue definitions there may differ from the legal ones.	E, K, M
98	-3.8	–	The problem was that we had a working solution of Quizalofop - Etil but not of the Quizalofop. All the standards of the different pesticides studied were checked and there weren't differences between old and new standards. ***Comments by the organizers:*** This happend to several labs. Please carefully read the Targt Pesticide List (TPL) of each PT carefully as the residue definitions there may differ from the legal ones.	E, K
125	3.3	–	No reasons provided.	–

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors
A: Problems with measurement (e.g. chromatography, sensitivity)
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of stock or working standard solution (e.g. due to degradation or precipitation); inappropriate / erroneous calibration approach
F: Misinterpretation of measurement data
G: Use of inappropriate analytical procedure (e.g. showing high bias or low sensitivity; conditions for reductive clevage of dithiocarbamates possibly too weak for propineb)
H: Degradation in homogenate prior to analysis (e.g. due to Inappropriate storage/pre-treatment of sample)

Quizalofop Assigned value: 0.171 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
4	-3.8	–	We searched for Quizalofop ethyl instead of Quizalofop free acid. ***Comments by the organizers:*** This happend to several labs. Please carefully read the Target Pesticide List (TPL) of each PT carefully as the residue definitions there may differ from the legal ones.	E, K, L
14	-3.8	Yes	Out of our scope. Confusion with quizalofop ethyl, also named as quizalofop ***Comments by the organizers:*** This happend to several labs. Please read the Targt Pesticide List (TPL) of each PT carefully as the residue definitions there may differ from the legal ones.	E, J, K
16	2.3	Vague initial uspicions	We didn't find the cause of our error (concentration of solutions ok, calculation and processing ok, QC ok, reporting ok. We did the experiment again and we found 172 ppb. This new experiment was realized with EURL-SRM blank and the previous one with EURL-FV blank. ***Comment by the organizers:*** The blank spinach of the EUPT-FV18 was different than that of the EUPT-SRM11. Although the spinach variety was the same the growing season was different as well as the harvesting stage. It is thus possible that the matrix effects were different.	C, E, L
32	-3.8	–	Auf diesen Wirkstoff wurde nicht geprüft We have not searched for this compound ***Comments by the organizers:*** According to the rules such explanations are not accepted if received a posteriori. The result is thus treated as a false negative.	E, I
63	4.2	?	In sample preparation we did not use a single residue method for Quizalofop but QuEChERS. We applied the raw-extract (without PSA) for the determination although the peak of Quizalofop showed a negative impact of matrix and a low sensitivity. The qualifier ratios were not stable in all measured solutions and the concentration of 3 repetitions showed a high variation. But the recovery seemed to be good with 104 %. We thought that with standard addition we could delete these effects. In a pre-experiment we measured the normal QuEChERS extract (with PSA) too and received a concentration of 0.147 mg/kg with decreasing recovery up to 60 %. The internal standard nicarbazine also showed reduced recovery. For this reason we ignored this concentration although the peak shows no negative impact of matrix (but low sensitivity). The report of this result would have been better. But our validation data are for the raw-extract without PSA. So we decided to report this content (0.349 mg/kg). ***Comments by the organizers:*** Skipping PSA in the cleanup step is helpfull as quizalofop is an acidic pesticide with a tendency to interact with PSA. Please check if the losses of Nicarbazin in your pre-experiment were related to the use of carbon in dSPE. The low sensitivity of the peak that you mentioned has surely compromized precission, so that your final result might be a spurious outlier. Consider measuring quizalofop in the ESI-Neg. mode, where sensitivity is better.	E, G, L
73	41.5	–	The reason for our very high z-score was the analytical standard used. We buy custom standard mixtures in concentration of 100 µg/ml with approximately 30 pesticides in each. By mistake from the company the concentration of cyhalofop was wrong. We have bought a new standard of quizalofop and now the result is OK. ***Comments by the organizers:*** For an initial check of the pesticide concentration and stability of purchased mixtures the exchange of standards with other labs would be an option to consider.	E, L, O

Appendix 7 (cont.) Possible Reasons Reported for Poor Performance (ordered by z-scores)

Category of Errors

I: Transcription/Documentation/Communication/Calculation error
J: Result not or not properly corrected for recovery; Losses of analyte during analysis (e.g due to degradation or unfavorable partitioning)
K: EUPT-residue definition of the analyte was not followed (e.g. wrong components targeted)
L: Problem due to the presence of the analyte in the EUPT-blank material provided by the organizers
M: (Tentative) Assigned value is questionable
N: Portion to portion variability (small portion size and few repetitions)
O: Poor QC measures not triggering corrective actions to avoid FNs, FPs or strongly biased results
Adv1: Consider checking calculations
( ): Suspicions by participants, not sure, or explanation not logical

Quizalofop Assigned value: 0.171 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
81	-3.8	–	The initial data transmission (target pesticide list) is unintentional mistake. We analyse residues of Quizalafop-P-tefuryl and Quizalafop-ethyl as Partial legal residue definition analysed for Quizalafop. Our mistake was that we equate Quizalafop as Quizalafop (free acid). ***Comments by the organizers:*** This happend to several labs. Please carefully read the Targt Pesticide List (TPL) of each PT carefully as the residue definitions there may differ from the legal ones.	E, K
91	-3.8	–	This substance are not analysed because it is not included in our scope, and because using the GCMSMS the ester quizalfop ethyl are analyses and it is a mistake by us giving quizalofop free acid as analyzed ***Comments by the organizers:*** This happend to several labs. Please carefully read the Targt Pesticide List (TPL) of each PT, as the residue definitions there may differ from the legal ones.	E, K, M
98	-3.8	–	The problem was that we had a working solution of Quizalofop - Etil but not of the Quizalofop. All the standards of the different pesticides studied were checked and there weren't differences between old and new standards. ***Comments by the organizers:*** This happend to several labs. Please carefully read the Targt Pesticide List (TPL) of each PT carefully as the residue definitions there may differ from the legal ones.	E, K
125	3.3	–	No reasons provided.	–

Triclopyr Assigned value: 0.177 mg/kg

Lab-Code	z-score	Error Source localized?	Reason / Remarks	
2	5.1	(NO)	no experience for these compounds in this matrix ***Comments by the organizers:*** As you have submitted several strongly overestimated results out of the acceptable range, it would make sense, additionally checking if there is any systematic error in the way you conduct/calculate the standard addition approach. Please also consider checking the correctness of your standard solution.	D, E, L, O
14	-3.8	Yes	Out of our scope, careless mistake	C, D, E
118	-3.8	Yes	not analysed for, transcription error Comment by the Organizer: Following the rules in the General Protocol transcription errors cannot be taken into account. The result is still counted as a false negative.	(L), (M)

GENERAL PROTOCOL

for EU Proficiency Tests on 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, DG-SANTE[1] by the four European Union Reference Laboratories (EURLs) responsible for pesticide residues in food and feed. These EUPTs are directed at laboratories belonging to the Network[2] of National Reference Laboratories (NRLs) and Official Laboratories (OfLs) of the EU Member States. OfLs from EFTA countries and EU-Candidate countries are also welcome to participate in the EUPTs. OfLs from Third countries may be permitted to participate on a case-by-case basis.

The following four EURLs for pesticide residues were appointed by DG-SANTE based on regulation 882/2004/EC[3]:

- EURL for Fruits and Vegetables (EURL-FV),
- EURL for Cereals and Feedingstuffs (EURL-CF),
- EURL for Food of Animal Origin and Commodities with High Fat Content (EURL-AO) and
- EURL for pesticides requiring Single Residue Methods (EURL-SRM).

The aim of these EUPTs is to obtain information regarding the quality, accuracy and comparability of pesticide residue data in food and feed reported to the European Union within the framework of the national control programmes and the EU multiannual co-ordinated control programme[4]. Participating laboratories will be provided with an assessment of their analytical performance that

[1] DG-SANTÉ = European Commission, Health and Food Safety Directorate-General

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

[3] 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

[4] European Commission Proficiency Tests for Pesticide Residues in Fruits and Vegetables, Trends in Analytical Chemistry, 2010, 29 (1), 70 – 83.

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they can use to demonstrate their analytical performance and compare themselves with other participating laboratories.

EUPT-Organisers and Scientific Committee

EUPTs are organised by individual EURLs, or by more than one EURL, in joint collaboration.

An **Organising Team** is appointed by the EURL(s) in charge. This team is responsible for all administrative and technical matters concerning the organisation of the PT, e.g. the PT-announcement, production of Test Item and Blank Material, the undertaking of homogeneity and stability tests, packing and shipment of the Test Item and Blank Material, handling and evaluation of the results and method information submitted by the participants and the drafting of the preliminary and final reports.

To complement the internal expertise of the EURLs, a group of external consultants that form the **EUPT-Scientific Committee** (EUPT-SC)[5] has been established and approved by DG-SANTE. The EUPT-SC consists of expert scientists with many years of experience in PTs and/or pesticide residue analysis. The actual composition of the EUPT-SC, the affiliation of each member is shown on the EURL-Website. The members of the EUPT-SC will also be listed in the Specific Protocol and the Final Report of each EUPT.

The EUPT-SC is made up of the following two subgroups:

a) An independent **Quality Control Group** (EUPT-QCG) and

b) An **Advisory Group** (EUPT-AG).

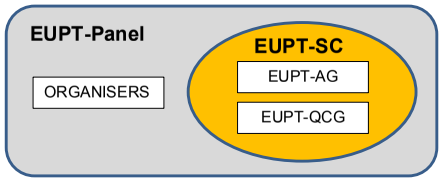
The EUPT-SC's role is to help the Organisers make decisions regarding the EUPT design: the selection of the commodity, the selection of pesticides to be included in the Target Pesticide List (see below), the establishment of the Minimum Required Reporting Levels (MRRLs), the statistical treatment and evaluation of participants results (in anonymous form), and the drafting and updating of documents such as the General and Specific PT Protocols and the Final EUPT-Reports.

The EUPT-QCG has the additional function of supervising the quality of EUPTs and of assisting the EURLs in confidential aspects such as the choice of the pesticides to be present in the Test Item and the concentrations at which they should be present.

[5] Link to the List of current members of the EUPT Scientific Committee: http://www.eurl-pesticides.eu/library/docs/allcrl/EUPT-SC.pdf

The EUPT-SC typically meets once a year, after the EUPTs of all four pesticide EURLs have been conducted, to discuss the evaluation of the EUPT-results and to consult with the EURLs in their decision making. Upcoming EUPTs are also planned during these meetings.

The EUPT-Organising Team and the EUPT-SC together form the **EUPT-Panel**.



The decisions of the EUPT-Panel will be documented.

This present EUPT General Protocol was jointly drafted by the EUPT-SC and the EURLs and was approved by DG-SANTE.

EUPT Participants

Within the European Union all NRLs operating in the same area as the organising EURL, as well as all OfLs whose scope overlaps with that of the EUPT, are legally obliged to participate in EUPTs. The legal obligation of NRLs and OfLs to participate in EUPTs arises from:

- Art. 28 of Reg. 396/2005/EC[6] (for all OfLs analysing for pesticide residues within the framework of official controls[7] of food or feed)
- Art. 33 of Reg. 882/2004/EC (for all NRLs)

The four EURLs will annually issue and distribute, via the EURL-website, a joint list of all OfLs that must participate in each of the EUPTs to be conducted within a given year. The list of obliged labs will be updated every year to take account of any changes in the lab profiles. Interim updates will be issued to eliminate any possible errors.

[6] 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.

[7] Official controls in the sense of Reg. 882/2004/EC, This includes labs involved in controls within the framework of national and/or EU-controlled programmes as well as labs involved in import controls according to Regulation 669/2009/EC.

NRLs are responsible for checking whether all relevant OfLs within their network are included in the list of obligated laboratories and whether the contact information and commodity-scopes are correct.

OfLs are furthermore urged to keep their own profiles within the EURL-DataPool up-to-date, especially their commodity and pesticide scopes and their contact information.

Labs that are obliged to participate in a given EUPT, and that are not able to participate, must provide the reasons for their non-participation without prejudice of any legal action taken against them for not participating. This also applies to any participating laboratories that then fail to report results.

Confidentiality and Communication

The proprietor of all EUPT data is DG-SANTE and as such has access to all information.

For each EUPT, the laboratories are given a unique code (lab code), initially only known to themselves and the Organisers. In the final EUPT-Report, the names of participating laboratories will not be linked to their laboratory codes. It should be noted, however, that the Organisers, at the request by DG-SANTE, may present the EUPT-results on a country-by-country basis. It may therefore be possible that a link between codes and laboratories could be made, especially for those countries where only one laboratory has participated. Furthermore, the EURLs reserve the right to share EUPT results and codes amongst themselves: for example, for the purpose of evaluating overall lab or country performance as requested by DG-SANTE.

As laid down in Regulation 882/2004, NRLs are responsible for evaluating and improving their own OfL-Network. On request from the NRLs, the EURLs will provide them with the PT-codes of the participating OfLs belonging to their OfL-Network. This will allow NRLs to follow the participation and performance of the laboratories within their network.

Communication between participating laboratories during the test on matters concerning a PT exercise is not permitted from the start of the PT exercise until the distribution of the preliminary report.

For each EUPT the organising EURL prepares a specific EUPT-Website where all relevant documents in their latest version are linked.

The official language used in all EUPTs is English.

Announcement / Invitation Letter

At least 3 months before the distribution of the Test Item the EURLs will publish an Announcement/Invitation letter on the EURL-web-portal and distribute it via e-mail to the NRL/OfL mailing list available to the EURLs. This letter will inform about the commodity to be used as Test Item, as well as links to the tentative EUPT-Target Pesticide List and the tentative EUPT-Calendar.

Target Pesticide List

This list contains all analytes (pesticides and metabolites) to be sought, along with the Minimum Required Reporting Levels (MRRLs) valid for the specific EUPT. The MRRLs are typically based upon the lowest MRLs found either in Regulation 396/2005/EC or Commission Directive 2006/125/EC (Baby Food Directive).

Labs must express their results as stated in the Target Pesticides List.

Specific Protocol

For each EUPT the organizing EURL will publish a Specific Protocol at least 2 weeks before the Test Item is distributed to the participating laboratories. The Specific Protocol will contain all the information previously included in the Invitation Letter but in its final version, information on payment and delivery, instructions on how to handle the Test Item upon receipt and on how to submit results, as well as any other relevant information.

Homogeneity of the Test Item

The Test Item will be tested for homogeneity typically before distribution to participants. The homogeneity tests involve the analysis of two replicate analytical portions, taken from at least ten randomly chosen units of treated Test Item. Both, sample preparation and measurements should be conducted in random order.

The homogeneity test data are statistically evaluated according to the International Harmonized Protocols published by ISO and IUPAC. The acceptance criterion for the Test Items to be sufficiently homogeneous for the Proficiency Test is that s_{sam}^2 is less than c with s_{sam} being the between-bottle sampling standard deviation and $c = F_1 \times \sigma_{all}^2 + F_2 \times s_{an}^2$. F_1 and F_2 are constants,

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with values of 1.88 and 1.01, respectively, if 10 samples are used. $\sigma_{all}^2 = 0.3 \times$ FFP-RSD[8] (FFP-RSD=0.25 × the mean of the homogeneity test), and s_{an} is the estimate of the analytical standard deviation.

The results of all homogeneity tests are presented to the EUPT-SC. In special cases where the above homogeneity test criteria are not met, the EUPT-SC considering all relevant aspects (e.g. the homogeneity results of other pesticides spiked at the same time, the overall distribution the participants' results, the analytical difficulties faced during the test, knowledge of the analytical behaviour of the pesticide question) may decide to overrule the test. The reasons of this overruling have to be transparently explained in the Final EUPT-Report.

Stability of the analytes contained in the Test Item

The Test Items will also be tested for stability - according to ISO 13528, Annex B. The time delay between the first and the last stability test must exceed the period of the EUPT-exercise. Typically the first analysis is carried out shortly before the shipment of the Test Items and the last one shortly after the deadline for submission of results. To better recognise trends and gain additional certainty one or more additional tests may be conducted by the Organisers. At least 6 sub-samples (analytical portions) should be analysed on each test day (e.g. 2 analytical portions withdrawn from three randomly chosen containers OR 6 portions withdrawn from a single container). In principle all pesticides contained in the Test Item should be checked for stability. However, in individual cases, where sufficient knowledge exists that the stability of a certain analyte is very unlikely to be significantly affected during storage (e.g. based on experience from past stability tests or knowledge of its physicochemical properties), the Organisers, after consultation with the EUPT-QCG, may decide to omit a specific stability test. The EUPT-SC will finally decide whether analytes for which the stability test was not undertaken will be included in the final report, considering all relevant aspects such as the distribution of the participant's results (CV*).

A pesticide is considered to be adequately stable if $|y_i - y| \leq 0.3 \times \sigma_{pt}$, where y_i the mean value of the last period of the stability test, y is the mean value of the first period of the stability test and σ_{pt} the standard deviation used for proficiency assessment (typically 25% of the assigned value).

The results of all stability tests are presented to the EUPT-SC. In special cases where the above stability test criteria are not met, the EUPT-SC considering all relevant aspects (e.g. the past experience with the stability of the compound, the overall distribution the participants' results, the

[8] FFP-RSD = fit for purpose relative standard deviation, see also p. 11.

analytical difficulties faced during the test, knowledge about the analytical behaviour of the pesticide question) may decide to overrule the test. The reasons of this overruling will be transparently explained in the Final EUPT-Report.

The Organisers may also decide to conduct additional stability tests at different storage conditions than those recommended to the participants e.g. at ambient temperature.

Considering knowledge about the expected susceptibility of pesticides in the Test Item to possible losses, the Organisers will chose the shipment conditions to be such that pesticide losses are minimised (e.g. shipment of frozen samples, addition of dry ice). As shipment time can differ between labs/countries it is recommended that the Organisers conduct additional stability tests at conditions simulating shipment. Should critical losses be detected for certain pesticides the EUPT-SC will be informed (or the EUPT-QCG before or during the test). Case-by-case decisions may be taken considering all relevant aspects including the shipment time of the samples to each laboratory.

Methodologies to be used by the participants

Participating laboratories are instructed to use the analytical procedure(s) that they would routinely employ in official control activities (monitoring etc.). Where an analytical method has not yet been established routinely this should be stated.

General procedures for reporting results

Participating laboratories are responsible for reporting their own quantitative results to the Organiser within the stipulated deadline. Any pesticide that was targeted by a participating laboratory should be reported as "analysed". Each laboratory will be able to report only one result for each analyte detected in the Test Item. The concentrations of the pesticides detected should be expressed in 'mg/kg' unless indicated otherwise in the specific protocol.

The Test Item is intentionally treated with pesticides whereas the Blank Material is analysed to ensure that it does not contain any of the pesticides in the Target Pesticides List, at or above, the specified MRRLs. Both the Test Item and Blank Material have to be analysed by the participating laboratories and any pesticide detected in them must be reported.

Correction of results for recovery

According to the Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed[9], it is common practice that pesticide analysis results are not corrected for recovery, but may be corrected if the average recovery is significantly different from 100 % (typically if outside the 70 – 120 % range, but also exhibiting good precision). Other approaches for recovery correction explicitly allowed in the SANTE document are the use of stable isotope labelled analogues of the target analytes used as Internal Standards (ISTDs), the 'procedural calibration' approach as well as the approach of 'standard addition' with additions of analyte(s) being made to analytical portions. Where reported residue data have been automatically adjusted for recovery by the method, or have subsequently been adjusted using a recovery factor, this must be indicated on the specific field of the 'Result Submission Form'. Results may be corrected for recovery only in cases where this correction is applied in routine practice (including cases of MRL-violations). Laboratories are required to report whether their results were adjusted for recovery and, if a recovery factor was used, the recovery (in percentage) must also be reported. No recovery data are required where correction for recovery is automatic by using the 'standard addition approach, or isotopically-labelled internal standards (in both cases with spiking into the Test Item at the beginning of the extraction procedures). In these cases, the laboratories should report the actual approach that was followed.

Methodology information

All laboratories are requested to provide information on the analytical method(s) they have used. A compilation of the methodology information submitted by all participants is presented in an Annex of the final report or in a separate report. Where necessary the methods are evaluated and discussed, especially in those cases where the result distribution is not unimodal or very broad (e.g. CV* > 35 %). If no sufficient information on the methodology used is provided, the Organiser reserves the right not to accept the analytical results reported by the participants concerned.

[9] Document N° SANTE/11945/2015; Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed

Results evaluation

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

– ***False Positive results***

These are results of pesticides from the Target Pesticides List, that are reported, at or above, their respective MRRL although they were: (i) not detected by the Organiser, even after repeated analyses, and/or (ii) not detected by the overwhelming majority (e.g. > 95 %) of the participating laboratories that had targeted the specific pesticides. In certain instances, case-by-case decisions by the EUPT-Panel may be necessary.

Any results reported lower than the MRRL will not be considered as false positives, even though these results should not have been reported.

– ***False Negative results***

These are results for pesticides reported by the laboratories as 'analysed' but without reporting numerical values although they were: a) used by the Organiser to treat the Test Item and b) detected by the Organiser as well as the majority of the participants that had targeted these specific pesticides at or above the respective MRRLs. Results reported as '< RL' (RL= Reporting Limit of the laboratory) will be considered as not detected and will be judged as false negatives. In certain instances, case-by-case decisions by the EUPT-Panel may be necessary.

In cases of the assigned value being less than a factor of 4 times the MRRL, false negatives will typically not be assigned. The EUPT-Panel may decide to take case-by-case decisions in this respect after considering all relevant factors such as the result distribution and the reporting limits of the affected labs.

– ***Estimation of the assigned value (x_{pt})***

In order to minimise the influence of out-lying results on the statistical evaluation, the assigned value x_{pt} (= consensus concentration) will typically be estimated using robust estimate of the participant's mean (x^*) as described in ISO 13528:2015[10]. In special justifiable cases, the EUPT-Panel may decide to eliminate certain results traceably associated with gross errors (see "Omission or Exclusion of results" below) or to use only the results of a subgroup consisting of laboratories that have repeatedly demonstrated good performance for the specific compound in the past.

[10] DIN ISO 13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons, International Organization for Standardization. Therein a specific robust method for determination of the consensus mean and standard deviation without the need for removal of deviating results is described (Algorithm A in Annex C).

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– ***Omission or Exclusion of results***

Before estimating the assigned value results associated with obvious mistakes have to be examined to decide whether they should be removed from the population. Such gross errors may include incorrect recording (e.g. due to transcription errors by the participant, decimal point faults or transposed digits, incorrect unit), calculation errors (e.g. missing factors), analysis of a wrong sample/extract (e.g. a spiked blank), use of wrong concentrations of standard solutions, incorrect data processing (e.g. integration of wrong peak), major deviations from the analytical procedure, inappropriate storage or transport conditions (in case of susceptible compounds), and the use of inappropriate procedures that demonstrably lead to significantly biased results (e.g. due to degradation or incomplete extraction). Where the Organisers (e.g. after the publication of the preliminary report) receive information of such gross errors, having a significant impact on a generated result, the affected results will be examined on a case-by-case basis to decide whether, or not, they should be excluded from the population used for robust statistics. Results may also be omitted e.g. if an inappropriate method has been used even if they are not outliers. All decisions to omit/exclude results will be discussed with the EUPT-SC and the reasoning for the omission of each result clearly stated in the final EUPT-Report. However, z scores will be calculated for all results irrespective of the fact that they were omitted from the calculation of the assigned value.

Omitted results might be interesting as they might give indications about possible source(s) of errors. The Organisers will thus ask the relevant lab(s) to provide feedback on possible sources of errors (see also "follow-up activities").

Uncertainty of the assigned value

The uncertainty of the assigned values $u(x_{pt})$ is calculated according to ISO 13528:2015 as:

$$u\left(x_{pt}\right) = 1{,}25 \times \frac{s^*}{\sqrt{p}}$$

where s^* is the robust standard deviation and p is the number of results.

In certain cases and considering all relevant factors (e.g. the result distribution, multimodality), the number of submitted results, information regarding analyte homogeneity/stability, information regarding the use of methodologies that might produce a bias that were used by the participants), the EUPT-Panel may consider the assigned value of a specific analyte to be too uncertain and decide that the results should not be evaluated, or only evaluated for informative purposes. The provisions of ISO 13528:2015 concerning the uncertainty of the assigned value will be taken into account.

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

The target standard deviation of the assigned value ($\mathrm{FFP}\text{-}\sigma_{pt}$) will be calculated using a Fit-For-Purpose approach with a fixed Relative Standard Deviation (FFP-RSD) of 25% as follows:

$$\mathrm{FFP}\text{-}\sigma_{pt} = 0.25 \times x_{pt}$$

The percentage FFP-RSD is set at 25% based on experience from results of previous EUPTs[11]. 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.

For informative purposes the robust relative standard deviation (CV^*) is calculated according to ISO 13528:2015; Chapter 7.7 (Consensus value from participant results) following Algorithm A in Annex C.

– ***z scores***

This parameter is calculated using the following formula:

$$z_i = \frac{(x_i - x_{pt})}{FFP\text{-}\sigma_{pt}}$$

where x_i is the value reported by the laboratory, x_{pt} is the assigned value, and $\mathrm{FFP}\text{-}\sigma_{pt}$ is the standard deviation using FFP approach. Z scores will be rounded to one decimal place. For the calculation of combined z scores (see below) the original z scores will be used and rounded to one decimal place after calculation.

[11] Comparative Study of the Main Top-down Approaches for the Estimation of Measurement Uncertainty in Multiresidue Analysis of Pesticides in Fruits and Vegetables. J. Agric. Food Chem., 2011, 59(14), 7609-7619.

Any z scores > 5 will be typically reported as '> 5' and a value of '5' will be used to calculate combined z scores (see below).

Z scores will be interpreted in the following way, as is set in the ISO 17043:2010[12]:

$\lvert z \rvert \leq 2.0$	Acceptable
$2.0 < \lvert z \rvert < 3.0$	Questionable
$\lvert z \rvert \geq 3.0$	Unacceptable

For results considered as 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 decide whether, or not, these values should appear in the z score histograms.

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

The EUPT-Panel will decide if and how to classify the laboratories into two categories - A or B. Currently, laboratories that are able to analyse at least 90% of the compulsory pesticides in the target pesticides list, have correctly detected and quantified a sufficiently high percentage of the pesticides present in the Test Item (at least 90 %) and reported no false positives will have demonstrated 'sufficient scope' and can therefore be classified into Category A. For the 90% criterion the number of pesticides needed to be correctly analysed to have sufficient scope will be calculated by multiplying the number of compulsory pesticides from the Target Pesticides List by 0.9 and rounding to the nearest full number with 0.5 decimals being rounded downwards (see some examples in Table 1).

Table 1. No. of pesticides from the Target Pesticides List needed to be targeted or pesticides present in the Test Item that need to be correctly detected and quantified to have sufficient scope.

No. of compulsory pesticides present in the Test Item / Target Pesticides List (N)	90 %	No. of pesticides needed to be correctly detected and quantified / targeted to have sufficient scope (n)	n
3	2.7	3	N
4	3.6	4	
5	4.5	4	N - 1
6	5.4	5	
7	6.3	6	
8	7.2	7	

[12] ISO/IEC 17043:2010. Conformity assessment – General requirements for proficiency testing

No. of compulsory pesticides present in the Test Item / Target Pesticides List (N)	90 %	No. of pesticides needed to be correctly detected and quantified / targeted to have sufficient scope (n)	n
9	8.1	8	
10	9.0	9	
11	9.9	10	
12	10.8	11	
13	11.7	12	
14	12.6	13	
15	13.5	13	
16	14.4	14	
17	15.3	15	
18	16.2	16	
19	17.1	17	N - 2
20	18	18	
21	18.9	19	
22	19.8	20	
23	20.7	21	
24	21.6	22	
25	22.5	22	N - 3
26	23.4	23	

– ***Overall performance of laboratories - combined z scores***

For evaluation of the overall performance of laboratories within Category A, the Average of the Squared z Score (AZ^2)[13,14] (see below) will be used. The AZ^2 is calculated as follows:

$$AZ^2 = \frac{\sum_{i=1}^{n} z_i^2}{n}$$

Where n is the number of z scores to be considered in the calculation. In the calculation of the AZ^2, z scores higher than 5 will be classified as 5. Based on the AZ^2 achieved, the laboratories are classified as follows:

$AZ^2 \leq 2.0$	Good
$2.0 < AZ^2 < 3.0$	Satisfactory
$AZ^2 \geq 3.0$	Unsatisfactory

[13] Formerly named "Sum of squared z scores (SZ^2)"

[14] Laboratory assessment by combined z score values in proficiency tests: experience gained through the EUPT for pesticide residues in fruits and vegetables. Anal. Bioanal. Chem., 2010, 397, 3061–3070.

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6th Edition: Revised 8th February, 2016

Combined z scores are considered to be of lesser importance than the individual z scores. The EUPT-Panel retains the right not to calculate AZ^2 if it is considered as not being useful or if the number of results reported by any participant is considered to be too low.

In the case of EUPT-SRMs, where only a few results per lab may be available, the Average of the Absolute z scores (AAZ) may be calculated for informative purposes, but only for labs that have reported enough results to obtain 5 or more z scores. For the calculation of the AAZ, z scores higher than 5 will also be classified as 5.

Laboratories within Category B will be ranked according to the total number of pesticides that they correctly reported to be present in the Test Item. The number of acceptable z scores achieved will be presented, too. The EURL-Panel retains the right to calculate combined z scores (see above) also for labs within Category B, e.g. for informative purposes, provided that a minimum number of results (z scores) have been reported.

Publication of results

The EURLs will publish a preliminary report, containing tentative assigned values and z score values for all pesticides present in the Test Item, within 2 months of the deadline for result submission.

The Final EUPT Report will be published after the EUPT-Panel has discussed the results. Taking into account that the EUPT-Panel meets normally only once a year (typically in late summer or autumn) to discuss the results of all EUPTs organised by the EURLs earlier in the year, the final report may be published up to 10 months after the deadline for results submission.

Certificates of participation

Together with the Final EUPT-Report, the EURL Organiser will deliver a Certificate of Participation to each participating laboratory showing the z scores achieved for each individual pesticide, the combined z scores calculated (if any), and the classification into Category A or B.

Feedback

At any time before, during or after the PT participants have the possibility to contact the Organisers and make suggestions or indicate errors. After the distribution of the Final EUPT-Report, participating laboratories will be given the opportunity to give their feedback to the Organisers and make suggestions for future improvements.

www.eurl-pesticides.eu

Correction of errors

Should errors be discovered in any of the documents issued prior to the EUPT (Calendar, Target Pesticides List, Specific Protocol, General Protocol) the corrected documents will be uploaded onto the website and in the case of substantial errors the participants will be informed. **Before starting the exercise participants should make sure to download the latest version of these documents.**

If substantial errors are discovered in the Preliminary EUPT-Report the Organisers will distribute a new corrected version, where it will be stated that the previous version is no longer valid.

Where substantial errors are discovered in the Final EUPT-Report the EUPT-Panel will decide whether a corrigendum will be issued and how this should look. The online version of the final report will be replaced by the new one and all affected labs will be contacted.

Where errors are discovered in EUPT-Certificates the relevant laboratories will be sent new corrected ones. Where necessary the laboratories will be asked to return the old ones.

Follow-up activities

Laboratories are expected to undertake follow-up activities to trace back the sources of erroneous or strongly deviating results (typically those with $|z| > 2.0$) - including all false positives. Even results within $|z| \leq 2.0$ may have to be checked if there is indications of a significant positive or negative bias.

Upon request, the laboratory's corresponding NRL and EURL are to be informed of the outcome of any investigative activities for false positives, false negatives and for results with $|z| \geq 3.0$. Concerning z scores between 2.0 and 3.0 the communication of the outcome of traceability activities is optional but highly encouraged where the source of deviation could be identified and could be of interest to other labs.

According to instructions from DG-SANTE, the "Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with EU Reference Laboratories (EURLs) activities" is to be followed.

NRLs will be considered as **underperforming in relation to scope** if in two EUPTs of the last four EUPTs falling within their responsibility area if they: a) haven't participated, or b) targeted less than 90% of the compulsory pesticides in the target lists (80% for SRM-compounds), or c) detected less than 90% of the compulsory compounds present in the test items (80% for SRM-compounds).

Additionally, NRLs that obtained AZ^2 higher than 3 in two consecutive EUPTs of the last four EUPTs, will be considered as **underperforming in accuracy**. A two-step protocol established by DG-SANTE will be applied as soon as underperformance of an NRL is detected[15]:

Phase 1:

- Identifying the origin of the bad results (failure in EUPTs).
- Actions: On the spot visits and training if necessary and repetition of the comparative test if feasible and close the assessment of results by the EURL.

Phase 2:

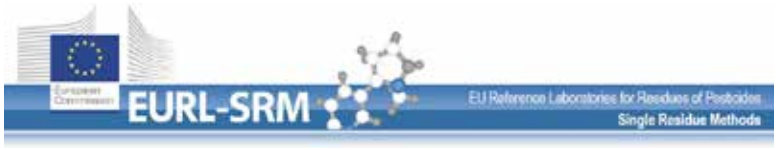
- If the results still reveal underperformance the Commission shall be informed officially by the EURL including a report of the main findings and corrective actions.
- The Commission shall inform the Competent Authority and require that appropriate actions are taken.

Underperformance rules for the OfLs will be established at a later stage.

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.

[15] Article 32 of the Regulation 882/2004



SPECIFIC PROTOCOL

for the 11th EU Proficiency Test
on Pesticides requiring Single Residue Methods
EUPT – SRM11 (2016)
(update on 27 April, 2016)

Introduction

This protocol is complementary to the "**General Protocol for EU Proficiency Tests for Pesticide Residues in Food and Feed**" covering all EUPTs.
The EUPT-SRM11 is organised by the EU Reference Laboratory for pesticides requiring Single Residue Methods (EURL–SRM) in cooperation with the EU Reference Laboratory for pesticide residues in Fruits and Vegetables (EURL-FV). Both EURLs are **accredited according to ISO 17043** as providers of proficiency tests.
The EUPT-SRM11 deals with the analysis of SRM-pesticides in spinach homogenate and is to be performed by all National Reference Laboratories for Single Residue Methods (NRL-SRMs) as well as by all official EU laboratories (OfLs) involved in official pesticide residue controls as far as their scope overlaps with that of the EUPT-SRM11. This includes laboratories involved in import control within the frame of Reg. 669/2009/EC. A special **EUPT-SRM11-Website** containing links to the most important documents of relevance was constructed.

Considering only the commodity scope (not the pesticide scope) of OfLs a **Tentative List of obliged labs for EUPTs in 2016** has been prepared by the EURLs and published on the **CIRCA BC-Platform**. As far as the EUPT-SRM11 is concerned, all OfLs analysing pesticides in fruits and vegetables were considered as obliged. The initial list has been updated considering all input received by the NRL-SRMs and the OfLs. OfLs listed as "obliged to participate in the EUPT-SRM11" but not intending to participate had to state their reasons for non-participation during the online registration the EUPT-SRM11 from 8 February till 11 March, 2016.

Test Item and Blank Material

This EUPT deals with the analysis of pesticide residues in **Spinach Homogenate**.

Participants will receive two bottles containing:

1) ca. 300 g **Test Item (with incurred or spiked analytes)**, containing pesticides from the **Target Pesticides List.**
2) ca. 300 g **Blank Material**, that can be used for recovery experiments as well as for the preparation of matrix-matched calibration standards

Using randomly chosen bottles, the Organizers will check the Test Item for sufficient homogeneity and for the stability of the pesticides contained over the period of the exercise. The Blank Material will be also checked to prove that none of the pesticides on the Target pesticides List is contained at relevant levels.

Target Analytes and MRRLs

The Test Item will contain several pesticides from the **EUPT-SRM11 Target Pesticides List.** Laboratories should read this list carefully, as it shows how the residues are expected to be reported as well as the **Minimum Required Reporting Levels (MRRLs)**. The MRRL values will be used to help identify false positive and false negative results and for the calculation of z-scores for false negatives. **Make sure to download the latest version of the** EUPT-SRM11 Target Pesticides List **before starting with analysis and reporting of results**.
It should not be assumed that only pesticides registered for use in spinach are present in the Test Item.

Shipment of Test Item

Test item and Blank Material are planned to be shipped on 4 April, 2016 to laboratories in Spain and Portugal and on 5 April, 2016 to laboratories in all other countries.
Frozen Test Item and Blank Material will be packed in thermo-boxes together with dry ice and shipped to the participants. Prior to shipment a reminder will be sent to the participating laboratories by e-mail.

Laboratories must make their own arrangements for the receipt of the package. They should **inform the Organisers of any public holidays in their country/city during the week of the shipment, and must make the necessary arrangements to receive the shipment, even if the laboratory is closed.**
Should any complications during shipment, delivery or the customs be expected, the participating laboratories should provide the Organizers with contact information of possible contact persons of the lab (e.g. mobile phone numbers) as well as instructions in local language explaining the need to keep the package in freezer during delay in transit. This information will be attached to the package.

Instructions on handling the Test Item

Once received, the Test Item should be stored deep frozen (at -18°C or lower) until analysis in order to avoid any possible deterioration/spoilage and to minimize pesticide degradation.

Before analytical portions are taken for analysis, it is recommended to mix the material thoroughly in its entirety. While mixing, try to keep temperatures as low as possible to avoid the loss of unstable pesticides.

Participating laboratories should use their routine standard operating procedures for extraction, clean-up and analytical measurement as well as their own reference standards for identification and quantification purposes. Laboratories may also employ methods not yet implemented routinely for example if they are in the test-phase of implementing them. In this case the limited experience and the non-inclusion of the analyte in the routine scope should be indicated in the **result submission website**.

The homogeneity tests will be conducted using 10 g analytical portions of Test Item for all analytes except for dithiocarbamates where expectedly 20 g will be used. Please note: Sub-sampling variability increases with decreasing analytical portion size, and sufficient homogeneity can only be guaranteed for sample portions ≥ 10 g.

Results submission website

Sample receipt acknowledgement, analytical results and method information are to be submitted via the following website: **EUPT-SRM11 result submission website.**

- **Sub-Page 0 (Sample receipt acknowledgement), accessible from 5 April, 2016**
- **Sub-Pages 1-3 (analytical results and method information) accessible from 7 April till 20 May, 2016.**

To access the data-submission forms participants must use their unique login data (username and password) that will be provided to them before sample shipment. The unique EUPT-SRM11 lab-codes will be provided in a separate e-mail.

The deadline for result submission is 20 May, 2016 at 16 h (CEST).

- Sample Receipt and Acceptance (Sub-Page 0)

Once the laboratory has received the Test Items it must report to the organiser via the **EUPT-SRM11** Result Submission Website (sub-page 0) the date of receipt, the condition of the Test Item, and its acceptance. For laboratories in the EU- and EFTA countries and EU candidate countries, the deadline for acceptance is the 8 April, 2016. If a laboratory does not respond by this deadline, the Organisers will assume that Test Item and Blank Material have been received and accepted.
If any participants have not received the Test Items by the 8 April in the afternoon, they must inform the Organiser via e-mail (EURL-SRM@cvuas.bwl.de**). The Organiser will consult the shipping company to localize the package and decide on further actions including new shipment, if necessary**.
Selected participants might be asked to provide information on the condition of the Test Item upon receipt (e.g. core temperature of Test Item etc.).

- Reporting qualitative and quantitative Results (Sub-Page 1 and 2)

To report their results, laboratories must access the **EUPT-SRM11 Result Submission Website**.
All results must be reported on this website by 20 May, 2016 at 16 h (CEST). The website will not be accessible after this deadline, and all results submitted afterwards will not be accepted.

Before entering the results, please study the Target Pesticide List carefully, in particular the residue definitions, which are not necessarily given on the Result Submission Website.

The following fields will be available for reporting the quantitative results:

- "**Concentration in mg/kg":** the pesticide concentrations that would be reported in routine work. Recovery-corrected results should be reported only where this reflects the routine lab's procedure; otherwise the non-recovery-corrected result should be reported. Results should not be reported where a pesticide was not detected, or was detected below the RL (Reporting Limit) of the laboratory or the MRRL. Results reported as "< RL" or "< #,# mg/kg" will be considered as „Not Detected".

  The residue levels of the pesticides must be reported in mg/kg using the following **significant figures**:
  - Levels <0.010 mg/kg to be expressed to 2 significant figures, e.g. 0.0058 mg/kg;
  - Levels ≥ 0.010 mg/kg to be expressed to 3 significant figures, e.g. 0.156, 1.64, 10.3 mg/kg.

- **"Conc. in blank in mg/kg":** concentration values of any pesticides from the Target Pesticide List determined in the Blank Material (even at levels below the MRRL).

- **"Experience with this compound":** Use the dropdown-menu to indicate for how many years you have been analysing for each compound using the method applied in this EUPT.

- **"Did you use an Internal standard (IS)":** Please only choose **one of the three "Yes" options if the IS was used for calculation of the result of the target analyte (not merely for quality control purposes**).
  Please choose "No" if the IS was only used for quality control purposes and not for the calculation of the target analyte result.
  - ***Yes, Isotope labelled analogue of target analyte (ILIS)*** if you have employed a real ILIS as defined in the SANTE document (e.g. Ethephon D_4 for Ethephon)
  - ***Yes, other IS*** if you have employed a compound other than ILIS as internal standard (e.g. MCPA or MCPA D_3 for 2,4-D or TPP, Chlorpyrifos D_{10}, Nicarbazin)

- **"At what stage of the procedure did you employ the IS":**
  - ***at the beginning*** if the IS was added to the sample portion directly or shortly following extraction solvent addition
  - ***to an aliquot of the final extract*** if the IS was added to an isolated aliquot of the final extract
  - ***at an intermediate stage*** if the IS was added at any stage in-between the above two

- **"Other means of recovery or matrix-effect correction used"**
  - ***None***
  - ***Procedural calibration***
  - ***Standard addition to sample portions***
  - ***Standard addition to extract aliquots***
  - ***Matrix-matched calibration***
  - ***Use of a recovery factor (please indicate recovery figure)***
  - ***Other (please specify the details)***

- **"Recovery figure (in %)":** Here laboratories can report any recovery figures (in %) obtained for the analyte in question. If a recovery factor was used to correct the result for recovery, the recovery figure (in %) used for the calculation MUST be reported.

- **Recovery details:** Please indicate here concisely how the recovery experiment(s) was/were conducted, e.g. spiking level, spiked compound.

  Additional information will be asked in separate fields.

- Reporting Information on Analytical Methodology (Sub-Page 3)

In **sub-page 3 of** the "**EUPT-SRM11 Result Submission Website"** the participating laboratories must provide complete information on the analytical method(s) applied to **all pesticides which were analysed, irrespective of whether they were detected or not**.

The participating laboratories are urged to thoroughly fill-in all requested information and control it carefully in order to minimize the administrative burden of collecting and correcting it a posteriori.

If no sufficient information on the methodology used is provided, the Organisers reserve the right not to accept the analytical results reported by the participant or to refuse participation is future EUPT-SRMs.

Subcontracting

The following task was subcontracted to the EURL-FV, Almería, Spain:

a) Production, preparation and shipment of Test Items and Blank Materials for the EUPT-SRM11

The following task was subcontracted to the EURL-CF, Søborg, Denmark:

a) Administration of EUPT-SRM11 registration and result submission website

Follow-up actions

After the distribution of the EUPT-SRM11 Preliminary Report , laboratories with poor results (high absolute z-scores, false negatives or false positives) will be asked to provide information concerning the reasons for this and possible corrective actions. This information will be forwarded to the corresponding NRL-SRMs upon request. All EUPT-SRM11-participants are welcome to ask the EURL-SRM for technical assistance.
According to instructions by DG-SANTE, the "**Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with Community reference laboratories (CRLs) activities**" will be followed by NRLs.

Documents

All documents related to the EUPT–SRM11 can be found in the **EURL-Document Repository (CIRCA/FIS-VL).** Links to the documents can also be found in the **EUPT-SRM11 Website.**
For further information please contact the organizers **EURL-SRM@cvuas.bwl.de**
Please check the **EUPT-SRM11 Website** before starting with the analysis to **make sure that you have the latest version of all documents available**. In case of major changes the participants will be informed via e-mail.

Participation fees and payment details

To cover the costs of production, handling and shipment of the PT-Materials the following fees will be charged for one unit of the PT-Material to the participating laboratories:

- OfLs (including NRLs) from EU countries, EU-candidate countries and EFTA countries: 230 €
- Labs based in third countries: 350 €

An invoice issued for the "invoice address" stated in the registration form will be sent to the e-mail address(es) responsible for the PT. Should the payment being take care of by another department/institution the participating laboratories are requested to forward the invoice accordingly. Details of payment will be given in the invoices.

Payment is expected to be made within 30 days upon the date of shipment.
If for any reason payment cannot be carried out before this date, please contact the Organizer to give explanations.
If no payment or no proof of payment is received and no explanation is given to the Organizers, the Organizers reserve the right not to exclude the results of the concerned laboratories from the Final EUPT-Report or to refuse participation in future EUPT-SRMs.

Please note:
The bank account of EURL-SRM has been changed since the end of October 2013! Please ask your financial department to update the bank account of EURL-SRM!

NEW Bank Details:

Bank account holder:	**Landesoberkasse Baden Wuerttemberg**
Bank Name :	**Baden Wuerttembergische Bank**
IBAN:	**DE 02 6005 0101 7495 5301 02**
BIC/SWIFT:	**SOLADESTXXX**
Payee identification text:	***See invoice (important and MUST be indicated!)***
VAT of CVUA Stuttgart	**DE 811 600 510**

To facilitate tracking of money transfer the special **payee identification text (= invoice number) as shown in the invoice MUST be indicated in the remittance.**

More details for bank-remittance will be given in the invoices.

Calendar of EUPT-SRM11

(please see: http://www.eurl-pesticides.eu/userfiles/file//EUPT-SRM11_Calendar.pdf)

Target Pesticides List of EUPT-SRM11

(please see: http://www.eurl-pesticides.eu/userfiles/file//EUPT-SRM11_TargetPesticideList.pdf)

Contact information

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Carmelo Rodríguez	University of Almería, Spain

Quality Control Group

Antonio Valverde	University of Almería, ES
Stewart Reynolds	Food and Environmental Research Agency, York, UK (retired in 2015)

CALENDAR for the EUPT – SRM11

Spinach Homogenate

(update on 13 April, 2016)

Activity	Who ?	Dates
Opening of the **EUPT-SRM11 Website** with links to all relevant documents (**List of obliged labs, Calendar, Target Pesticides List, General Protocol**)	EURL-SRM	Jan. 2016
Registration via "**EUPT-Registration Website**" (Note: obliged OfLs MUST enter this Website and either register or give **explanations for non-participation**)	**- Obliged OfLs from EU-MSs** **- OfLs from EFTA Countries** **- OfLs from EU-candidate C.** **- Labs from 3rd Countries**	**8 Feb. - 11 March 2016**
Dispatch of **EUPT-SRM11-Specific Protocol**	EURL-SRM	March 2016
Preparation of EUPT-SRM11-Test Item (preliminary tests Spiking / Homogenization)	EURL-SRM	Jan. – March 2016
Homogeneity Tests	EURL-SRM	March – Apr. 2016
Stability Tests	EURL-SRM	March – May 2016
Shipment of EUPT-SRM11 Test Item (+reminder of upcoming parcel arrival)	EURL-SRM	**4 Apr. 2016 (ES, PT)** **5 Apr. 2016 (all other countries)**
Confirmation of sample Receipt and acceptance via "**EUPT-SRM11 Result Submission Website**", (Sub-Page 0)	**Participating Labs**	**within 48 h of receipt**
Result Submission **(Pesticide scope, Results, Method Info)** in "**EUPT-SRM11 Result Submission Website**", (Sub-Pages 1 – 3)	**Participating Labs**	**7 Apr. – 20 May 2016**
Preliminary Report (only compilation of results)	EURL-SRM	June 2016
EUPT Evaluation Meeting	EUPT-SC, DG-SANTE	-
Survey to collect reasons for underperformance and missing information on methods	EURL-SRM / **Participating Labs**	June 2016
Final Report	EURL-SRM	Dec. 2016

REMARK: Please note that the dates mentioned above may be subject to minor **changes**. In the case of changes the participants will be informed via e-mail. But still **please check periodically our website for possible updates** in case the email does not get through to you.
Contact: **eurl-srm@cvuas.bwl.de**

The EUPT-SRM Team

TARGET PESTICIDE LIST

for the EUPT – SRM11 2016, Spinach Homogenate

update on 30.03.2016

Compounds Potentially Present in Test Item	In MACP	MRRL (mg/kg)
Compulsory Compounds (will be considered in Category A/B classification)		
2,4-D (free acid*)	MACP-Reg.	0.01
Cyromazine	MACP-Reg.	0.01
Dithiocarbamates (expressed as CS_2)	MACP-Reg.	0.03
Dodine	MACP-Reg.	0.01
Ethephon	MACP-Reg.	0.02
Fluazifop (free acid*)	MACP-Reg.	0.01
Glyphosate	MACP-Reg.	0.03
Haloxyfop (free acid*)	MACP-Reg.	0.01
TFNA (metabolite of flonicamid)	MACP-Reg.	0.01
TFNG (metabolite of flonicamid)	MACP-Reg.	0.01
Tolylfluanid (parent only)	MACP-Reg.	0.01
Optional Compounds (will NOT be considered in Category A/B classification)		
BAC-C10 (expressed as chloride salt)	MACP-WD	0.02
BAC-C12 (expressed as chloride salt)	MACP-WD	0.02
BAC-C14 (expressed as chloride salt)	MACP-WD	0.02
BAC-C16 (expressed as chloride salt)	MACP-WD	0.02
BAC-C18 (expressed as chloride salt)	MACP-WD	0.02
Chlorate (anion)	MACP-WD	0.02
DDAC-C10 (expressed as chloride salt)	MACP-WD	0.01
Dithianon *SHIFT FROM COMPULSORY TO OPTIONAL*	MACP-Reg.	0.01
Fosetyl	MACP-WD	0.02
Phosphonic acid	MACP-WD	0.05
MCPA (free acid*)	MACP-WD	0.01
MCPB (free acid*)	MACP-WD	0.01
Perchlorate (anion) *NEW!*	–	0.02
Pymetrozine *NEW!*	MACP-Reg.	0.01
Quizalofop (free acid*)	MACP-WD	0.01
Triclopyr	MACP-WD	0.01

MACP = EU Multi-Annual Coordinated Control Program;
MACP-Reg.: MACP Regulation; MACP-WD: MACP Working Document
* no hydrolysis

Note: This document may be subject to minor changes. In case of significant changes the organizers will send e-mails. In any case please check our website periodically to make sure you are using the latest available version.

For any further clarification don't hesitate to contact us under **eurl-srm@cvuas.bwl.de**
The EUPT-SRM11 Organising Team