European Commission

EURL-SRM

EU Reference Laboratories for Residues of Pesticides

Single Residue Methods

EU Proficiency Test on the Analysis of Spiked and Incurred Pesticides in Milled Dry Lentils

EUPT–SRM7

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Final Report

Chemisches und Veterinär-untersuchungsamt Stuttgart

cvua STUTTGART

EU PROFICIENCY TEST
EUPT-SRM7, 2012

Residues of Pesticides requiring Single Residue Methods

Test Item:
Milled Dry Lentils

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. These Proficiency Tests (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 programmes as well as national monitoring programmes. By participating in PTs laboratories can assess and at the same time demonstrate their analytical performance. The competitive nature of EUPTs and the attention to detail paid when analysing PT test items, together with the need to identify errors and take corrective actions in cases of underperformance, typically lead to improvements in the quality of data generated by participating laboratories.

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 Proficiency Tests (EUPTs) for pesticide residues. Each official laboratory 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 EUPT. Three of these 7 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) and apple purée (EUPT-SRM5, 2010) as selected test items; the other three were conducted in collaboration with the EURL for Pesticide Residues in Cereals and Feeding Stuff (EURL-CF) with wheat flour (EURL-C1/SRM2, 2007), oat flour (EURL-C3/SRM4, 2009) and rice flour (EURL-C5/SRM6, 2011) as the test items. The EUPT-SRM7 presented here was based on milled dry lentils.

Participation in the EUPT-SRM7 was mandatory for all National Reference Laboratories for pesticides requiring Single Residue Methods (NRL-SRMs) and for all Official Laboratories (OfLs) analysing pesticide residues in vegetables, cereals or feed within the framework of national and EU official control programmes. Official laboratories from EFTA countries (Iceland, Norway and Switzerland) also contributing data to the EU-coordinated multiannual control programme (MACP), as well as official laboratories from EU-candidate countries (Croatia, FYROM and Turkey), were also invited to take part in this EUPT. Selected laboratories from Third Countries were allowed to take part in this exercise following approval by DG-SANCO. However, only results submitted by labs from EU and EFTA countries were included in the calculation of the Assigned Values. A tentative list of EU-labs considered as being obliged to participate in the EUPT-SRM7 was published at the beginning of 2012. The list was drafted based on information about the commodity scope and NRL-status of the labs. The pesticide scope was not considered at this stage due to concerns that the data available in the EUPT-DataPool was not up-to-date. NRLs and OfLs that were listed as being obliged to participate in this exercise, but decided not to take part, were asked to state the reason(s) for their non-participation. Laboratories that originally had registered to participate in this PT but finally did not submit results were also asked to provide explanations.

DG-SANCO will have full access to all EUPTs data 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 for Animal Health and the Food Chain or during EURL-Workshops.

[1] Former Community Reference Laboratories (CRLs)

CONTENT

EUROPEAN COMMISSION –
EU-PROFICIENCY TEST ON RESIDUES OF PESTICIDES REQUIRING SINGLE RESIDUE METHODS
TEST ITEM: MILLED DRY LENTILS
EUPT-SRM7, 2012

INTRODUCTION

On February 1st 2012 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 Organizers were invited to participate in the 7th European Commission's Proficiency Test Requiring Single Residue Methods (EUPT-SRM7). The Announcement/Invitation Letter contained links to the Calendar of the EUPT-SRM7, as well as to the Target Pesticides List showing the compounds that could potentially be present in the Test Item (**Appendix 10** and **Appendix 11**). The Target Pesticides List contained 16 compounds requiring single residue methods. For each compound a residue definition valid for the PT was given and the minimum required reporting level (MRRL) was stipulated. A link to the "General EUPT Protocol", containing information common to all EUPTs, was also provided. The laboratories were able to register on-line from the 6th to the 24th of February 2012.

A tentative list of laboratories that, based on their commodity scope and NRL-status, were considered as being obliged to participate in the EUPT-SRM7 was distributed to NRLs and OfLs. To ensure that all relevant OfLs were informed about this EUPT, the NRLs were asked to additionally forward the invitation to all relevant laboratories within their countries. It was made clear that the list was only tentative and that the real obligation to participate was based on Reg. 396/2005 and Reg. 882/2004 EC. Obliged labs that did not intend to participate were asked to provide an explanation. In total 114 laboratories from EU and EFTA countries agreed to participate in the test with only 4 of them failing to submit results. 5 laboratories from Third Countries also registered for the present EUPT with 4 of them submitting results.

To prepare the Test Item, lentils of German origin from organic production were used. The lentils were first checked for the absence of the pesticides from the Target Pesticides List and spiked with 7 compounds (***2,4-D, potassium bromide, chlorothalonil, cyromazine, dithiocarbamates, ethephon and fenbutatin oxide***). Mixed standard solutions were used for spiking. A certain portion of conventionally produced lentils containing a high level of incurred ***glyphosate*** was also added to the material before milling, so that the final Test Item contained 8 compounds in total. More details are given in the Section "**Test Item**".

1. TEST ITEM

1.1 Analytical methods

The analytical methods described briefly below were used by the organisers to check the homogeneity and storage-stability of the pesticides contained in the Test Item:

2,4-D (acidic pesticide): QuEChERS-method [3] involving extraction after addition of acetonitrile, partitioning after addition of salts, and determinative analysis by LC-MS/MS in the ESI-neg. mode directly from the raw extract (no dispersive-SPE cleanup with PSA sorbent).

Bromide ion: method involving acidification of the test portion with H_2SO_4, derivatization with propylene oxide, partitioning of the derivative into ethyl acetate, desiccation with Na_2SO_4 and direct determination by GC-ECD.

Chlorothalonil (base-labile pesticide): modified QuEChERS-method for the analysis of ***chlorothalonil*** (see EURL-SRM website) involving acidification with sulphuric acid to pH~1 at the beginning of the sample preparation. Partitioning is induced by adding $MgSO_4$ / NaCl = 4:1 (no citrate buffer salts used). Determinative analysis is performed via LC-MS/MS in the APCI-neg. mode directly from the raw extract (no dispersive-SPE cleanup with PSA sorbent).

Dithiocarbamates (sum): method involving cleavage with HCl/$SnCl_2$ in a hot water bath with simultaneous partitioning of the formed CS_2 into iso-octane and determination by GC-MSD.

Ethephon and **glyphosate** (highly polar pesticides): QuPPe-M1.2 method as described in the EURL-SRM-website involving addition of isotope labelled analogues of the compounds as ISTDs, addition of methanol containing 1 % formic acid, extraction by shaking, centrifugation, filtration and determination by LC-MS/MS in the ESI-neg. mode using ion-pac AS11-HC column.

Cyromazine (highly polar pesticide): QuPPe-M4 method as described in the EURL-SRM-website involving addition of isotopically labelled ***cyromazine*** as ISTD, addition of methanol containing 1 % formic acid, extraction by shaking, centrifugation, filtration and determination by LC-MS/MS in the ESI-pos. mode.

Fenbutatin oxide (organotin compound): extraction by modified QuEChERS-method as described above for ***chlorothalonil*** followed by LC-MS/MS determination in the ESI-pos. mode using a gradient containing 1 % formic acid.

For more details on the above methods used, see http://www.eurl-pesticides.eu (EURL-SRM-website → Services → Methods).

The above described methods were also used to analyse all Blank Materials that might potentially be used for this exercise, to ensure the absence of all pesticides in the Target Pesticides List. The material containing high level of incurred ***glyphosate*** that was added at a small percentage to the Test Item prior to milling was also analysed to quantify ***glyphosate*** and to check for the absence of all other compounds. ***Avermectin***, ***propamocarb***, ***fluazifop***, ***haloxyfop*** and dichlorprop were analysed by the QuEChERS method (EN-15662) [3]. ***Chlormequat***, ***mepiquat*** were analyzed by the QuPPe method (QuPPe-M4).

1.2 Selection of pesticides for the Target Pesticides List

The pesticides 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 six points into account: 1) the present and upcoming scope of the EU-coordinated control programme; 2) a pesticide priority list ranking the pesticides according to their risk potential; 3) the relevance of pesticides to the specific commodity group (pulses); 4) the overall scope and capability of the OfLs as assessed in previous EUPTs or surveys; 5) the need of additional PT- data to gain the ability to evaluate the analytical proficiency of labs that offer analytical services via the SRM-PinBoard Service of the EURL-SRM[1]; and 6) labs needs as expressed via surveys or e-mail communications.

In some cases it was decided that the residue definitions valid for the EUPT should differ from those in the legislation (e.g. in the case of avermectin, where only the B1a component was included and in the case of the acids, where only the free acid had to be analysed). The minimum required reporting levels (MRRLs) were set at 0.01 mg/kg for ***chlorothalonil***; at 0.02 mg/kg for ***2,4-D***, ***cyromazine***, ***ethephon*** and ***fenbutatin oxide***; at 0.05 mg/kg for ***dithiocarbamates*** as CS_2 and ***glyphosate*** and at 3 mg/kg for ***bromide ion***.

1.3 Preparation of the Blank Material

The lentils used for the preparation of the Blank Material were purchased from an organic producer in South-Western Germany. After mixing the material in its entirety with a drum-hoop mixer for 2 h it was checked for the absence of the pesticides included in the Target Pesticides List. Part of the material was then used for the preparation of the Test Item and the rest was milled in 2 kg portions using a rotor beater mill (Retsch Rotor Beater Mill SR 300) equipped with a 0.5 µm sieve. The first 2 kg portion of the milled material was discarded. The milled material was re-mixed with a drum-hoop mixer over 2 h and weighed out in ca. 400 g portions into screw-capped polyethylene plastic bottles. The bottles were sealed and stored in a freezer at about -20 °C until packaging and distribution to the participants. A randomly chosen bottle was checked again to make sure that there was no cross-contamination during Test Item preparation.

1.4 Preparation of the Test Item

Before preparing this Test Item, the pesticides and their suitable, approximate target residue levels for the study were selected by the Organizers in coordination with the EUPT-QC-Group. The Test Item contained 8 different pesticides (see **Table 1-1**). As several analytical methods had to be applied to cover all compounds, it was decided to provide ca. 400 g Test Item and ca. 400 g Blank Material to each participating lab. Spiking in the laboratory was performed using pesticide standards except for ***glyphosate***, which was contained at high levels in lentils added at a small proportion to the Test Item.

One kilogram blank lentils (see **Section 1.3**) was spiked with 100 ml of a solution containing 100 mg thiram, 40 mg ***cyromazine***, 25 mg ***fenbutatin oxide***, 80 mg ***chlorothalonil***, 30 mg ***2,4-D*** and 25 mg ***ethephon*** all dissolved in acetone : water = 9 : 1. Another kilogram of the blank lentils was spiked with 5 g ***potassium bromide*** dissolved in 100 ml acetone : water = 1 : 1. Both spiked portions were dried separately using an orbital shaker, mixed with 10 kg commercial lentils containing ***glyphosate***, and then added to 75 kg blank lentils.

1 A service provided by the EURL-SRM to encourage and facilitate the cooperation between labs in the area of SRM-pesticides.It essentially consists of a list showing labs offering analytical services on a subcontract basis and labs interested to receive analytical services on a subcontract basis. The proficiency of the labs offering analytical services is evaluated based on results achieved in EUPT-SRMs.

Table 1-1: Compounds employed for the preparation of the Test Item.

Pesticide	Application in the field	Spiking in laboratory	Treatment Form
2,4-D		x	Standard solution
Potassium bromide		x	Standard solution
Chlorothalonil		x	Standard solution
Cyromazine		x	Standard solution
Thiram		x	Standard solution
Ethephon		x	Standard solution
Fenbutatin oxide		x	Standard solution
Glyphosate	x		contained in lentils purchased commercially

The spiked lentils (in total 87 kg) were then mixed thoroughly over 4 h using a drum-hoop mixer. For a preliminary check 1 kg of the mixed lentils were milled, and the concentrations of the pesticides contained were analytically determined. Since the concentrations of ***chlorothalonil*** and CS_2 declined dramatically, it was decided to spike with additional ***chlorothalonil*** (80 mg) and thiram (100 mg). This was accomplished in a similar way as described above by spiking 1 kg of the remaining spiked lentils, drying them and mixing them with the rest over 4 hours using a drum-hoop mixer. The mixed lentils were then milled in 2 kg portions. Regular pauses were required to allow the mill to cool down to avoid any effects of high temperatures on the material. The particle size distribution of the material was determined via Retsch Sieve Shaker AS 200 basic with a sieving tower of 1 mm, 500 µm, 250 µm, 125 µm and 63 µm mesh sieves running over 10 minutes at a frequency of 50 Hz and an amplitude of 3 cm. **Figure 1-1** shows the particle size distribution. The milled material was mixed again in its entirety over 4 h using the drum-hoop mixer. Subsequently, 400 g portions were weighed out into screw-capped polyethylene plastic bottles, sealed, numbered, and stored in a freezer at about -20 °C. Thereafter the homogeneity test was performed. Due to the unacceptable inter-bottle variance in the case of ***dithiocarbamates*** all protions of the spiked material, including those used for the homogeneity test, were taken out from the bottles and mixed again (= second mixing procedure) over night. During this step the susceptible pesticide ***chlorothalonil*** partially degraded, which explains the lower levels detected in the stability test compared to the homogeneity test. The materials were then re-portioned and stored in a freezer at about -20 °C until their packaging and distribution to the participants.

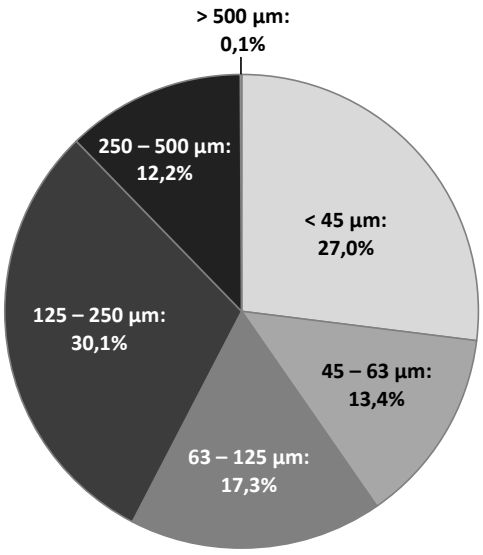

Figure 1-1: Particle size distribution of the milled lentils for the Test Item and Blank Material.

Table 1-2: Statistical evaluation of homogeneity test data (n = 20 analyses), see Appendix 2.

	2,4-D	Bromide	Chlorothalonil	Cyromazine	Dithiocarbamates	Ethephon	Fenbutatin oxide	Glyphosate
Analytical portion size [g]	5	5	5	5	15	5	5	5
Mean [mg/kg]	0.294 [1)]	33.7 [1)]	0.175 [1)]	0.356 [1)]	0.825 [2)]	0.227 [1)]	0.234 [1)]	0.855 [1)]
s_{sam}^2	4.62×10^{-5}	1.49	1.99×10^{-6}	1.69×10^{-4}	3.49×10^{-3}	0	0	1.80×10^{-3}
c	9.69×10^{-4}	21.9	4.52×10^{-5}	7.13×10^{-4}	8.97×10^{-3}	9.17×10^{-4}	6.50×10^{-4}	1.03×10^{-2}
Passed/Failed	passed	passed	passed	passed	passed	passed	passed	passed

s_{sam}^2 : sampling variance; c: critical value
1) analysed on 11.04.2012 before the second mixing procedure
2) analysed on 18.04.2012 after the second mixing procedure

1.5 Homogeneity test

Ten bottles of treated Test Item were randomly chosen and analyses were performed on duplicate portions taken from each bottle. The order of sample preparation and extract injection into the analytical instruments were also random. Quantification was performed using matrix-matched standards for calibration. The homogeneity test experiments were performed for all compounds using the material derived after the first mixing procedure. In the case of ***dithiocarbamates*** the homogeneity test was repeated after the second mixing procedure and the results of this test were used to judge homogeneity. Analytical sample portions of 5 g were used for all compounds except for ***dithiocarbamates*** where 20 g were used after the first mixing and 15 g after the second mixing.

The statistical evaluation of the homogeneity test data was performed according to the International Harmonized Protocols published by IUPAC, ISO and AOAC [4]. An overview of the statistical analyses of the homogeneity test is shown in **Table 1-2**. The individual residue data from the homogeneity tests, as well as the results of the statistical analyses, are given in **Appendix 2**.

The acceptance criterion for the Test Item to be sufficiently homogenous 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, when duplicate samples are taken from 10 bottles. $\sigma_{all}^2 = 0.3 \times$ FFP-RSD (25 %) $\times$ the analytical sampling mean for all pesticides, and s_{an} is the estimate of the analytical standard deviation.

As all pesticides passed the homogeneity test, the Test Item was considered sufficiently homogenous and suitable for the EUPT-SRM7.

1.6 Stability test

Following a simulated transport over 2 days (using the same containers and cooling elements as for the participants) 5 randomly chosen samples were analysed shortly before the start of the EUPT-exercise, ca. 2 weeks after and after the deadline for result submission. Due to its well-known stability ***bromide ion*** was only analysed on two occasions, before and after the EUPT-exercise skipping the second test. The samples were stored at -18 °C, the storage temperature recommended to the participants in the EUPT-SRM7 Specific Protocol.

Table 1-3: Stability test results (storage at -18 °C), see also Appendix 3

	2.4-D	Bromide	Chlorothalonil	Cyromazine	Dithiocarbamates*	Ethephon	Fenbutatin oxide	Glyphosate
Storage at -18 °C (mean values in mg/kg)								
Analysis 1 12.04.2012	0.294	33.4	0.112 [1)]	0.370	0.813 [2)]	0.223	0.235	0.873
Analysis 2 08.05.2012	0.299	–	0.119	0.366	0.774	0.235	0.226	0.861
Analysis 3 30.05.2012	0.307	32.1	0.119	0.377	0.680 [3)]	0.233	0.236	0.863
Deviation [%] Analysis 3 vs. Analysis 1	**4.48 %**	**-3.88 %**	**5.78 %**	**3.03 %**	**-16.4 % (9.7 % [4)])**	**4.26 %**	**0.71 %**	**-1.14 %**
Passed/Failed	Passed	Passed	Passed	Passed	**Failed (Passed [4)])**	Passed	Passed	Passed

1) analysed on 25.04.2012 after the second mixing procedure
2) analysed on 18.04.2012 after the second mixing procedure
3) due to technical difficulties analysed on 14.06.2012, 2 weeks after the deadline for results submission
4) calculated via intrapolation for the period starting two days after shipment and ending the day before the deadline for results submission (see text and Figure 1-1)

Analysis 1 (before or just after the shipment):
12 April 2012 (all compounds except ***dithiocarbamates*** and ***chlorothalonil***)
18 April 2012 (***dithiocarbamates***)
25 April 2012 (***chlorothalonil***)

Analysis 2 (two weeks after shipment):
8 May 2012 (all pesticides except ***bromide ion***)

Analysis 3 (after deadline for results submission):
30 May 2012 (all pesticides except ***dithiocarbamates***)
14 June 2012 (***dithiocarbamates***)*

*The final analysis of ***dithiocarbamates*** had to be postponed due to technical difficulties.

The results of the stability test of pesticides present in the Test Item are shown in **Table 1-3** and **Appendix 3**. Except for ***dithiocarbamates*** the test results did not indicate any significant degradation in the Test Item (stored at -18 °C, the recommended storage temperature) for the period of the PT. For ***dithiocarbamates*** the stability-test criteria were not achieved, but as the period between the first and the last measurement (18 April – 19 June, 58 days) was very long compared to the duration of the EUPT (23 April – 29 May, 37 days), the EUPT-Scientific Committee was consulted and it was agreed to calculate the losses during the duration of the exercise via interpolation.

As the ***dithiocarbamate*** losses during the stability test period followed a nearly linear trend (see **Figure 1-2**), a simple linear interpolation was considered as an acceptable approximation. Using the rule of three the loss of ***dithiocarbamates*** (determined as CS_2) during the 34 days of the EUPT-exercise was calculated to be ca. 9.7 %. Based on this data and considering that the Qn-RSD of ***dithiocarbamates*** did not exceed 25 %, the EUPT-SC considered that the ***dithiocarbamates*** were sufficiently stable during the test.

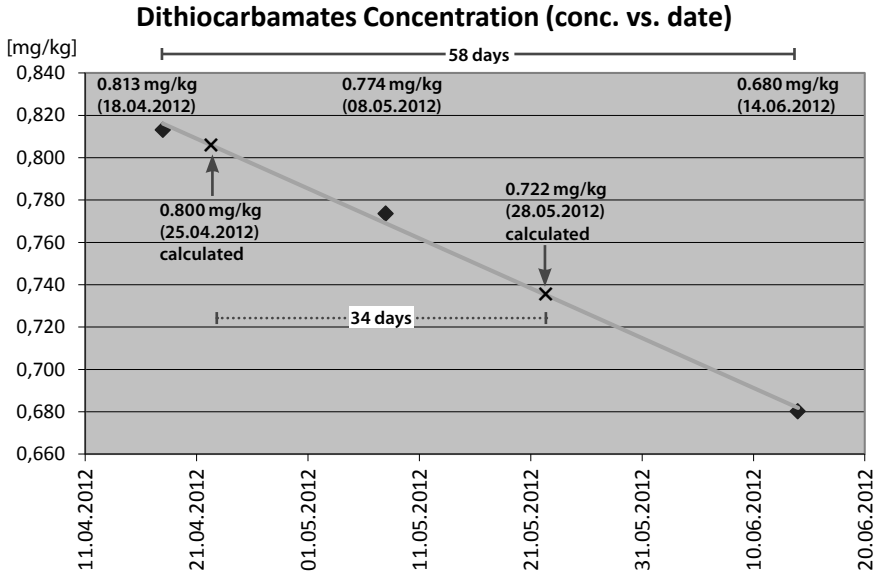

Figure 1-2: Decline of the dithiocarbamates (as CS_2) content in the Test Item during storage in the freezer. The values for 25.04.2012 (two days after sample shipment) and 28.05.2012 (the day before deadline for results submission) were calculated based on linear intrapolation.

1.7 Organisational details

1.7.1 Preparation and distribution of a tentative list of obliged labs

A tentative list of laboratories (NRLs and OfLs) that are obliged to participate in this EUPT was constructed based on information on NRL-status and commodity scope as recorded in the EURL-DataPool. The pesticide scope of the labs was not considered when drafting this list due to concerns that the available data is not up-to-date and/or not applicable to the present commodity (dry pulses). NRLs were additionally prompted to carefully check the status, commodity scope and contact data of the OfLs within their network and asked to amend and complement it, if necessary, and to ensure that all OfLs obliged to participate within their network were informed of this EUPT. The invited EU-laboratories were informed that the list of obliged labs was tentative and that the real obligation to participate in EUPTs derived from Art. 28 of Reg. 396/2005/EU (for OfLs) and from Art. 33 of Reg. 882/2005/EC (for NRL-SRMs). Following DG-SANCO instructions, obliged labs that were not intending to participate in the EUPT-SRM7 were instructed to provide explanations for their non-participation.

1.7.2 Announcement / Invitation and EUPT-SRM7-Website

An Announcement/Invitation Letter was sent in January 2012 to all NRL-SRMs as well as to any other OfLs analysing pesticide residues in fruit and vegetables, cereals or feeding stuff within the framework of official controls. The invitation letter was also sent to all OfLs for which no information regarding scope was available. OfLs from EFTA countries, as well as of EU-candidate states, were also invited to voluntarily participate if their contact data was available.

An EUPT-SRM7-Website was constructed within the EURL-web-portal with links to all documents relevant to this EUPT (i.e. Calendar, Target Pesticides List, Specific Protocol and General EUPT Protocol). These documents were uploaded to the EURL-web-portal and the CIRCA/FIS-VL platform.

1.7.3 Registration and confidentiality

An EUPT-SRM7 registration website was constructed in collaboration with the EURL-CF. All laboratories obliged to participate in the current EUPT, regardless of whether they were intending to participate in this exercise or not, were requested to register or to state their reasons for non-participation using the same website.

Upon registration the participating labs were automatically provided via e-mail with a unique laboratory code as well as with unique login information to be used to enter the online result-submission-website. This ensured confidentiality throughout the entire duration of the PT.

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

1.7.4 Distribution of the Test Item and the Blank Material

One bottle of treated Test Item (ca. 400 g) and one bottle of Blank Material (ca. 400 g) were shipped on 23 April 2012 to each participant in thermo-insulated polystyrene boxes each charged with two cryobags previously stored in the freezer. Laboratories were asked to check the integrity and condition of the material upon receipt and to report to the Organizers via the website any observations or complaints and whether they are accepted.

Instructions on how to treat the Test Items and Blank Material upon receipt were provided to the participating laboratories within the Specific Protocol (**Appendix 10**).

1.7.5 Submission of results and additional information

An online result submission tool allowed participants to submit their results via the Internet. Using their individual access-information all participants had access to the result-submission-website from a week after the sample shipment until the result submission deadline (29 May 2012). Participants were asked not only to report their analytical results but also to state whether the compounds in the Target Pesticides List are part of their routine scope and to indicate the experience with the analysis of these compounds. Furthermore the labs had to give information if they analyse any compounds routinely on behalf of another OfL or institution and whether they subcontract any compounds to another laboratory on a routine basis. In addition, laboratories had to provide details about the methods they had used and to provide their own reporting limits (RLs) for each pesticide they have analysed. After the deadline for results submission participating laboratories having submitted false negative results were asked to provide detailed information on their methods used for analysing those compounds. Where information on analytical methods, that is important for the evaluation, was missing, laboratories were requeseted to provide.

2. EVALUATION RULES

2.1 False positives and negatives

2.1.1 False positives (FP)

In principle, any result indicating the presence of a pesticide listed in the Target Pesticides List, which was (a) not used in the preparation of the Test Item; (b) not detected by the Organisers, even following a repetitive analysis; and (c) not detected by the overwhelming majority (e.g. > 95 %) of the participants that tested for this compound, is treated as a false positive, if it is reported at a concentration at or above the Minimum Required Reporting Level (MRRL). Results lower than the MRRL are ignored by the Organisers and are not considered as false positives. No z-scores are calculated for false positive results.

2.1.2 False negatives (FN)

These are results of pesticides reported as "analysed" but where no numerical values are reported, 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 majority of the participating laboratories. Z-scores for false negatives are calculated using the MRRL as the result. Any reporting-limits (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 (consensus) values

To establish the Assigned Values, the median levels of all reported results from EU and EFTA countries, excluding outliers, are used.

2.3 Fixed target standard deviation (FFP-approach)

Based on experience from previous EU Proficiency Tests on fruit and vegetables and cereals, a fixed fit-for-purpose relative standard deviation (FFP-RSD) of 25 % is applied. The target standard deviation (σ) for each individual pesticide is calculated by multiplying the Assigned Value by the FFP-RSD. In addition, the robust relative standard deviation (Qn-RSD) is calculated for informative purposes.

2.4 z-Scores

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

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

Where

- x_i is the result for the pesticide (i) as reported by the participant
  (For results considered 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.)
- μ_i is the Assigned Value for the pesticide (i)
- δ_i is the target standard deviation for the pesticide (i), which equals 25 % of the Assigned Value (FFP-approach)
  Any z-scores > 5 are set at "5" in calculations of combined z-scores (see 2.5.2).

The z-scores are classified as follows:

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

For results considered as 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 Lab ranking and classification

2.5.1 Category A and B classification

Based on the scope of pesticides covered by the labs, 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 reported concentration values for at least 90 % of the pesticides present in the Test Item,
b) not have reported any false positive results.

2.5.2 Combined z-scores

For informative purposes and to allow comparison as measure of the overall performance the Average of the Absolute z-Score (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.
For the calculation, any z-score > 5 is set at "5".

The AAZ-scores were classified as follows:

$AAZ \leq 2$	good
$2 < AAZ \leq 3$	satisfactory
$AAZ > 3$	unsatisfactory

3. RESULTS

3.1 Participation

119 laboratories from 32 countries (25 EU-Member States, 2 EFTA-States and 5 Third Countries) registered for participation in the EUPT-SRM7. Out of those laboratories 114 (108 from EU-Member States, 2 from EFTA-States and 4 from Third Countries) submitted at least one result. An overview of the participating labs and countries is given in **Table 3-1**.

A list of all individual laboratories that registered for this EUPT is presented in **Appendix 1**. Out of the EU Member States only Malta and Romania were not represented among the participating labs. As far as NRL-SRMs are concerned Romania and Italy were not represented whereas Malta was represented by its proxy-NRL in the UK and a subcontracted lab for official control in Germany.

In total 6 laboratories from non-EU countries submitted results (2 from EFTA Countries and 4 from Third Countries). The results submitted by the 4 laboratories from the Third Countries were not taken into account when calculating the Assigned Values.

In total, 228 EU-OfLs (including NRL-SRMs) were considered as being obliged to participate in the present EUPT and were thus included in a tentative list distributed to the network labs prior to the registration period for this EUPT. The list included all NRL-SRMs, regardless of their commodity scope, and all EU-OfLs analyzing pesticide residues in fruit and vegetables, cereals or feed. The pesticide scope of the labs was not taken into account due to concerns that the data available in the EURL-DataPool was not up-to-date or not applicable to the matrix in question. It was emphasized to the labs that this list was only indicative and that the real obligation is stipulated in Reg. 396/2005/EC for OfLs and in Reg. 882/2004/EC for NRLs.

All labs that were listed as obliged to participate had to either participate or to provide an explanation for their non-participation. Out of 117 obliged laboratories that did not register for this PT, 52 (from 14 EU countries) provided explanations for their non-participation. The most frequent reason stated by the laboratories to explain their non-participation in the EUPT-SRM7 was that the pesticides to be targeted in this EUPT were out of their scope. Other reasons concerned limitations in capacity (time, personnel, and instrument availability) and the non-inclusion of dried pulses in their routine scope. All statements provided by the labs to explain their non-participation were forwarded to DG-SANCO as requested. **Table 3-2** gives an overview on the participating and non-participating EU-labs that were obliged to participate in the EUPT-SRM7.

Upon request, 3 of the 4 EU-laboratories (3× IT, 1× FR) that had originally registered for the EUPT-SRM7, but then failed to submit results, provided explanations for their non-submission of results. Only one Italian laboratory did not provide any explanation.

Table 3-1: Number of laboratories obliged to participate in the EUPT-SRM7, labs that registered, and labs that finally submitted results (grouped by country)

Contracting Country	No. of obliged labs [1]	Registered for Participation		Submitted Results		Provided Explanations [2]		Notes
		Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	
Austria	**3**	1	1	1	1	**2**	**0**	
Belgium	**9**	6	1	6	1	**1**	**0**	One lab based in NL was subcontracted by BE and NL but is only listed here
Bulgaria	**9**	1	1	1	1	**0**	**0**	
Cyprus	**2**	1	1	1	1	**1**	**0**	
Czech Republic	**4**	3	1	3	1	**0**	**0**	
Denmark	**2**	2	1	2	1	**0**	**0**	
Estonia	**2**	2	1	2	1	**0**	**0**	
Finland	**3**	2	1	2	1	**0**	**0**	
France	**16**	7	1	6	1	**4 + 1** [3]	**0**	
Germany	**30**	24	1	24	1	**6**	**0**	CVUA Stuttgart hosting the EURL organizing this PT was not considered as an obliged lab.
Greece	**10**	4	2	4	2	**5**	**0**	Greece has appointed two NRL-SRMs.
Hungary	**7**	3	1	3	1	**1**	**0**	
Ireland	**1**	1	1	1	1	**0**	**0**	
Italy	**35**	12	1	9	0	**10 + 2** [3]	**1** [3]	
Latvia	**1**	1	1	1	1	**0**	**0**	
Lithuania	**2**	1	1	1	1	**1**	**0**	
Luxembourg	**1**	1	1	1	1	**0**	**0**	
Malta		–	–	–	–	–	–	MT-NRL represented by the UK-NRL (however, not in terms of controls) and a subcontracted lab in Germany
Netherlands	**2**	2	1	2	1	**0**	**0**	
Poland	**34**	12	1	12	1	**10**	**0**	
Portugal	**4**	3	1	3	1	**0**	**0**	
Romania	**6**	0	0	0	0	**1**	**1**	
Slovakia	**2**	2	1	2	1	**1**	**0**	One of the two participating labs wasn't obliged to participate.
Slovenia	**4**	3	1	3	1	**1**	**0**	
Spain	**32**	12	2	12	2	**7**	**0**	Spain has appointed two NRL-SRMs.
Sweden	**2**	2	1	2	1	**0**	**0**	
UK	**5**	4	1	4	1	**0**	**0**	
EU Total	**228**	112	23	108	22			
Norway		1	1	1	1			
Switzerland		1	–	1	–			
EU+EFTA Total	**228**	114	24	110	23			
Australia		1	–	1	–			
Egypt		1	–	1	–			
Singapore		1	–	1	–			
USA		1	–	1	–			
Zambia		1	–	0	–			
Third Countries		5		4				
Overall Sum	**228 + (6)**	119		114				

1) The obliged labs were tentatively defined based on their function (NRL-SRMs) and the commodity-scope covered (vegetables, cereals or feed). Obliged labs that did not participate were requested to provide an explanation.
2) Explanation for non-participation or for non-submission of results
3) Explanation for non-submission of results

Table 3-2: Overview of EU-labs with a mandatory obligation to participate in the EUPT-SRM7

Total Number of Obliged EU-labs [1)]	228	100 %
Thereof		
- Registered for Participation	**112**	**49 %**
- Submitting results *	108	**47 %**
- Not submitting results / providing explanation for non-submission	4 / 3	2 % / 1 %
- Not Registered for Participation	**116**	**51 %**
- Providing explanations for non-participation	52	23 %
- No feedback	65	29 %

1) Tentative number of OfLs (including NRLs) of EU-member states that were included in the list of labs that were considered as obliged to participate in the EUPT-SRM7 (see Section 1.7.1)

3.2 Overview of results

An overview of the results reported for the pesticides present in the sample is shown in **Table 3-3**.

Table 3-4 gives an overview of all results submitted by each laboratory. For the individual results reported by the laboratories see **Table 3-8**. The detailed information about the analytical methods used by the laboratories is shown in **Appendix 7**.

Table 3-3: Percentage of EU and EFTA labs that have analysed the compounds present in the Test Item.

Pesticides present in Test Item	Labs reporting results		
	No.	% (based on N = 110 [1)])	% (based on N = 228 [2)])
2,4-D (free acid)	70	64 %	30 %
Bromide	45	41 %	20 %
Chlorothalonil	77	70 %	34 %
Cyromazine	55	50 %	24 %
Dithiocarbamates	87	79 %	38 %
Ethephon	33	30 %	14 %
Fenbutatin Oxide	44	40 %	19 %
Glyphosate	39	35 %	17 %

1) based on 110 laboratories from EU and EFTA countries having submitted at least one result
2) 228 EU-laboratories were included in the tentative list of labs considered to be obliged to participate in the EUPT-SRM7

Table 3-4: Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results)

Compound listed in Target List			2.4-D (free acid)	Avermectin B1a	Bromide ion	Chlormequat (cation)	*Chlorothalonil*	*Cyromazine*	Dichlorprop (2,4-DP) incl. Dichl.-P (free acids)	Dithiocarbamates (as CS_2)	Ethephon	*Fenbutatin Oxide*	Fluazifop incl. Fluazifop-P (free acids)	Glyphosate	Haloxyfop incl. Haloxyfop-R (free acids)	MCPA (free acid)	Mepiquat (cation)	Propamocarb	Compounds analysed / correctly found out of those...	
																			... within EUPT-Pesticide Target List	... present in EUPT-Test-Material
within MACP			√	√	√	√	√	√		√	√	√	√	√	√		√	√		
present in Test Item			√		√		√	√		√	√	√		√						
Evaluated within this PT			√		√					√	√			√						
Lab-Code SRM7-	NRL-SRM	Cat.																		
1		A	V	ND		ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	15 / 7	7 / 7
2		B	V	ND			V	V	ND		V	V#	ND	V	ND	ND		ND	12 / 6	6 / 6
3		A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
4	x	A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
6	x	B	V	ND	V	ND	V	V	ND	V		V	ND		ND	ND	ND	ND	14 / 6	6 / 6
7		A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
8		B				ND				V							ND		3 / 1	1 / 1
9		B	V	ND	V	ND	V	V	ND				ND		ND	ND	ND	ND	12 / 4	4 / 4
10	x	B	V	ND		ND			ND	FN	V	V	ND	V	ND	ND	ND	ND	13 / 4	5 / 4
11		B	V	ND	V	ND		V		V			ND	V	ND		ND	ND	11 / 5	5 / 5
12		A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
13		B	V	ND			V	V	ND	V	V#‡	V	ND			ND		ND	11 / 6	6 / 6
14	x	A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
15		B	V			ND		V	ND	V			ND		ND	ND	ND	ND	10 / 3	3 / 3
17		A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
18		B	V	ND	V	ND	V	V	ND	FN	FN	V	ND	V	ND	ND	ND	ND	16 / 6	8 / 6
19	x	B	V	ND			V	V	ND			V	ND		ND	ND		ND	10 / 4	4 / 4
20	x	B	V	ND		ND	V	V	ND		V	V	ND	V	ND	ND	ND	ND	14 / 6	6 / 6
21		A	V	ND	V‡	ND	V		ND	V	V	V	ND	V	ND	ND	ND	ND	15 / 7	7 / 7
22		B	V		V	ND		V	ND	V				V		ND	ND	ND	10 / 5	5 / 5
23	x	B	V	ND		ND	FN	V	ND	V		V	ND		ND	ND	ND	ND	13 / 4	5 / 4
24	x	B	V			ND	V	V	ND	V	V		ND	V	ND	ND	ND		12 / 6	6 / 6
25		A	V		V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	15 / 8	8 / 8
26		B					V												1 / 1	1 / 1
27	x																		0 / 0	0 / 0
28		A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
29		A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
30	x	A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
31		A	V	ND	V	ND	V	FN	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 7	8 / 7

MACP = EU Mutiannual Community Control Program (2012-14)
V = analysed for and submitted concentration **V**alue > MRRL
ND = analysed for and correctly **N**ot **D**etected
Empty cells: not analysed
FN = analysed for but falsely not detected (**F**alse **N**egative result)
V# : Outlier according to the General Protocol (z-score > 5)
V‡: Outlier according to Grubbs' test, alpha = 0.01

Table 3-4 (cont.): Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results)

Compound listed in Target List			2.4-D (free acid)	Avermectin B1a	Bromide ion	Chlormequat (cation)	*Chlorothalonil*	*Cyromazine*	Dichlorprop (2,4-DP) incl. Dichl.-P (free acids)	Dithiocarbamates (as CS_2)	Ethephon	*Fenbutatin Oxide*	Fluazifop incl. Fluazifop-P (free acids)	Glyphosate	Haloxyfop incl. Haloxyfop-R (free acids)	MCPA (free acid)	Mepiquat (cation)	Propamocarb	Compounds analysed / correctly found out of those...	
																			... within EUPT-Pesticide Target List	... present in EUPT-Test-Material
within MACP			√	√	√	√	√	√		√	√	√	√	√	√		√	√		
present in Test Item			√		√		√	√		√	√	√		√						
Evaluated within this PT			√		√					√	√			√						
Lab-Code SRM7-	NRL-SRM	Cat.																		
32	x	B	V	ND		ND	V	V	ND		V	V	ND	V	ND	ND	ND	ND	14 / 6	6 / 6
33	x	B					V			V								ND	3 / 2	2 / 2
34		B	V	ND			V	V	ND	V		V	ND	V	ND	ND		ND	12 / 6	6 / 6
35		B								V									1 / 1	1 / 1
36		B	V	ND	V	ND			ND	V			ND	V	ND	ND	ND		11 / 4	4 / 4
37	x	B	V	ND		ND	V		ND	V‡	V	V	ND		ND	ND	ND	ND	13 / 5	5 / 5
38		B	V	ND	V#‡		V	V	ND	V			ND		ND	ND		ND	11 / 5	5 / 5
39		B					FN												1 / 0	1 / 0
40		B								V									1 / 1	1 / 1
41		B	V			ND		V	ND				ND		ND	ND	ND	ND	9 / 2	2 / 2
42		B								V									1 / 1	1 / 1
43		B	V	ND	V	ND			ND	V			ND	V	ND	ND	ND		11 / 4	4 / 4
44		B			V					V									2 / 2	2 / 2
45		B			V														1 / 1	1 / 1
46		B			V	ND	V			V							ND		5 / 3	3 / 3
47	x	A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
48																			0 / 0	0 / 0
49		B	V	ND	V	ND			ND	V			ND		ND	ND	ND	ND	11 / 3	3 / 3
50	x	B	V	ND	V	ND	V	V	ND	V		V	ND		ND	ND	ND	ND	14 / 6	6 / 6
52		B								V									1 / 1	1 / 1
53		B	V		V	ND	V		ND	V		V	ND		ND	ND	ND		11 / 5	5 / 5
54	x	B	V				V		ND				ND		ND	ND		ND	7 / 2	2 / 2
55	x	B				ND	V	V		V	V						ND	ND	7 / 4	4 / 4
56		B	V	ND	FN		V	V	ND	V			ND		ND	ND		ND	11 / 4	5 / 4
57		B				ND				V				V					3 / 2	2 / 2
58		B								V									1 / 1	1 / 1
60		A	V	ND	V	ND	V	V	ND	V	V		ND	V	ND	ND	ND	ND	15 / 7	7 / 7
61		B		ND			V	V										ND	4 / 2	2 / 2
62	x	B	V	ND	V	ND	V		ND	V		V	ND		ND	ND	ND	ND	13 / 5	5 / 5

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Table 3-4 (cont.): Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results)

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																			... within EUPT-Pesticide Target List	... present in EUPT-Test-Material
within MACP			√	√	√	√	√	√		√	√	√	√	√	√		√	√		
present in Test Item			√		√		√	√		√	√	√		√						
Evaluated within this PT			√		√					√	√			√						
Lab-Code SRM7-	NRL-SRM	Cat.																		
64		B								V								ND	2 / 1	1 / 1
66		A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
67		B								V									1 / 1	1 / 1
70		B					V												1 / 1	1 / 1
72		B	V	ND		ND	V	V	ND	V			ND		ND	ND	ND	ND	12 / 4	4 / 4
73		B			V		V			V									3 / 3	3 / 3
74		B	V	ND		ND				V							ND		5 / 2	2 / 2
76		B								V									1 / 1	1 / 1
77		B	V	ND		ND	V	V		V			ND		ND	ND	ND	ND	11 / 4	4 / 4
78		B	V#‡				V	V				V							4 / 4	4 / 4
79	x	B	V	ND		ND	V	V		V	V		ND	V	ND		ND	ND	12 / 6	6 / 6
80		B	V	ND	V	ND	V	V	ND	V		V	ND		ND	ND	ND	ND	14 / 6	6 / 6
82		B								V									1 / 1	1 / 1
84		A	V	ND	V	ND	V	V	ND	V		V	ND	V	ND	ND	ND	ND	15 / 7	7 / 7
85		B		ND		ND	V	V		V		V	ND		ND		ND	ND	10 / 4	4 / 4
88		B	V	ND		ND	V	V	ND	V		V	ND		ND	ND	ND	ND	13 / 5	5 / 5
89		B	V	ND	V	ND	V#	V	ND	V		V#	ND		ND	ND	ND	ND	14 / 6	6 / 6
90		B					V							V					2 / 2	2 / 2
91		B	V	ND			V			V			ND					ND	6 / 3	3 / 3
92		B	V	ND	V	ND	V	V	ND				ND		ND	ND	ND	ND	12 / 4	4 / 4
93		A	V	ND	V	ND	V	V	ND	V	V		ND	V	ND	ND	ND	ND	15 / 7	7 / 7
94		B								V									1 / 1	1 / 1
95		B					V						ND		ND				3 / 1	1 / 1
96	x	A	V	ND	V	ND	V			V	V	V	ND	V	ND	ND	ND	ND	14 / 7	7 / 7
97		B		ND			V			V									3 / 2	2 / 2
98		B			V					V									2 / 2	2 / 2
99		A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
100		B								V									1 / 1	1 / 1
101	x	B		ND		ND		V			V			V			ND		6 / 3	3 / 3
102		B	V	ND	V	ND	V		ND	V	V		ND		ND	ND	ND	ND	13 / 5	5 / 5

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Table 3-4 (cont.): Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results)

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																			... within EUPT-Pesticide Target List	... present in EUPT-Test-Material
within MACP			√	√	√	√	√	√		√	√	√	√	√	√		√	√		
present in Test Item			√		√		√	√		√	√	√		√						
Evaluated within this PT			√		√					√	√			√						
Lab-Code SRM7-	NRL-SRM	Cat.																		
103	x	A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
104		B	V	ND			V	V	ND	V			ND			ND		ND	9 / 4	4 / 4
105		B								V									1 / 1	1 / 1
107		B					FN			V									2 / 1	2 / 1
108		B	V	ND			V			FN			ND		ND	ND		ND	8 / 2	3 / 2
109	x	B	V	ND	V	ND	V		ND	V		V	ND		ND	ND	ND	ND	13 / 5	5 / 5
110	x	B	V				FN		ND	V			ND		ND	ND		ND	8 / 2	3 / 2
111		B					V												1 / 1	1 / 1
112		B								V									1 / 1	1 / 1
113	x	B	V	ND		ND	V	V	ND	V		V	ND		ND	ND	ND	ND	13 / 5	5 / 5
114		B								V									1 / 1	1 / 1
115		B								V									1 / 1	1 / 1
116		B	V				V			V			ND		ND	ND			6 / 3	3 / 3
118	x	B	V	ND		ND	V	V	ND	FN		V	ND		ND	ND	ND		12 / 4	5 / 4
119		B		ND			V			V								ND	4 / 2	2 / 2
120																			0 / 0	0 / 0
121	x	B	V	ND		ND	V	V	ND				ND	V	ND	ND	ND		11 / 4	4 / 4
122		B			V		V												2 / 2	2 / 2
123		A	V	ND	V	ND	V	V	ND	V	V	V	ND	V	ND	ND	ND	ND	16 / 8	8 / 8
125		B								V									1 / 1	1 / 1
126	x	B								V									1 / 1	1 / 1
127		B	V	ND		ND	V	V	ND			V	ND		ND	ND	ND	ND	12 / 4	4 / 4
128		B		ND		ND								V			ND		4 / 1	1 / 1
129																			0 / 0	0 / 0
130		B	V	ND		ND	V		ND	V		V	ND		ND	ND	ND	ND	12 / 4	4 / 4
133		B	V				V		ND							ND			4 / 2	2 / 2
135		B								V									1 / 1	1 / 1
136		B			V					V	V								3 / 3	3 / 3
137		A	V	ND	V	ND	FN	V		V	V	V		V		ND	ND	ND	13 / 7	8 / 7
138		B	V	ND	V	ND	V	V	ND	V	V					ND	ND	ND	12 / 6	6 / 6
139																			0 / 0	0 / 0

MACP = EU Mutiannual Community Control Program (2012-14)
V = analysed for and submitted concentration **V**alue > MRRL
ND = analysed for and correctly **N**ot **D**etected
Empty cells: not analysed
FN = analysed for but falsely not detected (**F**alse **N**egative result)
V# : Outlier according to the General Protocol (z-score > 5)
V‡: Outlier according to Grubbs' test, alpha = 0.01

3.3 Assigned Values, target standard deviations and outliers

To establish the Assigned Values for each pesticide the medians of all results submitted by labs from EU and EFTA countries were calculated and used. Results from Third Country laboratories were not included. Prior to the calculation of the median values outliers were excluded. Results with z-scores > 5 were eliminated as outliers. The results of the remaining population were then subjected to the Grubbs' test (alpha = 0.01) to identify and eliminate any further outliers. The Assigned Values are shown in **Table 3-5**.

The results of ***chlorothalonil***, ***cyromazine*** and ***fenbutatin*** *oxide* showed a very broad distribution with Qn-RSD values being 46 %, 45 % and 58 %, respectively. The broad distribution for these three compounds can be attributed to the fact that a substantial number of labs applied methodologies leading to biased (typically underestimated) results without applying a correction of results for recovery. In the case of ***chlorothalonil*** and ***cyromazine*** the result distribution appears to be visibly bimodal (see kernel density estimate curves in **Appendix 4**) whereas in the case of ***fenbutatin oxide*** the non-unimodality of the results becomes apparent when looking at the results in detail (see **Section 3.5.4**). Taking the median of the entire result population of these three compounds as hypothetical assigned value the associated uncertainties calculate as shown in **Table 3-5.** The uncertainty was unacceptable in the case of ***fenbutatin oxide*** and ***cyromazine*** and just acceptable in the case of ***chlorothalonil***. Still, taking all facts into account the EUPT-Scientific Committee considered that any assigned value established using the median of the entire population or a sub-population of the results would be too uncertain and decided that the quantitative results of ***chlorothalonil, cyromazine*** and ***fenbutatin oxide*** should be presented as "for information only". Nevertheless, it was decided that the qualitative results of these three compounds should still be considered in the classification of the labs based on scope (see **Section 3.4.4**).

Excluding the above mentioned 3 compounds the average of the Qn-RSDs was 25.7 %, which is close to the FFP-RSD of 25 %.

Table 3-5: Assigned Values and RSDs for all pesticides present in the Test Item and used for results evaluation

Compound	No. of NDs	No. of Outliers	Assigned Value [mg/kg]	No. of numerical results (EU+EFTA)	Uncertainty of Assigned Value (UAV) [§] [mg/kg]	UAV-Threshold (=0.3*FFP-SD) [mg/kg]	Qn-RSD [%]
2,4-D (free acid)	0	1 [#]	0.278	70	0.012 (acceptable)	0.021	27.9
Bromide	1	1 [#] + 1 [‡]	41.4	44	1.41 (acceptable)	3.11	18.0
Dithiocarbamates	4	1 [‡]	0.615	83	0.020 (acceptable)	0.046	23.1
Ethephon	1	1 [#]	0.210	32	0.012 (acceptable)	0.016	25.2
Glyphosate	0	0	0.827	39	0.054 (acceptable)	0.062	34.5
Chlorothalonil	*4*	*1 [#]*	*0.104 **	*73*	*0.0070 (acceptable)*	*0.0078*	*45.7*
Cyromazine	*1*	*0*	*0.351 **	*54*	*0.027 (unacceptable)*	*0.026*	*45.3*
Fenbutatin Oxide	*0*	*3 [#]*	*0.186 **	*44*	*0.021 (unacceptable)*	*0.014*	*58.0*
Average							**25.7 [§]**

#: Outliers due to z-score > 5
‡: Outliers according to Grubbs' test, alpha value = 0.01
*: Median of all reported results excluding outliers (too uncertain to be defined as assigned value)
§: Chlorothalonil, cyromazine and fenbutatin oxide were not included.
§: Uncertainty of Assigned Value (μ_i) is calculated according to ISO 13528:2009-01 as
$\mu_i = 1.25 * [(Qn\text{-}SD)/\sqrt{n}]$, where *Qn-SD* is the robust standard deviation and *n* is the number of results

Table 3-6: Overview of false negative results reported by participating labs from EU and EFTA countries

Compound	PT-Code	Analysed	Reported Result [mg/kg]	RL [mg/kg]	MRRL [mg/kg]	Assigned Value [mg/kg]	Judgement
Bromide ion	SRM7-56	yes	–	7.0	3.0	41.4	False Negative
Chlorothalonil	SRM7-23	yes	–	0.05	0.01	– [1]	False Negative
	SRM7-39	yes	–	0.01			False Negative
	SRM7-107	yes	–	0.1			False Negative
	SRM7-110	yes	–	0.01			False Negative
Cyromazine	SRM7-31	yes	–	–	0.02	– [1]	False Negative
Dithiocarbamates	SRM7-10	yes	–	0.05	0.05	0.615	False Negative
	SRM7-18	yes	–	0.5			False Negative
	SRM7-108 [2]	yes	–	1.0			False Negative
	SRM7-118	yes	–	0.05			False Negative
Ethephon	SRM7-18	yes	–	0.05	0.02	0.210	False Negative

1) Due to statistical uncertainty no assigned value could be established for chlorothalonil and cyromazine. The median values (see Table 3-5), even considering the uncertainty, are however sufficiently distant from the MRRL, thus allowing safe judgement of false negatives.
2) This lab (SRM7-108) reported that it had analysed, but not detected (= ND) dithiocarbamates. The Reporting Limit (RL) submitted by this lab is much higher than the MRRL and the assigned value. Following the General EUPT Protocol (Appendix 9) the result was still judged as a "false negative" and the MRRL was thus used to calculate the z-score.

3.4 Assessment of laboratory performance

3.4.1 False Positives

No false positive results were submitted in the EUPT-SRM7.

3.4.2 False Negatives

In 11 cases (1× ***bromide***, 4× ***chlorothalonil***, 1× ***cyromazine***, 4× dithiocabamates, 1x ***ethephon***) participating EU and EFTA labs reported "analysed, but not detected" (**Table 3-6**) for pesticides present in the Test Item. This represents only 2.4 % of all 450 reported results concerning pesticides present in the Test Item (including results for ***chlorothalonil***, ***cyromazine*** and ***fenbutatin oxide***). In all cases the Assigned Values were sufficiently distant from the MRRLs stipulated in the Specific Protocol. One false negative result was also reported by a Third Country Lab (Lab Code 137).

3.4.3 Laboratory performance based on z-scores

All individual z-scores were calculated using the FFP-RSD of 25 %. **Table 3-7** shows the overall classification of z-scores achieved by the participating laboratories. The respective classification rules are shown in **Section 2.4**. Disregarding ***chlorothalonil***, ***cyromazine*** and ***fenbutatin oxide***, where no trustworthy assigned values could be established, "Acceptable" z-scores were achieved by 87 – 93 % of the labs (90 % on average).

Table 3-7: Overall classification of z-scores of EU and EFTA labs

Compound	No. of results	Acceptable		Questionable		Unacceptable [1)]		FNs
		No.	(%)	No.	(%)	No.	(%)	No.
2,4-D (free acid)	70	64	(91 %)	2	(3 %)	4	(6 %)	0
Bromide	45	42	(93 %)	0	(0 %)	3	(7 %)	1
Dithiocarbamates (as CS_2)	87	76	(87 %)	3	(3 %)	8	(9 %)	4
Ethephon	33	30	(91 %)	0	(0 %)	3	(9 %)	1
Glyphosate	39	34	(87 %)	4	(10 %)	1	(3 %)	0
Overall	**274**	**246**	(**90** %)	**9**	(**3** %)	**19**	(**7** %)	6

1) Including false negatives (FNs)

Table 3-8: Results reported by all laboratories* and the respective z-scores calculated using the FFP-RSD of 25 %

Compound				2,4-D (free acid)		Bromide ion		Dithiocarbamates (sum) expr. as CS_2	
Assigned Value [mg/kg]				0.278		41.4		0.615	
MRRL [mg/kg]				0.02		3.0		0.05	
Qn-RSD				27.9 %		18.0 %		23.1 %	
Lab code SRM7-	NRL-SRM	No. Compounds * Analysed / Correctly Found	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		15 / 7	A	0.367	***1.28***			0.680	***0.42***
2		12 / 6	B	0.312	***0.49***				
3		16 / 8	A	0.355	***1.11***	29.0	***-1.19***	0.621	***0.04***
4	x	16 / 8	A	0.352	***1.06***	46.6	***0.51***	0.371	***-1.59***
6	x	14 / 6	B	0.155	***-1.77***	40.4	***-0.09***	0.607	***-0.05***
7		16 / 8	A	0.315	***0.53***	45.4	***0.39***	0.655	***0.26***
8		3 / 1	B					0.559	***-0.36***
9		12 / 4	B	0.561	***4.07***	46.3	***0.48***		
10	x	13 / 4	B	0.304	***0.37***			FN	***-3.68***
11		11 / 5	B	0.202	***-1.09***	42.8	***0.14***	0.743	***0.83***
12		16 / 8	A	0.314	***0.52***	41.2	***-0.01***	0.591	***-0.16***
13		11 / 6	B	0.174	***-1.50***			0.360	***-1.66***
14	x	16 / 8	A	0.230	***-0.69***	53.8	***1.20***	1.100	***3.15***
15		10 / 3	B	0.289	***0.16***			0.835	***1.43***
17		16 / 8	A	0.323	***0.65***	55.0	***1.32***	0.531	***-0.55***
18		16 / 6	B	0.239	***-0.56***	37.0	***-0.42***	FN	***-3.68***
19	x	10 / 4	B	0.286	***0.12***				
20	x	14 / 6	B	0.280	***0.03***				
21		15 / 7	A	0.272	***-0.09***	77.3‡	***3.48***	0.650	***0.23***
22		10 / 5	B	0.200	***-1.12***	40.3	***-0.10***	0.740	***0.81***
23	x	13 / 4	B	0.216	***-0.89***			0.574	***-0.27***
24	x	12 / 6	B	0.222	***-0.81***			0.635	***0.13***
25		15 / 8	A	0.254	***-0.35***	45.6	***0.41***	0.632	***0.11***
26		1 / 1	B						
27	x	0 / 0							
28		16 / 8	A	0.294	***0.23***	34.5	***-0.66***	0.401	***-1.39***

* including chlorothalonil, cyromazine and fenbutatin oxide. #: outliers due to |z| > 5; ‡: outliers based on Grubbs' test with alpha = 0.01
** Categorisation based on scope (see Section 3.4.4)

A compilation of all individual results and z-scores for each laboratory is shown in **Table 3-8**. The corresponding kernel density histograms showing the distribution of the reported results are shown in **Appendix 4**. A graphic representation of the z-score distribution of each pesticide present in the Test Item can be seen in **Appendix 5**.

In **Table 3-9** all laboratories are ranked based on the individual z-scores obtained for each of the analytes present in the Test Item.

	Compound			Ethephon		Glyphosate		Submitted Results [mg/kg]		
	Assigned Value [mg/kg]			0.210		0.827				
	MRRL [mg/kg]			0.02		0.02				
	Qn-RSD			25.2 %		34.5 %				
Lab code SRM7-	NRL-SRM	No. Compounds * Analysed / Correctly Found	Cat.**	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Chlorothalonil	Cyromazine	Fenbutatin Oxide
1		15 / 7	A	0.250	***0.76***	1.020	***0.93***	*0.123*	*0.437*	*0.389*
2		12 / 6	B	0.243	***0.63***	0.905	***0.38***	*0.137*	*0.448*	*0.550*
3		16 / 8	A	0.117	***-1.77***	0.690	***-0.66***	*0.016*	*0.390*	*0.254*
4	x	16 / 8	A	0.205	***-0.10***	0.837	***0.05***	*0.097*	*0.459*	*0.201*
6	x	14 / 6	B					*0.172*	*0.145*	*0.140*
7		16 / 8	A	0.131	***-1.50***	0.457	***-1.79***	*0.154*	*0.280*	*0.116*
8		3 / 1	B							
9		12 / 4	B					*0.073*	*0.546*	
10	x	13 / 4	B	0.194	***-0.30***	0.602	***-1.09***			*0.042*
11		11 / 5	B			0.596	***-1.12***		*0.559*	
12		16 / 8	A	0.208	***-0.04***	0.842	***0.07***	*0.109*	*0.380*	*0.311*
13		11 / 6	B	0.630	***8.00***			*0.052*	*0.555*	*0.199*
14	x	16 / 8	A	0.182	***-0.53***	1.010	***0.89***	*0.153*	*0.418*	*0.175*
15		10 / 3	B						*0.299*	
17		16 / 8	A	0.241	***0.59***	1.030	***0.98***	*0.060*	*0.129*	*0.045*
18		16 / 6	B	FN	***-3.62***	1.110	***1.37***	*0.095*	*0.120*	*0.210*
19	x	10 / 4	B					*0.113*	*0.443*	*0.162*
20	x	14 / 6	B	0.211	***0.02***	1.370	***2.63***	*0.182*	*0.467*	*0.306*
21		15 / 7	A	0.126	***-1.60***	0.515	***-1.51***	*0.068*		*0.137*
22		10 / 5	B			0.746	***-0.39***		*0.333*	
23	x	13 / 4	B					*FN*	*0.400*	*0.170*
24	x	12 / 6	B	0.197	***-0.25***	0.768	***-0.29***	*0.054*	*0.423*	
25		15 / 8	A	0.197	***-0.25***	1.140	***1.51***	*0.093*	*0.398*	*0.261*
26		1 / 1	B					*0.061*		
27	x	0 / 0								
28		16 / 8	A	0.145	***-1.24***	0.723	***-0.50***	*0.114*	*0.108*	*0.289*

Table 3-8 (cont.): Results reported by the laboratories* and the respective z-scores calculated using the FFP-RSD of 25 %

Compound				2,4-D (free acid)		Bromide ion		Dithiocarbamates (sum) expr. as CS_2	
Assigned Value [mg/kg]				0.278		41.4		0.615	
MRRL [mg/kg]				0.02		3.0		0.05	
Qn-RSD				27.9 %		18.0 %		23.1 %	
Lab code SRM7-	NRL-SRM	No. Compounds * Analysed / Correctly Found	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 %)
29		16 / 8	A	0.265	***-0.19***	36.4	***-0.48***	0.741	***0.82***
30	x	16 / 8	A	0.269	***-0.13***	27.4	***-1.35***	0.625	***0.07***
31		16 / 7	A	0.296	***0.26***	47.4	***0.59***	0.310	***-1.98***
32	x	14 / 6	B	0.238	***-0.58***				
33	x	3 / 2	B					0.655	***0.26***
34		12 / 6	B	0.310	***0.46***			0.776	***1.05***
35		1 / 1	B					0.650	***0.23***
36		11 / 4	B	0.303	***0.36***	41.7	***0.03***	0.497	***-0.77***
37	x	13 / 5	B	0.278	***0.00***			1.380‡	***4.98***
38		11 / 5	B	0.150	***-1.84***	126.0#‡	***8.19***	0.720	***0.68***
39		1 / 0	B						
40		1 / 1	B					0.488	***-0.83***
41		9 / 2	B	0.384	***1.53***				
42		1 / 1	B					0.384	***-1.50***
43		11 / 4	B	0.340	***0.89***	41.8	***0.04***	0.595	***-0.13***
44		2 / 2	B			40.5	***-0.08***	0.590	***-0.16***
45		1 / 1	B			30.5	***-1.05***		
46		5 / 3	B			31.5	***-0.95***	0.610	***-0.03***
47	x	16 / 8	A	0.146	***-1.90***	55.1	***1.33***	0.684	***0.45***
48		0 / 0							
49		11 / 3	B	0.256	***-0.32***	39.5	***-0.18***	0.581	***-0.22***
50	x	14 / 6	B	0.245	***-0.47***	36.6	***-0.46***	0.703	***0.57***
52		1 / 1	B					0.663	***0.31***
53		11 / 5	B	0.328	***0.72***	44.5	***0.30***	0.694	***0.51***
54	x	7 / 2	B	0.219	***-0.85***				
55	x	7 / 4	B					0.590	***-0.16***
56		11 / 4	B	0.245	***-0.47***	FN	***-3.71***	0.555	***-0.39***
57		3 / 2	B					1.240	***4.07***
58		1 / 1	B					0.588	***-0.18***
60		15 / 7	A	0.303	***0.36***	29.6	***-1.14***	0.650	***0.23***
61		4 / 2	B						
62	x	13 / 5	B	0.300	***0.32***	34.0	***-0.71***	0.620	***0.03***
64		2 / 1	B					0.496	***-0.77***
66		16 / 8	A	0.338	***0.86***	42.3	***0.09***	0.585	***-0.20***
67		1 / 1	B					0.590	***-0.16***
70		1 / 1	B						
72		12 / 4	B	0.360	***1.18***			0.870	***1.66***
73		3 / 3	B			43.0	***0.16***	0.460	***-1.01***

* including chlorothalonil, cyromazine and fenbutatin oxide. #: outliers due to |z| > 5; ‡: outliers based on Grubbs' test with alpha = 0.01
** Categorisation based on scope (see Section 3.4.4)

	Compound			Ethephon		Glyphosate		Submitted Results [mg/kg]		
	Assigned Value [mg/kg]			0.210		0.827				
	MRRL [mg/kg]			0.02		0.02				
	Qn-RSD			25.2 %		34.5 %				
Lab code SRM7-	NRL-SRM	No. Compounds * Analysed / Correctly Found	Cat.**	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Chlorothalonil	Cyromazine	Fenbutatin Oxide
29		16 / 8	A	0.220	***0.19***	0.988	***0.78***	*0.098*	*0.035*	*0.230*
30	x	16 / 8	A	0.210	***0.00***	0.347	***-2.32***	*0.122*	*0.287*	*0.323*
31		16 / 7	A	0.144	***-1.26***	0.236	***-2.86***	*0.134*	*FN*	*0.090*
32	x	14 / 6	B	0.043	***-3.18***	1.020	***0.93***	*0.099*	*0.335*	*0.082*
33	x	3 / 2	B					*0.093*		
34		12 / 6	B			0.956	***0.62***	*0.054*	*0.412*	*0.193*
35		1 / 1	B							
36		11 / 4	B			0.964	***0.66***			
37	x	13 / 5	B	0.268	***1.10***			*0.148*		*0.190*
38		11 / 5	B					*0.215*	*0.125*	
39		1 / 0	B					*FN*		
40		1 / 1	B							
41		9 / 2	B						*0.421*	
42		1 / 1	B							
43		11 / 4	B			0.880	***0.26***			
44		2 / 2	B							
45		1 / 1	B							
46		5 / 3	B					*0.195*		
47	x	16 / 8	A	0.245	***0.67***	0.900	***0.35***	*0.098*	*0.200*	*0.042*
48		0 / 0								
49		11 / 3	B							
50	x	14 / 6	B					*0.155*	*0.186*	*0.153*
52		1 / 1	B							
53		11 / 5	B					*0.142*		*0.134*
54	x	7 / 2	B					*0.130*		
55	x	7 / 4	B	0.225	***0.29***			*0.091*	*0.350*	
56		11 / 4	B					*0.140*	*0.490*	
57		3 / 2	B			0.827	***0.00***			
58		1 / 1	B							
60		15 / 7	A	0.250	***0.76***	0.420	***-1.97***	*0.139*	*0.340*	
61		4 / 2	B					*0.124*	*0.343*	
62	x	13 / 5	B					*0.050*		*0.110*
64		2 / 1	B							
66		16 / 8	A	0.287	***1.47***	0.708	***-0.58***	*0.117*	*0.409*	*0.070*
67		1 / 1	B							
70		1 / 1	B					*0.075*		
72		12 / 4	B					*0.080*	*0.390*	
73		3 / 3	B					*0.140*		

Table 3-8 (cont.): Results reported by the laboratories* and the respective z-scores calculated using the FFP-RSD of 25 %

Compound				2,4-D (free acid)		Bromide ion		Dithiocarbamates (sum) expr. as CS_2	
Assigned Value [mg/kg]				0.278		41.4		0.615	
MRRL [mg/kg]				0.02		3.0		0.05	
Qn-RSD				27.9 %		18.0 %		23.1 %	
Lab code SRM7-	NRL-SRM	No. Compounds * Analysed / Correctly Found	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 %)
74		5 / 2	B	0.286	***0.12***			0.800	***1.20***
76		1 / 1	B					0.727	***0.73***
77		11 / 4	B	0.029	***-3.58***			0.345	***-1.76***
78		4 / 4	B	0.790#‡	***7.37***				
79	x	12 / 6	B	0.239	***-0.56***			0.660	***0.29***
80		14 / 6	B	0.206	***-1.04***	42.4	***0.10***	0.591	***-0.16***
82		1 / 1	B					0.480	***-0.88***
84		15 / 7	A	0.248	***-0.43***	41.0	***-0.03***	0.579	***-0.23***
85		10 / 4	B					0.479	***-0.88***
88		13 / 5	B	0.210	***-0.98***			0.705	***0.59***
89		14 / 6	B	0.146	***-1.90***	45.8	***0.43***	0.723	***0.70***
90		2 / 2	B						
91		6 / 3	B	0.310	***0.46***			0.626	***0.07***
92		12 / 4	B	0.210	***-0.98***	41.1	***-0.02***		
93		15 / 7	A	0.277	***-0.01***	40.9	***-0.04***	0.553	***-0.40***
94		1 / 1	B					0.550	***-0.42***
95		3 / 1	B						
96	x	14 / 7	A	0.363	***1.22***	41.3	***0.00***	0.934	***2.07***
97		3 / 2	B					0.498	***-0.76***
98		2 / 2	B			41.4	***0.00***	0.440	***-1.14***
99		16 / 8	A	0.362	***1.21***	46.5	***0.50***	0.460	***-1.01***
100		1 / 1	B					0.570	***-0.29***
101	x	6 / 3	B						
102		13 / 5	B	0.345	***0.96***	42.7	***0.13***	0.725	***0.72***
103	x	16 / 8	A	0.272	***-0.09***	42.0	***0.06***	0.695	***0.52***
104		9 / 4	B	0.209	***-0.99***			1.000	***2.50***
105		1 / 1	B					0.620	***0.03***
107		2 / 1	B					0.450	***-1.07***
108		8 / 2	B	0.260	***-0.26***			FN	***-3.68***
109	x	13 / 5	B	0.325	***0.68***	56.0	***1.42***	0.773	***1.03***
110	x	8 / 2	B	0.350	***1.04***			0.350	***-1.72***
111		1 / 1	B						
112		1 / 1	B					0.640	***0.16***
113	x	13 / 5	B	0.369	***1.31***			0.189	***-2.77***

* including chlorothalonil, cyromazine and fenbutatin oxide. #: outliers due to |z| > 5; ‡: outliers based on Grubbs' test with alpha = 0.01
** Categorisation based on scope (see Section 3.4.4)

	Compound			Ethephon		Glyphosate		Submitted Results [mg/kg]		
	Assigned Value [mg/kg]			0.210		0.827				
	MRRL [mg/kg]			0.02		0.02				
	Qn-RSD			25.2 %		34.5 %				
Lab code SRM7-	NRL-SRM	No. Compounds * Analysed / Correctly Found	Cat.**	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Chlorothalonil	Cyromazine	Fenbutatin Oxide
74		5 / 2	B							
76		1 / 1	B							
77		11 / 4	B					*0.126*	*0.181*	
78		4 / 4	B					*0.110*	*0.560*	*0.280*
79	x	12 / 6	B	0.267	***1.09***	0.576	***-1.21***	*0.103*	*0.078*	
80		14 / 6	B					*0.100*	*0.254*	*0.214*
82		1 / 1	B							
84		15 / 7	A			0.202	***-3.02***	*0.030*	*0.411*	*0.038*
85		10 / 4	B					*0.079*	*0.236*	*0.145*
88		13 / 5	B					*0.108*	*0.267*	*0.035*
89		14 / 6	B					*0.263*	*0.157*	*0.507*
90		2 / 2	B			0.412	***-2.01***	*0.050*		
91		6 / 3	B					*0.065*		
92		12 / 4	B					*0.033*	*0.111*	
93		15 / 7	A	0.227	***0.32***	0.694	***-0.64***	*0.128*	*0.141*	
94		1 / 1	B							
95		3 / 1	B					*0.043*		
96	x	14 / 7	A	0.212	***0.04***	0.456	***-1.79***	*0.146*		*0.169*
97		3 / 2	B					*0.087*		
98		2 / 2	B							
99		16 / 8	A	0.166	***-0.84***	0.813	***-0.07***	*0.195*	*0.392*	*0.216*
100		1 / 1	B							
101	x	6 / 3	B	0.265	***1.05***	0.940	***0.55***		*0.343*	
102		13 / 5	B	0.250	***0.76***			*0.076*		
103	x	16 / 8	A	0.199	***-0.21***	0.978	***0.73***	*0.123*	*0.327*	*0.416*
104		9 / 4	B					*0.121*	*0.186*	
105		1 / 1	B							
107		2 / 1	B					*FN*		
108		8 / 2	B					*0.190*		
109	x	13 / 5	B					*0.194*		*0.150*
110	x	8 / 2	B					*FN*		
111		1 / 1	B					*0.008*		
112		1 / 1	B							
113	x	13 / 5	B					*0.057*	*0.400*	*0.320*

Table 3-8 (cont.): Results reported by the laboratories* and the respective z-scores calculated using the FFP-RSD of 25 %

Compound				2,4-D (free acid)		Bromide ion		Dithiocarbamates (sum) expr. as CS_2	
Assigned Value [mg/kg]				0.278		41.4		0.615	
MRRL [mg/kg]				0.02		3.0		0.05	
Qn-RSD				27.9 %		18.0 %		23.1 %	
Lab code SRM7-	NRL-SRM	No. Compounds * Analysed / Correctly Found	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 %)
114		1 / 1	B					0.677	***0.40***
115		1 / 1	B					0.590	***-0.16***
116		6 / 3	B	0.422	***2.07***			1.170	***3.61***
118	x	12 / 4	B	0.040	***-3.42***			FN	***-3.68***
119		4 / 2	B					0.825	***1.37***
120		0 / 0							
121	x	11 / 4	B	0.270	***-0.12***				
122		2 / 2	B			32.9	***-0.82***		
123		16 / 8	A	0.400	***1.76***	38.0	***-0.32***	0.780	***1.07***
125		1 / 1	B					0.457	***-1.03***
126	x	1 / 1	B					0.593	***-0.14***
127		12 / 4	B	0.297	***0.27***				
128		4 / 1	B						
129		0 / 0							
130		12 / 4	B	0.125	***-2.20***			0.569	***-0.30***
133		4 / 2	B	0.150	***-1.84***				
135		1 / 1	B					0.550	***-0.42***
136		3 / 3	B			34.7	***-0.64***	0.542	***-0.47***
137		13 / 7	A	0.180	***-1.41***	35.0	***-0.61***	0.770	***1.01***
138		12 / 6	B	0.380	***1.47***	42.0	***0.06***	0.740	***0.81***
139		0 / 0							

* including chlorothalonil, cyromazine and fenbutatin oxide. #: outliers due to |z| > 5; ‡: outliers based on Grubbs' test with alpha = 0.01
** Categorisation based on scope (see Section 3.4.4)

	Compound			Ethephon		Glyphosate		Submitted Results [mg/kg]		
	Assigned Value [mg/kg]			0.210		0.827				
	MRRL [mg/kg]			0.02		0.02				
	Qn-RSD			25.2 %		34.5 %				
Lab code SRM7-	NRL-SRM	No. Compounds * Analysed / Correctly Found	Cat.**	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Chlorothalonil	Cyromazine	Fenbutatin Oxide
114		1 / 1	B							
115		1 / 1	B							
116		6 / 3	B					*0.075*		
118	x	12 / 4	B					*0.123*	*0.397*	*0.226*
119		4 / 2	B					*0.058*		
120		0 / 0								
121	x	11 / 4	B			1.070	***1.18***	*0.142*	*0.454*	
122		2 / 2	B					*0.079*		
123		16 / 8	A	0.190	***-0.38***	0.620	***-1.00***	*0.025*	*0.380*	*0.350*
125		1 / 1	B							
126	x	1 / 1	B							
127		12 / 4	B					*0.133*	*0.351*	*0.181*
128		4 / 1	B			0.962	***0.65***			
129		0 / 0								
130		12 / 4	B					*0.056*		*0.087*
133		4 / 2	B					*0.105*		
135		1 / 1	B							
136		3 / 3	B	0.163	***-0.90***					
137		13 / 7	A	0.500	***5.52***	1.130	***1.47***	*FN*	*0.330*	*0.067*
138		12 / 6	B	0.190	***-0.38***			*0.170*	*0.440*	
139		0 / 0								

Table 3-9: EU and EFTA laboratories ranked by the absolute z-scores achieved for each compound
(where 2 < |z| ≤ 3 – "questionable" – the ranking position is shown in bold, and where |z| > 3 – "unacceptable" – in bold and italic)

Compound				2,4-D (free acid)	Bromide ion	Dithiocarbamates (sum) expr. as CS_2	Ethephon	Glyphosate
Assigned Value [mg/kg]				0.278	41.4	0.615	0.210	0.827
MRRL [mg/kg]				0.02	3.0	0.05	0.02	0.02
Qn-RSD				27.9 %	18.0 %	23.1 %	25.2 %	34.5 %
No. Labs reporting results				70	45	87	33	42
Lab code SRM7-	NRL-SRM	No. Compounds* Analysed / Corr. Found	Cat.	ranking position	ranking position	ranking position	ranking position	ranking position
1		15 / 7	A	55		38	18	21
2		12 / 6	B	27			16	8
3		16 / 8	A	50	37	4	30	16
4	x	16 / 8	A	48	29	71	5	2
6	x	14 / 6	B	60	12	5		
7		16 / 8	A	29	21	26	28	32
8		3 / 1	B			33		
9		12 / 4	B	***69***	26			
10	x	13 / 4	B	21		***82 (FN)***	11	25
11		11 / 5	B	49	16	55		26
12		16 / 8	A	28	3	12	3	4
13		11 / 6	B	57		72	***33***	
14	x	16 / 8	A	35	38	***80***	14	20
15		10 / 3	B	10		69		
17		16 / 8	A	33	39	42	15	23
18		16 / 6	B	30	23	***82 (FN)***	***32 (FN)***	29
19	x	10 / 4	B	6				
20	x	14 / 6	B	3			2	**37**
21		15 / 7	A	4	***43***	22	29	30
22		10 / 5	B	51	13	52		9
23	x	13 / 4	B	40		28		
24	x	12 / 6	B	37		9	8	6
25		15 / 8	A	18	22	8	8	31
26		1 / 1	B					
27	x	0 / 0						
28		16 / 8	A	12	31	68	25	10
29		16 / 8	A	11	27	53	6	19
30	x	16 / 8	A	9	41	6	1	**36**
31		16 / 7	A	13	30	76	26	**38**
32	x	14 / 6	B	32			***31***	21
33	x	3 / 2	B			26		
34		12 / 6	B	23		62		13
35		1 / 1	B			22		
36		11 / 4	B	19	5	50		16
37	x	13 / 5	B	1		***87***	24	
38		11 / 5	B	61	***45***	45		
39		1 / 0	B					
40		1 / 1	B			54		

#: outliers due to |z| > 5; ‡: outliers based on Grubbs' test with alpha = 0.01

Table 3-9 (cont.): EU and EFTA laboratories ranked by the absolute z-scores achieved for each compound
(where 2 < |z| ≤ 3 – "questionable" – the ranking position is shown in bold, and where |z| > 3 – "unacceptable" – in bold and italic)

Compound				2,4-D (free acid)	Bromide ion	Dithiocarbamates (sum) expr. as CS_2	Ethephon	Glyphosate
Assigned Value [mg/kg]				0.278	41.4	0.615	0.210	0.827
MRRL [mg/kg]				0.02	3.0	0.05	0.02	0.02
Qn-RSD				27.9 %	18.0 %	23.1 %	25.2 %	34.5 %
No. Labs reporting results				70	45	87	33	42
Lab code SRM7-	NRL-SRM	No. Compounds* Analysed / Corr. Found	Cat.	ranking position	ranking position	ranking position	ranking position	ranking position
41		9 / 2	B	58				
42		1 / 1	B			70		
43		11 / 4	B	40	7	9		5
44		2 / 2	B		10	14		
45		1 / 1	B		35			
46		5 / 3	B		34	1		
47	x	16 / 8	A	63	40	39	17	7
48		0 / 0						
49		11 / 3	B	16	18	21		
50	x	14 / 6	B	25	25	43		
52		1 / 1	B			32		
53		11 / 5	B	36	19	40		
54	x	7 / 2	B	38				
55	x	7 / 4	B			14	10	
56		11 / 4	B	25	***44 (FN)***	34		
57		3 / 2	B			***86***		1
58		1 / 1	B			19		
60		15 / 7	A	19	36	22	18	34
61		4 / 2	B					
62	x	13 / 5	B	16	32	1		
64		2 / 1	B			51		
66		16 / 8	A	39	11	20	27	12
67		1 / 1	B			14		
70		1 / 1	B					
72		12 / 4	B	52		72		
73		3 / 3	B		17	58		
74		5 / 2	B	6		66		
76		1 / 1	B			48		
77		11 / 4	B	***68***		75		
78		4 / 4	B	***70***#‡				
79	x	12 / 6	B	30		29	23	28
80		14 / 6	B	46	13	12		
82		1 / 1	B			56		
84		15 / 7	A	22	5	25		***39***
85		10 / 4	B			57		
88		13 / 5	B	43		44		
89		14 / 6	B	63	24	46		
90		2 / 2	B					**35**

#: outliers due to |z| > 5; ‡: outliers based on Grubbs' test with alpha = 0.01

Table 3-9 (cont.): EU and EFTA laboratories ranked by the absolute z-scores achieved for each compound (where 2 < |z| ≤ 3 – "questionable" – the ranking position is shown in bold, and where |z| > 3 – "unacceptable" – in bold and italic)

Compound				2,4-D (free acid)	Bromide ion	Dithiocarbamates (sum) expr. as CS_2	Ethephon	Glyphosate
Assigned Value [mg/kg]				0.278	41.4	0.615	0.210	0.827
MRRL [mg/kg]				0.02	3.0	0.05	0.02	0.02
Qn-RSD				27.9 %	18.0 %	23.1 %	25.2 %	34.5 %
No. Labs reporting results				70	45	87	33	42
Lab code SRM7-	NRL-SRM	No. Compounds* Analysed / Corr. Found	Cat.	ranking position	ranking position	ranking position	ranking position	ranking position
91		6 / 3	B	23		7		
92		12 / 4	B	43	4			
93		15 / 7	A	2	8	35	12	14
94		1 / 1	B			37		
95		3 / 1	B					
96	x	14 / 7	A	54	2	**77**	3	33
97		3 / 2	B			49		
98		2 / 2	B		1	65		
99		16 / 8	A	53	28	58	21	3
100		1 / 1	B			29		
101	x	6 / 3	B				22	11
102		13 / 5	B	42	15	47	18	
103	x	16 / 8	A	4	9	41	7	18
104		9 / 4	B	45		**78**		
105		1 / 1	B			1		
107		2 / 1	B			63		
108		8 / 2	B	14		***82 (FN)***		
109	x	13 / 5	B	34	42	60		
110	x	8 / 2	B	46		74		
111		1 / 1	B					
112		1 / 1	B			14		
113	x	13 / 5	B	56		**79**		
114		1 / 1	B			36		
115		1 / 1	B			14		
116		6 / 3	B	**65**		***81***		
118	x	12 / 4	B	***67***		***82 (FN)***		
119		4 / 2	B			67		
120		0 / 0						
121	x	11 / 4	B	8				27
122		2 / 2	B		33			
123		16 / 8	A	59	20	63	13	24
125		1 / 1	B			60		
126	x	1 / 1	B			11		
127		12 / 4	B	15				
128		4 / 1	B					15
129		0 / 0						
130		12 / 4	B	**66**		31		
133		4 / 2	B	61				

#: outliers due to |z| > 5; ‡: outliers based on Grubbs' test with alpha = 0.01

3.4.4 Laboratory classification based on scope

All participating laboratories that have reported results were classified into Category A or B based on their scope as reflected by the number of pesticides analysed out of the total number of pesticides present in the Test Item. ***Chlorothalonil***, ***cyromazine*** and ***fenbutatin oxide***, the quantitative performance evaluation of which is only presented for informative purposes were also included in the classification based on scope. Following the rules defined in the General Protocol (3rd Edition, see **Appendix 9**) a laboratory should have a) detected at least 7 out of the 8 pesticides present in the Test Item, and b) not reported any false positive results in order to be classified into Category A. In total 23 EU and EFTA labs (21 %) were classified into Category A and 87 (79 %) were classified into Category B. One of the 4 Third Country laboratories was classified into Category A, and the other 3 were classified into Category B.

Table 3-10 and **Table 3-11** show the laboratories classified into Category A and B, respectively. For informative purposes the AAZ was calculated for all laboratories within Category A having obtained z-scores for each of the 5 compounds for which z-scores were assigned (***2,4-D***, ***bromide***, ***dithiocarbamates***, ***ethephon*** and ***glyphosate***). ***Chlorothalonil***, ***cyromazine*** and ***fenbutatin oxide*** were excluded from this AAZ evaluation as no valid z-scores were calculated.

Table 3-10: Category A laboratories ordered by lab-codes

Lab-code SRM7-	NRL-SRM	No. Compounds analysed / corr. found	z-scores					AAZ [1]	Submitted results [mg/kg]		
			2.4-D (free acid)	Bromide ion	Dithiocarbamates (as CS_2)	Ethephon	Glyphosate		*Chlorothalonil*	*Cyromazine*	*Fenbutatin Oxide*
1		15 / 7	1.28		0.42	0.76	0.93	not calc.[3]	***0.123***	***0.437***	***0.389***
3		16 / 8	1.11	-1.19	0.04	-1.77	-0.66	0.96	***0.016***	***0.390***	***0.254***
4	x	16 / 8	1.06	0.51	-1.59	-0.10	0.05	0.66	***0.097***	***0.459***	***0.201***
7		16 / 8	0.53	0.39	0.26	-1.50	-1.79	0.90	***0.154***	***0.280***	***0.116***
12		16 / 8	0.52	-0.01	-0.16	-0.04	0.07	0.16	***0.109***	***0.380***	***0.311***
14	x	16 / 8	-0.69	1.20	3.15	-0.53	0.89	1.29	***0.153***	***0.418***	***0.175***
17		16 / 8	0.65	1.32	-0.55	0.59	0.98	0.82	***0.060***	***0.129***	***0.045***
21		15 / 7	-0.09	3.48	0.23	-1.60	-1.51	1.38	***0.068***		***0.137***
25		15 / 8	-0.35	0.41	0.11	-0.25	1.51	0.53	***0.093***	***0.398***	***0.261***
28		16 / 8	0.23	-0.66	-1.39	-1.24	-0.50	0.81	***0.114***	***0.108***	***0.289***
29		16 / 8	-0.19	-0.48	0.82	0.19	0.78	0.49	***0.098***	***0.035***	***0.230***
30	x	16 / 8	-0.13	-1.35	0.07	0.00	-2.32	0.77	***0.122***	***0.287***	***0.323***
31		16 / 7	0.26	0.59	-1.98	-1.26	-2.86	1.39	***0.134***	***FN***	***0.090***
47	x	16 / 8	-1.90	1.33	0.45	0.67	0.35	0.94	***0.098***	***0.200***	***0.042***
60		15 / 7	0.36	-1.14	0.23	0.76	-1.97	0.89	***0.139***	***0.340***	
66		16 / 8	0.86	0.09	-0.20	1.47	-0.58	0.64	***0.117***	***0.409***	***0.070***
84		15 / 7	-0.43	-0.03	-0.23		-3.02	not calc.[3]	***0.030***	***0.411***	***0.038***
93		15 / 7	-0.01	-0.04	-0.40	0.32	-0.64	0.29	***0.128***	***0.141***	
96	x	14 / 7	1.22	0.00	2.07	0.04	-1.79	1.03	***0.146***		***0.169***
99		16 / 8	1.21	0.50	-1.01	-0.84	-0.07	0.72	***0.195***	***0.392***	***0.216***
103	x	16 / 8	-0.09	0.06	0.52	-0.21	0.73	0.32	***0.123***	***0.327***	***0.416***
123		16 / 8	1.76	-0.32	1.07	-0.38	-1.00	0.91	***0.025***	***0.380***	***0.350***
137		13 / 7	-1.41	-0.61	1.01	5.52	1.47	1.90	***FN***	***0.330***	***0.067***

1) AAZ: Average of Absolute z-scores, calculated for informative purposes only for the labs in Category A with 5 or more z-scores. For the calculation of the AAZ the value "5" was applied where the z-score was higher than 5. Chlorothalonil, cyromazine and fenbutatin oxide were not considered in the AAZ calculation, because no assigned values could be established.
2) [FN]: false negative results
3) AAZ was not calculated as the number of available z-scores is smaller than 5

Table 3-11: Category B laboratories ordered by their lab-codes

Lab code SRM7-	NRL-SRM	No. Compounds analysed / corr. found	z-scores					Submitted results [mg/kg]		
			2.4-D (free acid)	Bromide ion	Dithiocarbamates (as CS_2)	Ethephon	Glyphosate	*Chlorothalonil*	*Cyromazine*	*Fenbutatin Oxide*
2		12 / 6	0.49			0.63	0.38	***0.137***	***0.448***	***0.550***
6	x	14 / 6	-1.77	-0.09	-0.05			***0.172***	***0.145***	***0.140***
8		3 / 1			-0.36					
9		12 / 4	4.07	0.48				***0.073***	***0.546***	
10	x	13 / 4	0.37		-3.68 (FN)	-0.30	-1.09			***0.042***
11		11 / 5	-1.09	0.14	0.83		-1.12		***0.559***	
13		11 / 6	-1.50		-1.66	8.00		***0.052***	***0.555***	***0.199***
15		10 / 3	0.16		1.43				***0.299***	
18		16 / 6	-0.56	-0.42	-3.68 (FN)	-3.62 (FN)	1.37	***0.095***	***0.120***	***0.210***
19	x	10 / 4	0.12					***0.113***	***0.443***	***0.162***
20	x	14 / 6	0.03			0.02	2.63	***0.182***	***0.467***	***0.306***
22		10 / 5	-1.12	-0.10	0.81		-0.39		***0.333***	
23	x	13 / 4	-0.89		-0.27			***FN***	***0.400***	***0.170***
24	x	12 / 6	-0.81		0.13	-0.25	-0.29	***0.054***	***0.423***	
26		1 / 1						***0.061***		
32	x	14 / 6	-0.58			-3.18	0.93	***0.099***	***0.335***	***0.082***
33	x	3 / 2			0.26			***0.093***		
34		12 / 6	0.46		1.05		0.62	***0.054***	***0.412***	***0.193***
35		1 / 1			0.23					
36		11 / 4	0.36	0.03	-0.77		0.66			
37	x	13 / 5	0.00		4.98	1.10		***0.148***		***0.190***
38		11 / 5	-1.84	8.19	0.68			***0.215***	***0.125***	
39		1 / 0						***FN***		
40		1 / 1			-0.83					
41		9 / 2	1.53						***0.421***	
42		1 / 1			-1.50					
43		11 / 4	0.89	0.04	-0.13		0.26			
44		2 / 2		-0.08	-0.16					
45		1 / 1		-1.05						
46		5 / 3		-0.95	-0.03			***0.195***		
49		11 / 3	-0.32	-0.18	-0.22					
50	x	14 / 6	-0.47	-0.46	0.57			***0.155***	***0.186***	***0.153***
52		1 / 1			0.31					
53		11 / 5	0.72	0.30	0.51			***0.142***		***0.134***
54	x	7 / 2	-0.85					***0.130***		
55	x	7 / 4			-0.16	0.29		***0.091***	***0.350***	
56		11 / 4	-0.47	-3.71 (FN)	-0.39			***0.140***	***0.490***	
57		3 / 2			4.07		0.00			
58		1 / 1			-0.18					
61		4 / 2						***0.124***	***0.343***	
62	x	13 / 5	0.32	-0.71	0.03			***0.050***		***0.110***
64		2 / 1			-0.77					
67		1 / 1			-0.16					
70		1 / 1						***0.075***		
72		12 / 4	1.18		1.66			***0.080***	***0.390***	
73		3 / 3		0.16	-1.01			***0.140***		

(FN): false negative result

Table 3-11 (cont.): Category B laboratories ordered by their lab-codes

Lab code SRM7-	NRL-SRM	No. Compounds analysed / corr. found	z-scores					Submitted results [mg/kg]		
			2.4-D (free acid)	Bromide ion	Dithiocarbamates (as CS_2)	Ethephon	Glyphosate	*Chlorothalonil*	*Cyromazine*	*Fenbutatin Oxide*
74		5 / 2	0.12		1.20					
76		1 / 1			0.73					
77		11 / 4	-3.58		-1.76			***0.126***	***0.181***	
78		4 / 4	7.37					***0.110***	***0.560***	***0.280***
79	x	12 / 6	-0.56		0.29	1.09	-1.21	***0.103***	***0.078***	
80		14 / 6	-1.04	0.10	-0.16			***0.100***	***0.254***	***0.214***
82		1 / 1			-0.88					
85		10 / 4			-0.88			***0.079***	***0.236***	***0.145***
88		13 / 5	-0.98		0.59			***0.108***	***0.267***	***0.035***
89		14 / 6	-1.90	0.43	0.70			***0.263***	***0.157***	***0.507***
90		2 / 2					-2.01	***0.050***		
91		6 / 3	0.46		0.07			***0.065***		
92		12 / 4	-0.98	-0.02				***0.033***	***0.111***	
94		1 / 1			-0.42					
95		3 / 1						***0.043***		
97		3 / 2			-0.76			***0.087***		
98		2 / 2		0.00	-1.14					
100		1 / 1			-0.29					
101	x	6 / 3				1.05	0.55		***0.343***	
102		13 / 5	0.96	0.13	0.72	0.76		***0.076***		
104		9 / 4	-0.99		2.50			***0.121***	***0.186***	
105		1 / 1			0.03					
107		2 / 1			-1.07			***FN***		
108		8 / 2	-0.26		-3.68 (FN)			***0.190***		
109	x	13 / 5	0.68	1.42	1.03			***0.194***		***0.150***
110	x	8 / 2	1.04		-1.72			***FN***		
111		1 / 1						***0.008***		
112		1 / 1			0.16					
113	x	13 / 5	1.31		-2.77			***0.057***	***0.400***	***0.320***
114		1 / 1			0.40					
115		1 / 1			-0.16					
116		6 / 3	2.07		3.61			***0.075***		
118	x	12 / 4	-3.42		-3.68 (FN)			***0.123***	***0.397***	***0.226***
119		4 / 2			1.37			***0.058***		
121	x	11 / 4	-0.12				1.18	***0.142***	***0.454***	
122		2 / 2		-0.82				***0.079***		
125		1 / 1			-1.03					
126	x	1 / 1			-0.14					
127		12 / 4	0.27					***0.133***	***0.351***	***0.181***
128		4 / 1					0.65			
130		12 / 4	-2.20		-0.30			***0.056***		***0.087***
133		4 / 2	-1.84					***0.105***		
135		1 / 1			-0.45					
136		3 / 3		-0.65	-0.50	-0.90				
138		12 / 6	1.47	0.06	0.77	-0.38		***0.170***	***0.440***	

(FN): false negative result

3.4.5 Laboratory feedback in case of poor performance

As a follow-up measure to this EUPT, participating laboratories that had achieved questionable or unacceptable z-scores were asked to provide, where possible, explanations for their poor performance. By asking laboratories to provide this information the Organizers aimed to emphasize to the laboratories the importance of tracing back potential sources of errors so that these can be avoided in the future. A compilation of this information is given in **Appendix 8**. The main aim of this compilation is to inform the laboratories about possible sources of errors that should be avoided. This information furthermore provides input to NRLs on how to better assist labs to improve their performance. In the case of ***chlorothalonil***, ***cyromazine*** and ***fenbutatin oxide*** the laboratories were asked to provide their explanations for underperformance based on the z-scores distributed in the preliminary report, which were calculated using the median of the entire population, but excluding outliers.

In many cases the laboratories were not able to fully clarify the reasons for their bad performance. The most common explanations for poor performance provided by the laboratories concerned: a) the use of inappropriate procedures (15×, mainly concerning ***cyromazine*** and ***fenbutatin oxide***); b) the lack of experience with the analyte or the matrix in question (11×); c) no or inappropriate correction for recovery (10×, mainly concerning ***cyromazine*** and ***fenbutatin oxide***); d) wrong concentration of standard solutions (5×); e) wrong evaluation or interpretation of the measured data (5×); f) analyte concentration too close to Reporting Limit or LOQ of the lab (4×) and g) errors when applying the analytical procedure (4×). Additional reasons included instrumental difficulties, non-consideration of matrix effects and cross contamination.

3.5 Methodological Information

3.5.1 Analytical methods used

Detailed information about the analytical methods used by the laboratories can be found in **Appendix 7**.

2,4-D analysis was undertaken by 70 laboratories with none of them reporting any false negative results. All laboratories provided information about the method-type used. 56 of the labs (80 %) employed methods involving acetonitrile-based extraction, 54 labs thereof (77 % overall) employed QuEChERS-type methodologies and 2 labs "dilute and shoot" approaches. Out of the 54 labs using QuEChERS type methods 3 employed the original (unbuffered) approach and 51 a buffered one (48× citrate buffered and 3× acetate buffered). A further 7 labs (10 %) employed methods involving extraction with methanol, 2 of them using the ChemElut method and the other 4 "dilute and shoot" approaches (not involving liquid-liquid partitioning). 3 labs (4 %) used ethyl acetate-based methods and a further 3 labs (4 %) employed S19 / Luke type methods involving extraction with acetone followed by partitioning into dichloromethane or cyclohexane/ethyl acetate. 1 lab employed a method involving extraction with water, derivatization and solid supported liquid/liquid extraction (SLE) with dichloromethane.

Although the residue definition stated in the Pesticides Target List referred to the free acid only, implying that no cleavage step was necessary, 10 labs (14 %) still conducted alkaline hydrolysis with 8 of them employing the QuEChERS-based method for acidic pesticides involving alkaline hydrolysis published on the EURL-website.

Furthermore, 3 labs (4 % of all) employed dispersive SPE cleanup using PSA, which is not recommended when dealing with acidic analytes as PSA has the tendency to remove organic acids from the extracts thus leading to substantial losses and low recoveries. These 3 labs reported low recoveries as well as negative z-scores despite applying a correction for recovery via recovery factors.

63 labs (90 % overall) indicated the use of LC-MS/MS and 1 lab the use of LC-ITD. 3 labs (5 %) employed GC-techniques following derivatization with pentafluorobenzyl***bromide***, trimethylsulfonium hydroxide or tetrabutylammonium hydroxide/iodomethane.

Bromide was analysed by 45 laboratories with 1 of them reporting a false negative result. All laboratories provided information about the method-type used. 33 labs (71 % overall) employed methods involving derivatization and partitioning into a non-polar solvent (32× ethyl acetate and 1× hexane) and gas chromatographic analysis (7× GC-ECD and 6× GC-MSD). 28 of these 33 labs (62 % overall) employed 1,2-propylene oxide and 5 labs ethylene oxide for derivatization. 12 labs employed methods involving extraction with water (in 1 case water/methanol mixture) followed by direct determinative analysis. 9 of these labs employed ion-chromatography combined with conductivity detection, two labs employed LC-UV/DAD and one lab ICP-MS.

Dithiocarbamates were analysed by 87 laboratories with 4 of them reporting false negative results. All but one lab provided information about the methodology used. Out of these labs 38 (44 % overall) employed methods involving reductive cleavage to CS_2 followed by its derivatization and spectrophotometric detection, 23 of them (26 % overall) derivatized the released CS_2 with MeOH/KOH to xanthogenate (EN-12396-3-type methods) and 15 labs (17 % overall) with copper-(II)-acetate to diethanolamine/ethanol (EN-12396-1-type methods). 33 laboratories (38 % overall) indicated the use of methods involving cleavage to CS_2 and liquid-liquid-partitioning (LLP) into iso-octane followed by GC-analysis in combination with various detectors as follows: MSD (16×), FPD/PFPD (9×) and ECD (6×). 16 laboratories (18 % overall) employed methods involving cleavage to CS_2, headspace sampling and GC-analysis, 12 of them performed direct headspace sampling (EN-12396-2-type methods) and the other 4 labs headspace sampling with SPME fibres.

Out of the 87 labs analysing ***dithiocarbamates*** 38 labs (44 % overall) employed spectrophotometeric detection, 25 labs (29 %) GC-MSD, 13 labs (15 %) GC-FPD, 8 labs (9 %) GC-ECD and 2 labs GC-ITD. Internal standards were employed by 8 labs as follows: thiophene (3×), chloroform (2×), iodoethane, dichloro-methane, $^{13}CS_2$ and a PCB.

Ethephon was analysed by 33 laboratories with one of them reporting a false negative result. All 33 laboratories provided information about the method-type used. Out of these labs 27 (82 % overall) employed QuPPe-type methods involving extraction/dilution with a water-miscible solvent and/or water followed directly by determinative analysis via LC-MS/MS (26×) or LC-MS (1×). 25 of these labs extracted the sample following addition of water/methanol, in most cases acidified with formic acid and in one case partitioned with dichloromethane for cleanup. 2 labs extracted purely with water. 22 of the labs employed QuPPe-type methods (66 % overall) according to the protocol published by the EURL-SRM. 5 labs (14 %) employed methods involving cleavage to ethylene under alkaline conditions followed by headspace sampling and determinative analysis by GC-FID (4×) or GC-MSD (1×). One lab employed an approach involving derivatization of ***ethephon*** with diazomethane and partitioning into ethyl acetate followed by GC-FPD analysis.

27 labs (82 % overall) indicated the use of LC with mass spectrometric detection (MS/MS or MS) and 6 labs (18 % overall) the use of GC-techniques, thereof 5 (15 % overall) in combination with headspace sampling.

Out of the 27 labs (N) employing QuPPe-type methods 20 labs (67 % of N) indicated the use of isotopically labelled ***ethephon*** as ISTD and the other 7 (33 % of N) did not. One of the labs employed isotope labelled ***glyphosate*** as ISTD, which is not recommended for the compensation of matrix effects on ***ethephon***. All 7 labs not employing isotopically labelled ***ethephon*** as ISTD employed matrix-matched calibrations using the Blank Material provided by the Organizers. Isotopically labelled ***ethephon*** as ISTD was also used by one of the labs that conducted cleavage to ethylene followed by GC-MSD analysis.

Glyphosate was analysed by 39 laboratories with none of them reporting a false negative result and all of them delivering data on the methodology applied. 21 of the labs (54 % overall) employed QuPPe-type methods involving extraction with a water-miscible solvent and/or water followed by direct determinative analysis using LC-MS/MS (19 labs), LC-MS (1 lab) or LC-orbitrap (1 lab). 17 labs extracted their samples with methanol/water (1× acidified with hydrochloric acid and 16× acidified with formic acid, thereof 1× partitioned with dichloromethane for cleanup) and 4 labs extracted their samples with water (2× pure and 2× acidified with formic acid). 15 labs (38 % overall) followed the QuPPe-protocol published on the EURL-website. 14 labs (36 %) employed methods involving extraction with methanol or methanol/water in presence of dichloromethane or ethyl acetate for cleanup followed by derivatization with FMOC and determination by LC-MS/MS (13×) or LC-FLD (1×). 3 labs employed methods involving LC-separation and post-column oxidation with OPA, and 1 lab a method involving derivatization with isobutyl chloroformate followed by LC-MS/MS analysis.

Overall 35 of the 39 labs (90 %) indicated the use of LC with mass spectrometric detection (including MS/MS, MS and orbitrap), whereas 4 labs (10 %) employed LC-FLD.

Overall 28 labs (72 % of all) employed isotope labelled ***glyphosate*** as ISTD. Out of the 21 labs (N) employing QuPPe-type methods without any derivatization 19 labs (90 % of N) indicated the use of isotopically labelled ***glyphosate*** as ISTD, whereas the other 2 labs employed matrix-matched calibrations using the Blank Material provided by the Organizer. Isotopically labelled ***glyphosate*** was also employed by 8 out of the 13 labs employing derivatization with FMOC followed by LC-MS/MS analysis as well as by the lab applying derivatization with isobutyl chloroformate.

Chlorothalonil was analysed by 77 laboratories with 4 of them reporting a false negative result. All laboratories provided information about the method-type used. 43 of the labs (56 % overall) employed methods involving acetonitrile extraction with 40 of them (52 % overall) employing QuEChERS-type methodologies. Lentils proved to be a quite challenging commodity for the analysis of ***chlorothalonil***. Compared to EUPT-FV12 (with the equally challenging leek homogenate as test item) there has been a clear shift away from using the standard (buffered or original) QuEChERS approaches towards the use of the modified QuEChERS approach published on the EURL-website specific, which involves extraction under acidic conditions. In parallel there has also been a clear trend towards ethyl acetate-based and S19 / Luke-type methodologies, that have been shown to be more suitable for this compound than the buffered or the original QuEChERS methodologies. Out of the 40 labs employing QuEChERS-type methodologies 23 labs conducted the extraction/partitioning step under acidic conditions. 21 of these labs employed the modified QuEChERS approach for ***chlorothalonil*** published on the EURL-Website involving acidification with sulfuric acid with one of them additionally employing buffering salts in the partitioning step. The other two labs employed formic or acetic acid for acidification with the latter additionally employing buffering salts in the partitioning step. 14 labs (18 % overall) employed ethyl acetate-based methods with 2 of them acidifying the sample with acetic acid and one with sulfuric acid during the extraction step. A further 16 labs (21 % overall) used methods involving extraction with acetone (S19 / Luke-type methods) and 4 labs used other types of methods.

Out of the 40 labs employing QuEChERS-type methodologies 19 used PSA sorbent during the dSPE-cleanup, which is not recommended as it can lead to losses of ***chlorothalonil*** that is sensitive to high pH-values. 7 out of these 19 labs acidified during the extraction/partitioning step and were thus less affected by such PSA-induced ***chlorothalonil*** losses as the acidity of the extract prevented the pH from rising too high during cleanup with PSA. Most of the labs employing PSA reported results with negative z-scores and in 3 cases false negative results.

2 labs (3 % overall) indicated the use of LC-MS/MS whereas 75 labs employed GC approaches as follows: GC/MSD (25×); GC-MS/MS (25×); GC [μ]ECD (15×); GC-ITD (8×); GC-NPD (1×) and GC-TOF (1×).

Cyromazine was analysed by 55 laboratories with one of them reporting a false negative result. 24 of the labs (43 % overall) employed methods involving acetonitrile extraction with 23 labs (42 % overall) employing QuEChERS-type methodologies. 26 labs (9 %) employed "dilute and shoot" approaches. In 25 cases the sample was extracted with a methanol/water mixture (thereof in 21 cases following the QuPPe protocol published by the EURL-SRM which involves extraction with methanol/water acidified with formic acid), in 2 cases with methanol and in one case with acetonitrile. 4 labs (7 % overall) employed ethyl acetate-based methods and 1 lab (2 % overall) a method involving extraction with acetone (S19 / Luke type).

53 labs (96 % overall) indicated the use of LC-MS/MS, 1 lab the use of GC-MS/MS and further 1 lab the use of GC-MSD.

Fenbutatin Oxide was analysed by 44 laboratories with none of them reporting a false negative result. All laboratories provided information about the method-type used. 33 of the labs (75 % overall) employed methods involving acetonitrile extraction with one lab employing a "dilute and shoot" approach and 32 labs (73 % overall) employing QuEChERS-type methodologies. Out of these 32 labs employing QuEChERS type methodologies 2 conducted the extraction/partitioning step under acidic conditions and further one conducted the extraction under acidic conditions followed by a partitioning step using the buffering salts. All other labs employed the original (4×) or a buffered (20× citrate, 3× acetate) QuEChERS approach. Most of the labs employing QuEChERS-type methodologies experienced too low recoveries and had, therefore, to correct their results for recovery. 7 labs (16 %) employed ethyl acetate-based methods with 2 of them acidifying the sample with acetic acid during the extraction step. 2 labs (4 %) used methods involving extraction with acetone (S19 / Luke type). 3 labs employed "dilute and shoot" approaches using methanol (2×) and acetonitrile (1×) for dilution.

39 of the labs (89 % overall) indicated the use of LC-MS/MS, 2 labs used LC-MS, 2 labs used LC-ITD and one lab employed GC-MS following methylation of ***fenbutatin oxide*** with t-butyl methyl ether/methyl magnesium chloride reagent.

3.5.2 Calibration approaches

Matrix-matched calibrations were employed in 73 % of the cases, including 15 % of the cases where the approach of standard additions was used. In 27 % of the cases solvent-based calibration solutions were employed by the participants. Among the 64 cases where standard additions approaches were employed 49 concerned standard additions to sample portions (where correction of results for recovery is included) and 15 to aliquots of sample extracts.

Furthermore, more than 98 % of the reported results were derived from multi-level calibrations (including those cases where standard additions approaches were used). Single level calibrations were applied in just 6 of the 439 cases.

In 58 cases laboratories employed isotopically labelled analogues of the target compounds to correct for recovery and/or to compensate for the influence of matrix on measurement or derivatization. Although the use of isotopically labelled ISTDs in principle obviates the need for matrix-matching, laboratories employed matrix-matching in 43 (= 74 %) of those 58 cases (this includes all cases where the approach of standard additions was employed).

3.5.3 Correction of results for recovery

As shown in **Table 3-12** correction of results for recovery approaches were applied in 156 cases, which correspond to 36 % of all results received.

In the case of **chlorothalonil**, **cyromazine** and **fenbutatin oxide**, for which the recoveries achieved using multiresidue methods were in many cases quite low, laboratories have frequently corrected their results for recovery using a recovery factor (10×, 11× and 10×, respectively) or via standard additions to sample portions (10×, 10× and 11×, respectively). For ***chlorothalonil*** and ***fenbutatin oxide*** there are, to our knowledge, currently no isotopically labelled analogues available on the market that could be used for correction of results for recovery. For ***cyromazine*** there is an isotope labelled analogue available, but only 8 out of the 55 laboratories analysing this compound used it in the current PT.

In the case of **2,4-D** only one lab used the commercially available isotopically labelled ***2,4-D*** as ISTD, however, several labs employed other acidic compounds with similar physico-chemical behavior to achieve a rough correction of results for recovery, namely 4-chloro-2,5-dimethyl-phenoxy-acetic acid, MCPA-D6, MCPA-D3 and bentazone-D6. Correction of results for recovery for this compound was mostly performed using a recovery factor (7×) or the standard addition approach (9×).

Glyphosate and **ethephon** were mostly analysed by "dilute and shoot" type methods which provide good recoveries but are typically affected by strong matrix-induced effects in LC-MS/MS measurement. In 79 % and 75 % of the cases, respectively, recovery-correction was applied with isotopically labelled ISTDs being the predominant approach. If added at the beginning of the procedure the isotopically labelled ISTD can help to automatically compensate for recovery and matrix-effect. In many labs the use of isotopically labelled ISTDs was combined with the standard addition approach. Out of the 28 labs using isotopically labelled ***glyphosate*** as ISTD 19 employed "dilute and shoot" methodologies and 9 applications involving derivatization. In the case of ***ethephon*** 20 labs employed "dilute and shoot" approaches and just 1 lab an application involving derivatization.

Result corrections for recovery were rather the exception in the case of **bromide** (7 % of all results) and **dithiocarbamates (as CS_2)** (14 % of all results) as the recoveries achieved by the laboratories for these two compounds were within the range of 70 % and 120 % in the vast majority of the cases. Also, matrix effects have a rather miner impact on the analysis of these two compounds.

Table 3-12: Overview concerning correction of results for recovery applied by labs on their submitted results

Are results recovery corrected?	2.4-D (free acid)	Bromide ion	Dithiocarbamates	Ethephon	Glyphosate	Chlorothalonil	Cyromazine	Fenbutatin oxide	Sum
Yes	16 (23 %)	3 (7 %)	12 (14 %)	24 (75 %)	31 (79 %)	20 (27 %)	29 (54 %)	21 (48 %)	156 (36 %)
Yes-1: via recovery factor	7 (10 %)	–	5 (6 %)	1 (3 %)	–	10 (14 %)	11 (20 %)	10 (23 %)	**44 (10 %)**
Yes-2: via Standard addition	8	3	6	2	2	10	10	11	**52 (12 %)**
Yes-3: via IL-ISTD	–	–	–	12	18	–	5	–	**35 (8 %)**
Yes-4: via combination of 2 and 3	1	–	–	9	10	–	3	–	**23 (5 %)**
Yes-5: via procedural calibration	–	–	1	–	1	–	–	–	**2 (0.5 %)**
No	54	41	71	8	8	53	25	23	**283 (64 %)**
Overall SUM	**70**	**44**	**83**	**32**	**39**	**73**	**54**	**44**	**439**

In the 44 cases where correction of results for recovery using a recovery figure was applied the respective recovery experiments were conducted in all cases within the same batch using the Blank Material provided by the Organizers. 16 labs used a factor based on just one recovery experiment, 14 labs based on 2 replicates, 9 labs based on 3 replicates, and one lab each based on 4, 5 or > 5 replicate recovery experiments. Looking at the recovery figures used to correct for recovery they were in 4 cases between 10 % and 20 %; in 8 cases between 20 % and 30 %; in 7 cases between 30 % and 40 %; in 4 cases between 40 % and 50 %; in 7 cases between 50 % and 60 %; in 4 cases between 60 % and 70 %; and in 9 cases between 70 % and 90 %. In one case no recovery rate was reported and in another case a recovery of 100 % was reported. The latter 2 cases are not shown in **Table 3-13**.

Table 3-13 shows 42 cases of correction via recovery factors concerning ***cyromazine*** (11 cases), ***fenbutatin oxide*** (10 cases), ***chlorothalonil*** (9 cases), ***2,4-D*** (6 cases), ***dithiocarbamates*** (5 cases) and ***ethephon*** (1 case). Correction of results for recovery leads in most cases to a result that was closer to the assigned value compared to the result that would have been reported if no correction of results for recovery was applied (Note: in the case of ***chlorothalonil***, ***cyromazine*** and ***fenbutatin oxide*** hypothetical assigned values were used to calculate the z-scores). As shown in **Table 3-13** laboratories applying a recovery factor were able to "shift" their z-scores from unacceptable to acceptable in 6 cases, from questionable to acceptable in 14 cases and from unacceptable to questionable in 1 case. Furthermore, in 12 cases z-scores remained within the acceptable range, in 5 cases within the questionable range and in 1 case within the unacceptable range. There were also 2 cases where the z-score shifted from acceptable to questionable. When comparing the AAZ calculated using the submitted results with the overall AAZ calculated using the results that would have been submitted if no correction of results for recovery was applied we see a drastic decline from 2.19 to 1.05. Similar observations were made in EUPT-C5/SRM6.

3.5.4 Methodology-related bias and bimodal distribution of results

As mentioned in **Section 3.3** a non-unimodal and quite broad distribution of the submitted results was observed for ***chlorothalonil***, ***cyromazine*** and ***fenbutatin oxide*** (see also **Appendix 5**). This broad distribution is related to the fact that many laboratories employed methods that produce low recoveries with no correction for recovery being applied.

Looking at the methodology information submitted by the labs for **cyromazine** (overall median of submitted results[1] = 0.351 mg/kg, Qn-RSD = 45.3 %) the recovery figures reported by the labs were in many cases quite low and in 45 % of the cases lower than 70 % (see also **Table 3-14**). Among the 54 submitted results for ***cyromazine*** 29 were corrected for recovery and 25 were not. A close look at these two sub-populations reveals that the overall median of the results submitted by labs correcting for recovery (0.398 mg/kg) is much higher than the median of the sub-population not correcting for recovery (0.287 mg/kg). The difference of these two sub-populations to the overall median is +13 % and -18 %, respectively. We have checked how the correction of certain results based on the delivered recovery figures and how the elimination of a sub-population of results, impacts the overall median and the Qn-RSD. By correcting the non-corrected results using the submitted recovery factors and mixing all "corrected" results together, the median of the new population rises to 0.395 mg/kg and is thus 13 % higher than the overall median of the submitted results. The Qn-RSD falls from 45.3 % based on the originally submitted results to 31.6 % for the new population using all "corrected" results. By excluding from the total population 10 results reported by labs using QuEChERS-type methodologies but without applying correction for recovery the median of the new sub-population increases to 0.380 mg/kg with a Qn-RSD of 31.7 %.

[1] Excluding outliers

Table 3-13: Compilation of results where correction of results for recovery using a recovery figure was applied

Pesticide	LabCode	Submitted Recovery figure [%]	Recovery replicates considered	Submitted result [mg/kg]	z-score derived from submitted result	z-scores (if non-corrected results were used)*
2.4-D (free acid) Assigned Value = 0.278 mg/kg	3	66.8	2	0.355	1.11	-0.59
	13	27	1	0.174	-1.50	-3.34
	24	10.2	1	0.222	-0.81	-3.68
	96	62	3	0.363	1.22	-0.76
	113	58	1	0.369	1.31	-0.92
	118	58	2	0.040	-3.42	-3.67
Chlorothalonil "Assigned Value"= 0.122 mg/kg	13	87.5	1	0.052	-2.30	-2.52
	34	68.1	3	0.054	-2.23	-2.82
	72	61	1	0.139	0.56	-1.25
	77	35	2	0.126	0.13	-2.56
	96	59	3	0.146	0.79	-1.18
	109	40	1	0.190	2.23	-1.51
	113	25	3	0.194	2.36	-2.43
	118	53	1	0.123	0.03	-1.87
	121	82	2	0.058	-2.10	-2.46
Cyromazine "Assigned Value"= 0.395 mg/kg	1	40	2	0.437	0.43	-2.24
	3	39	2	0.390	-0.05	-2.46
	13	21	1	0.555	1.62	-2.83
	34	72.1	3	0.412	0.17	-0.99
	50	26	2	0.421	0.26	-2.90
	56	40	4	0.350	-0.46	-2.58
	60	31	1	0.490	0.96	-2.47
	77	71	3	0.390	-0.05	-1.21
	91	13	2	0.181	-2.17	-3.77
	113	47	1	0.400	0.05	-2.10
	130	30	1	0.454	0.60	-2.62
Dithiocarbamates (as CS_2) Assigned Value= 0.615 mg/kg	3	45	2	0.621	0.01	-2.19
	96	83	2	0.626	0.04	-0.62
	100	51	3	0.934	2.03	-0.90
	108	83.6	5	0.570	-0.32	-0.90
	133	53.8	2	0.569	-0.33	-2.01
Ethephon Assigned Value= 0.210 mg/kg	30	20.7	1	0.210	0.00	-3.18
Fenbutatin Oxide "Assigned Value"= 0.214 mg/kg	3	83	2	0.389	3.27	2.02
	6	10.7	2	0.254	0.75	-3.50
	12	51	1	0.140	-1.38	-2.67
	13	45	1	0.311	1.81	-1.40
	24	43	1	0.199	-0.28	-2.41
	34	33.3	>5	0.323	2.04	-2.00
	41	82.6	3	0.193	-0.39	-1.03
	55	25	3	0.153	-1.14	-3.29
	118	16	1	0.320	1.98	-3.05
	119	26	2	0.226	0.22	-2.92
Overall	**27 labs**	**42 cases**	1 repl. (16×) 2 repl. (14×) 3 repl. (9×) 3 repl. (1×) 5 repl. (1×) > 5 repl. (1×)		**AAZ = 1.05** 8× Acceptable 1× Questionable 33× Unacceptable	**AAZ = 2.19** 20× Acceptable 8× Questionable 14× Unacceptable

* Calculated using the current Assigned Values

Nevertheless, the EUPT-Scientific Committee considered that any of the above alternative approaches would deliver assigned values that are still assosiated with too large uncertainty and decided that z-scores should be calculated based on hypothetical assigned values but presented only for information purposes. For informative purposes z-scores were calculated based on a) the median of all submitted results (0.351 mg/kg), b) the median of all results following correction of recovery by the Organizers where this was not already done by the lab (0.395 mg/kg), and c) the median of the sub-population remaining after exclusion of all results submitted by labs using QuEChERS methodologies without applying correction of results for recovery (0.380 mg/kg). As regards second case it should be noted that in many cases correction for recovery was based on recovery factors derived from only 1 or 2 replicates of the recovery experiments. The respective histograms, the kernel density curves and the z-scores based on Assigned Values established from different sub-populations are shown in **Appendix 4 – Appendix 6**.

For **chlorothalonil** (overall median of submitted results = 0.104 mg/kg, Qn-RSD = 45.7 %) there were 11 labs (18 %) reporting recovery rates lower than 70 % (see **Table 3-14**). Among the total 73 results reported for ***chlorothalonil*** 25 were corrected for recovery and 48 were not. Comparing these two sub-populations we can observe some differences. The overall median of the results submitted by the labs correcting for recovery is 0.121 mg/kg whereas the median of the result sub-population of the labs not correcting for recovery is 0.100 mg/kg. The difference of these two sub-populations to the overall median is +16 % and -4 %, respectively. By correcting the uncorrected results using the recovery factors submitted by the labs and using all "corrected" results together the median of the new sub-population is 0.122 mg/kg and thus 17 % higher than the overall median of the submitted results. The Qn-RSD of the new population falls to 42.5 %, which is slightly lower than the original value resulting from the submitted results (Qn-RSD = 45.7 %). Nevertheless, the EUPT-Scientific Committee till decided not to use this overall corrected median as the assigned value for ***chlorothalonil*** due to the large uncertainty associated with this value. For informative purposes z-scores were calculated based on a) the median of all submitted results (0.104 mg/kg), and b) the median of all results following correction for recovery where this was not already performed by the lab (0.122 mg/kg). For the latter case it should be noted that in many cases correction for recovery was based on just 1 or 2 recovery replicates. The respective histograms, the kernel density curves and the z-scores based on Assigned Values established from different sub-populations are shown in **Appendix 4 – Appendix 6**.

Looking at the results obtained by different methodology types we can observe some differences between the respective median values. The median of the results generated by QuEChERS-based methods (all types) is 0.122 mg/kg (n = 40). The median of results submitted by the labs using acidified QuEChERS approaches is 0.128 mg/kg (n = 23) and of the labs using non-acidified QuEChERS approaches is 0.075 mg/kg (n = 17). Labs using ethyl acetate based methods (n = 14) had a median of 0.098 mg/kg and labs applying Luke (n = 16) had a median of 0.084 mg/kg. Removing the results of those 17 labs applying non-acidified QuEChERS from the total population we obtain a median value of 0.109 mg/kg (at n = 46).

Table 3-14: Recovery figures submitted by the participating EU laboratories for each of the compounds present in the Test Item

	2.4-D (free acid)	Bromide ion	Dithiocarbamates	Ethephon	Glyphosate	Chlorothalonil	Cyromazine	Fenbutatin oxide
No Data	7	5	9	4	6	7	7	6
10 % – 30 %	1 (2 %)	0 (0 %)	0 (0 %)	1 (4 %)	1 (3 %)	1 (2 %)	5 (11 %)	6 (16 %)
30 % – 50 %	0 (0 %)	0 (0 %)	1 (1 %)	1 (4 %)	1 (3 %)	3 (5 %)	10 (21 %)	6 (16 %)
50 % – 70 %	8 (13 %)	0 (0 %)	5 (7 %)	0 (0 %)	0 (0 %)	7 (11 %)	6 (13 %)	7 (18 %)
70 % – 120 %	**54 (86 %)**	**39 (100 %)**	**67 (91 %)**	**26 (93 %)**	**31 (94 %)**	**53 (80 %)**	**25 (53 %)**	**18 (47 %)**
> 120 %	0 (0 %)	0 (0 %)	1 (1 %)	0 (0 %)	0 (0 %)	2 (3 %)	1 (2 %)	1 (3 %)
Sum	63 (100 %)	39	74	28	33	66 (100 %)	47 (100 %)	38 (100 %)

Experiments conducted by the Organizer revealed that significant losses of ***chlorothalonil*** occur when lentils are wetted with pure, non-acidified water. Swelling for 15 minutes with water resulted in a ca. 50 % loss of ***chlorothalonil*** both in recovery experiments using the Blank Material as well as using the Test Item. Swelling with acidified water (5 g lentils + 10 ml water + 150 µl conc. H_2SO_4) resulted in much higher recoveries.

For **fenbutatin oxide** (overall median of submitted results = 0.175 mg/kg, Qn-RSD = 58.2 %) approximately half of the labs reported recovery rates below 70 %. No clear bimodality could be observed in the kernel density curve, but still a very broad distribution of the results was apparent. Among the 44 results reported for ***fenbutatin oxide*** 21 were corrected for recovery and 23 were not. The overall median of the results subpopulation submitted by the labs correcting for recovery is 0.226 mg/kg, whereas the median of the result sub-population of the labs not correcting for recovery is 0.145 mg/kg. The difference of these two subpopulations to the overall median is -22 % and +22 %, respectively. By correcting the uncorrected results using the recovery factors submitted by the labs and mixing all "corrected" results together the median of the new sub-population is 0.214 mg/kg and thus 15 % higher than the overall median of the submitted results. The Qn-RSD of the new population falls to 45 %. This figure is still high but clearly lower than the value from the original results (Qn-RSD = 58.2 %). Nevertheless, the EUPT-Scientific Committee still decided not to use this overall corrected median as the assigned value for ***fenbutatin oxide*** due to the large uncertainty associated with this value. For informative purposes z-scores were calculated based on a) the median of all submitted results (0.175 mg/kg), and b) the median of all results following correction for recovery where this was not already done by the lab (0.214 mg/kg). It should be noted, however, that correction for recovery was in many cases based on just 1 or 2 replicate recovery experiments and is thus also associated with some uncertainty. The median of the sub-population derived after exclusion of all results submitted by labs using QuEChERS methodologies without acidification was 0.212 mg/kg, that is very close to case b). The respective histograms, the kernel density curves and the z-scores based on Assigned Values established from different sub-populations are shown in **Appendix 4 – Appendix 6**.

Lentils proofed to be an analytically challenging commodity for the analysis of ***fenbutatin oxide*** using QuEChERS with recovery rates ranging significantly lower than those typically achieved with fruits and vegetables. Experiments conducted by the Organizers revealed that the recovery rates achieved using the citrate buffered QuEChERS are around 45 % – 55 % but can rise to 85 % – 95 % when the sample is acidified prior to extraction, e.g. with sulfuric acid as described in the method for the analysis for ***chlorothalonil*** published on the EURL-website, or with formic acid as described in another document on the analysis of organotin compounds also published on the EURL-SRM website under "Analytical Observations". It should be noted that experiments performed by the Organizers have shown that "aged" ***fenbutatin oxide*** residues, as contained in the Test Item, seem to be more difficult to extract from lentils than when freshly spiked. This essentially means that the use of recovery factors will only partially correct results. Out of the 21 labs (48 % of all) that corrected their results for recovery 17 labs employed QuEChERS based approaches. Out of these 17 labs correction for recovery was accomplished using a recovery factor (10×) or standard additions to sample portions (7×).

As can be seen in **Appendix 4** the 10 laboratories employing alkaline hydrolysis in the case of **2,4-D** (assigned concentration 0.278 mg/kg) reported tentatively overestimated results with the median of this subpopulation being 0.315 mg/kg and thus ca. 13 % higher than the overall median of 0.278 mg/kg. This correlates very well with the observations of the Organizers who determined a shift of ca. 9 % when alkaline hydrolysis is employed. Excluding the results of the labs employing alkaline hydrolysis shifts the median of the remaining population to 0.272 mg/kg. Due to the very minor shift of the overall median, the EUPT-Scientific Committee decided to use the entire population of results for the establishment of the Assigned Value in the case of ***2,4-D***. The laboratories are urged to study the Target Pesticides List more carefully, in which the residue definitions that apply to each PT are provided. In future EUPTs the Organizers will emphasize clearly that no hydrolysis should be performed if the residue definition includes the free acids only.

In contrast to previous EUPT-SRMs containing ***dithiocarbamates*** there was no clear trend towards reporting significantly biased results when using any of the analytical approaches. The median of the results submitted by labs using the spectrophotometry-based methods was 0.59 mg/kg and thus ca. 10 % lower than the median derived from results submitted by labs using methods involving LLP into iso-octane or headspace sampling (in both cases median = 0.65 mg/kg). Interestingly, however, the results submitted by laboratories using spectrophotometric approaches (EN-12396-1- and EN-12396-3-type) showed clearly a lower variation (AAZ = 0.59 excluding the 3 false negative results) compared to those employing LLP (AAZ = 1.05) or headspace sampling (AAZ = 1.00). Among the spectrophotometric approaches the results generated by the xanthogenate method were more narrowly distributed (AAZ = 0.48) compared to those using the copper-(II)-acetate approach (AAZ = 0.78). Among the 4 labs reporting false negative results, two employed the copper-(II)-acetate approach, one employed the xanthogenate approach and one employed the LLP to iso-octane approach.

3.5.5 Coverage of compounds in routine scope and the experience of labs

As can be seen in **Figure 3-1** the percentage of participating labs that covered the various compounds in the EUPT-SRM7 Target Pesticides List varied a lot ranging from 30 % for ***ethephon*** to 79 % for ***dithiocarbamates***. The percentages become much lower when calculated against the total number of labs that were considered as being obliged to take part in this test based on their commodity scope or function (n = 228). There is obviously still room for substantial progress in the official controls of SRM-pesticides.

In 93 % of all cases compounds covered routinely by labs participating in this EUPT were also targeted by those labs in this exercise (**Table 3-15**). Many participating labs have even analysed compounds although they were not, or are not yet, included in their routine scope (176 cases overall and 90 cases concerning compounds contained in the Test Item). This indicates that many labs are in the process of expanding their scope with additional SRM-compounds. In the case of ***cyromazine*** and ***fenbutatin oxide*** a substantial per-

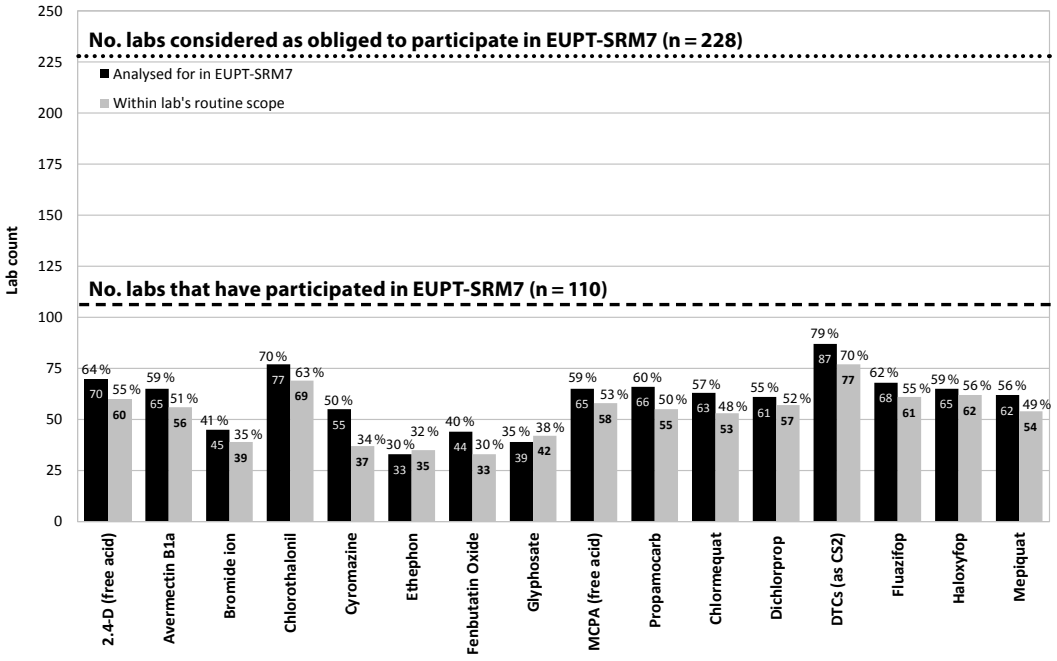

Figure 3-1: Inclusion of analytes in the routine scope of labs

Table 3-15: Inclusion of EUPT-SRM7 compounds in the routine scope of laboratories

Pesticide is	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
2.4-D (free acid)	58 (97 %)	2	12 (24 %)	38
Avermectin B1a	54 (96 %)	2	11 (20 %)	43
Bromide ion	36 (92 %)	3	9 (13 %)	62
Chlorothalonil	67 (97 %)	2	10 (24 %)	31
Cyromazine	33 (89 %)	4	22 (30 %)	51
Ethephon	27 (77 %)	8	6 (8 %)	69
Fenbutatin Oxide	29 (88 %)	4	15 (19 %)	62
Glyphosate	32 (76 %)	10	7 (10 %)	61
MCPA (free acid)	54 (93 %)	4	11 (21 %)	41
Propamocarb	53 (96 %)	2	13 (24 %)	42
Chlormequat	50 (94 %)	3	13 (23 %)	44
Dichlorprop	53 (93 %)	4	8 (15 %)	45
DTCs (as CS_2)	77 (100 %)		10 (30 %)	23
Fluazifop	58 (95 %)	3	10 (20 %)	39
Haloxyfop	58 (94 %)	4	7 (15 %)	41
Mepiquat	50 (93 %)	4	12 (21 %)	44
Sum	**783 (93 %)**	**59 (7 %)**	**176 (19 %)**	**736 (81 %)**

centage of the results received (47 % and 46 %, respectively) originated from labs with less than one year's experience, or no experience at all. ***Glyphosate*** and ***ethephon*** were the compounds most frequently not covered by participating labs despite being part of their routine scope (10 of 42 and 8 of 35 cases, respectively). This might be because the labs analysing these two compounds focus on other types of commodities, not in lentils.

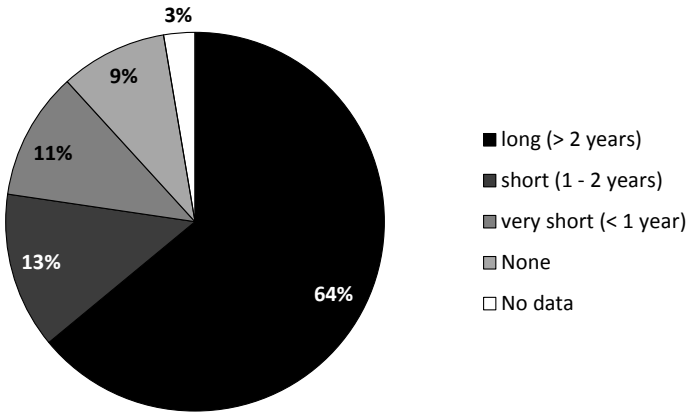

Figure 3-2: Experience of labs with the analysis of pesticides presend in the Test Item (overall)

Table 3-16: Experience of labs with the analysis of individual compounds

Pesticides	Experience	No. of Labs	% of Labs
2.4-D (free acid)	> 2 years	50	71 %
	1 – 2 years	11	16 %
	< 1 year	4	6 %
	None	5	7 %
Bromide ion	> 2 years	26	58 %
	1 – 2 years	10	22 %
	< 1 year	4	9 %
	None	3	7 %
	No Data	2	4 %
Chlorothalonil	> 2 years	61	79 %
	1 – 2 years	3	4 %
	< 1 year	6	8 %
	None	3	4 %
	No Data	4	5 %
Cyromazine	> 2 years	23	42 %
	1 – 2 years	5	9 %
	< 1 year	10	18 %
	None	16	29 %
	No Data	1	2 %
DTCs (as CS_2)	> 2 years	77	89 %
	1 – 2 years	3	3 %
	< 1 year	2	2 %
	None	1	1 %
	No Data	4	5 %
Ethephon	> 2 years	16	48 %
	1 – 2 years	9	27 %
	< 1 year	5	15 %
	None	2	6 %
	No Data	1	3 %
Fenbutatin Oxide	> 2 years	18	41 %
	1 – 2 years	10	23 %
	< 1 year	9	20 %
	None	7	16 %
Glyphosate	> 2 years	17	44 %
	1 – 2 years	9	23 %
	< 1 year	9	23 %
	None	4	10 %

In 64 % of the cases labs indicated that they had more than 2 years of analytical experience with the compounds that they reported results for (**Figure 3-2**). In 13 % of the cases, labs reported shorter experience (1 – 2 years), in 15 % of the cases they reported experience less than 1 year and in 9 % of the cases no experience at all. As far as the individual compounds are concerned (see **Table 3-16**), ***dithiocarbamates***, ***chlorothalonil*** and ***2,4-D*** are the analytes with which labs have the most experience. 89 %, 79 % and 71 % of the labs indicated more than 2 years of experience with analysing ***dithiocarbamates***, ***chlorothalonil*** and ***2,4-D***, respectively. The compounds with which the participating labs had the least experience were ***cyromazine*** (47 % of the labs reported less than 1 year of experience), ***fenbutatin oxide*** (36 %) and ***glyphosate*** (33 %). For ***dithiocarbamates***, ***chlorothalonil*** and ***2,4-D*** the percentage of labs indicating less than 1 year of experience were just 3 %, 12 % and 13 %, respectively.

3.5.6 Size of analytical portions

The size of the analytical portions employed by the participants ranged between 1 g and 5 g for ***fenbutatin oxide***, between 1 g and 6 g for ***ethephon***, between 1 g and 25 g for ***2,4-D***, ***bromide ion***, ***chlorothalonil***, ***cyromazine*** and ***glyphosate***, and between 1 g and 200 g for ***dithiocarbamates*** (see **Figure 3-3**). There were several cases where the sample portions employed by the laboratories were smaller than those used by the Organizers in the homogeneity test, i.e., 5 g for ***2,4-D***, ***bromide ion***, ***chlorothalonil***, ***cyromazine***, ***ethephon***, ***fenbutatin oxide*** and ***glyphosate*** and 15 g for ***dithiocarbamates***. Subsampling (= portion by portion) variation increases as the weight of the analytical portions decreases. Where the analytical portions employed were significantly smaller than those used in the homogeneity test, sufficient homogeneity cannot be guaranteed. Analytical portions smaller than those tested by the Organizers were employed by 17 out of 70 labs (24 %) in the case of ***2,4-D***; 37 out of 45 labs (82 %) in the case of ***bromide ion***; 24 out of 73 labs (31 %) in the case of ***chlorothalonil***; 13 out of 55 labs (23 %) in the case of ***cyromazine***; 64 out of 87 labs (74 %) in the case of ***dithiocarbamates***; 7 out of 33 labs (21 %) in the case of ***ethephon***; 13 out of 44 labs (29 %) in the case of ***fenbutatin oxide***, and 14 out of 39 labs (35 %) in the case of ***glyphosate***. In future EUPTs concerning dry commodities the Organizers will reduce the analytical portions size used to test the homogeneity of ***bromide*** and ***dithiocarbamates*** with the aim to cover a larger number of labs. Nevertheless, the Organizers would also like to emphasize that laboratories should avoid using very small analytical portions sizes (e.g. < 3 g) as sub-sampling variability increases the smaller the sample size becomes. This does not only apply to EUPTs, it also applies to routine work applications.

3.5.7 Comparison of Reporting Limits, Assigned Values and MRRLs

Figure 3-4 shows a compilation of the reporting limits (RLs) reported by the labs for each of the compounds present in the sample. In all cases the RLs were lower than the assigned concentrations of the compounds that were present in the Test Item.

In some cases high RLs could be linked to the reporting of false negative results (FNs). Lab 108, which reported a false negative result for ***dithiocarbamates***, stated a RL of 1 mg/kg, which is greater than the assigned value of 0.620 mg/kg and well above many RLs for ***dithiocarbamates***. Labs 107 and 110 reported false negative results for ***chlorothalonil***. Both stated a RL of 0.1 mg/kg, which is marginally lower than the tentative assigned value of 0.104 mg/kg. In all other cases of false negative results the stated RLs were clearly lower than the respective assigned values.

In the majority of the cases the laboratories were able to reach the required MRRLs. The MRRLs were not met by 11 labs (25 % of the cases) reporting results for ***bromide*** with an MRRL of 3 mg/kg, by 8 labs (24 %) analysing for ***ethephon*** with an MRRL of 0.02 mg/kg, by 8 labs (18 %) analysing for ***fenbutatin oxide*** with an MRRL of 0.02 mg/kg, by 12 labs (17 %) analysing for ***dithiocarbamates*** with an MRRL of 0.05 mg/kg, by 6 labs (16 %) analysing for ***chlorothalonil*** with an MRRL of 0.01 mg/kg, by 9 labs (13 %) analysing for ***2,4-D*** with an MRRL of 0.02 mg/kg, by 7 labs (13 %) analysing for ***cyromazine*** with an MRRL of 0.02 mg/kg and by 4 labs (10 %) analysing for ***glyphosate*** with an MRRL of 0.05 mg/kg. In the case of ***bromide*** it should be noted that the MRRL was lower than levels naturally encountered in some types of crops.

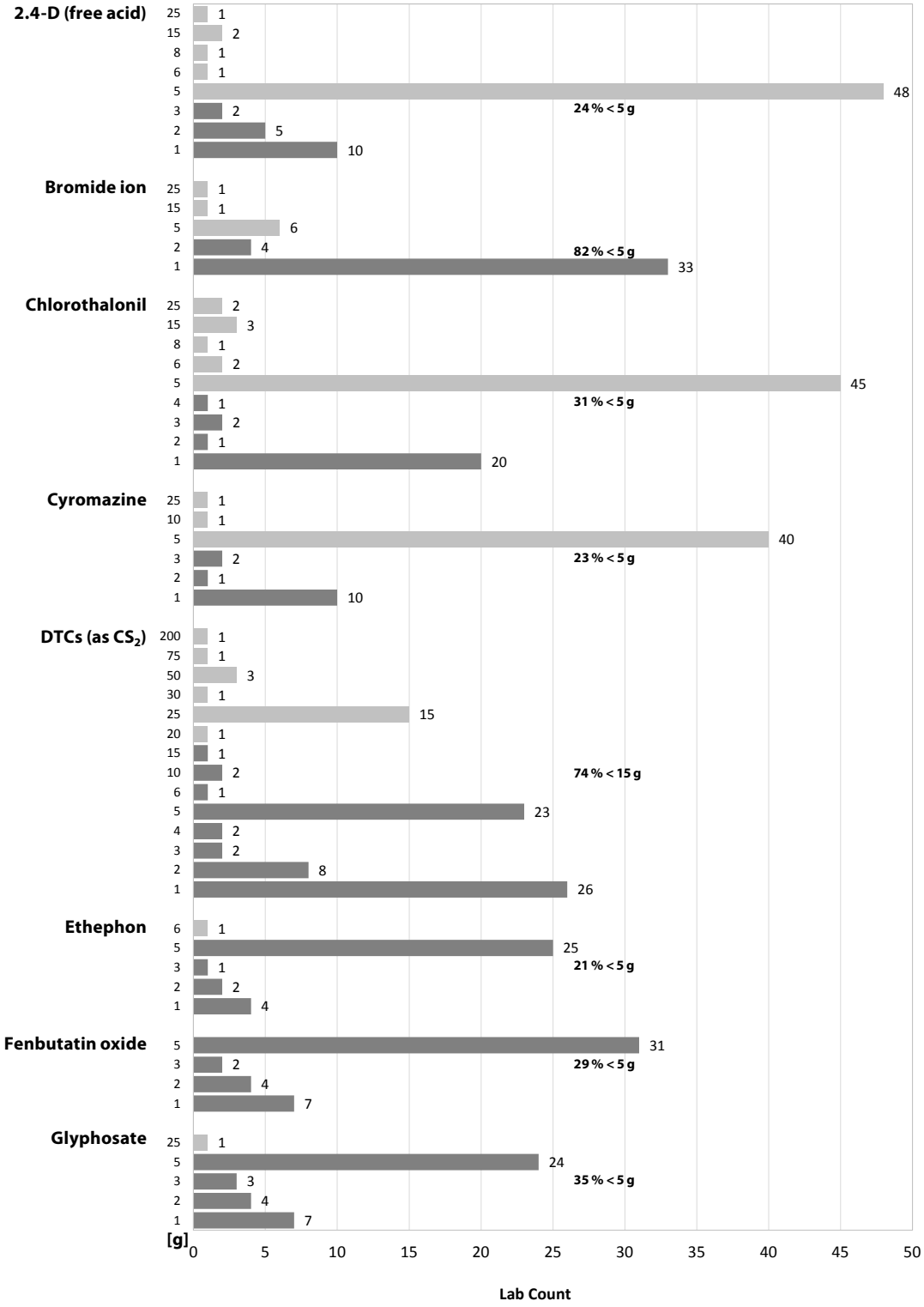

Figure 3-3: Size of analytical portions [g] employed by labs and percentage of analytical portions smaller than those used to test homogeneity.

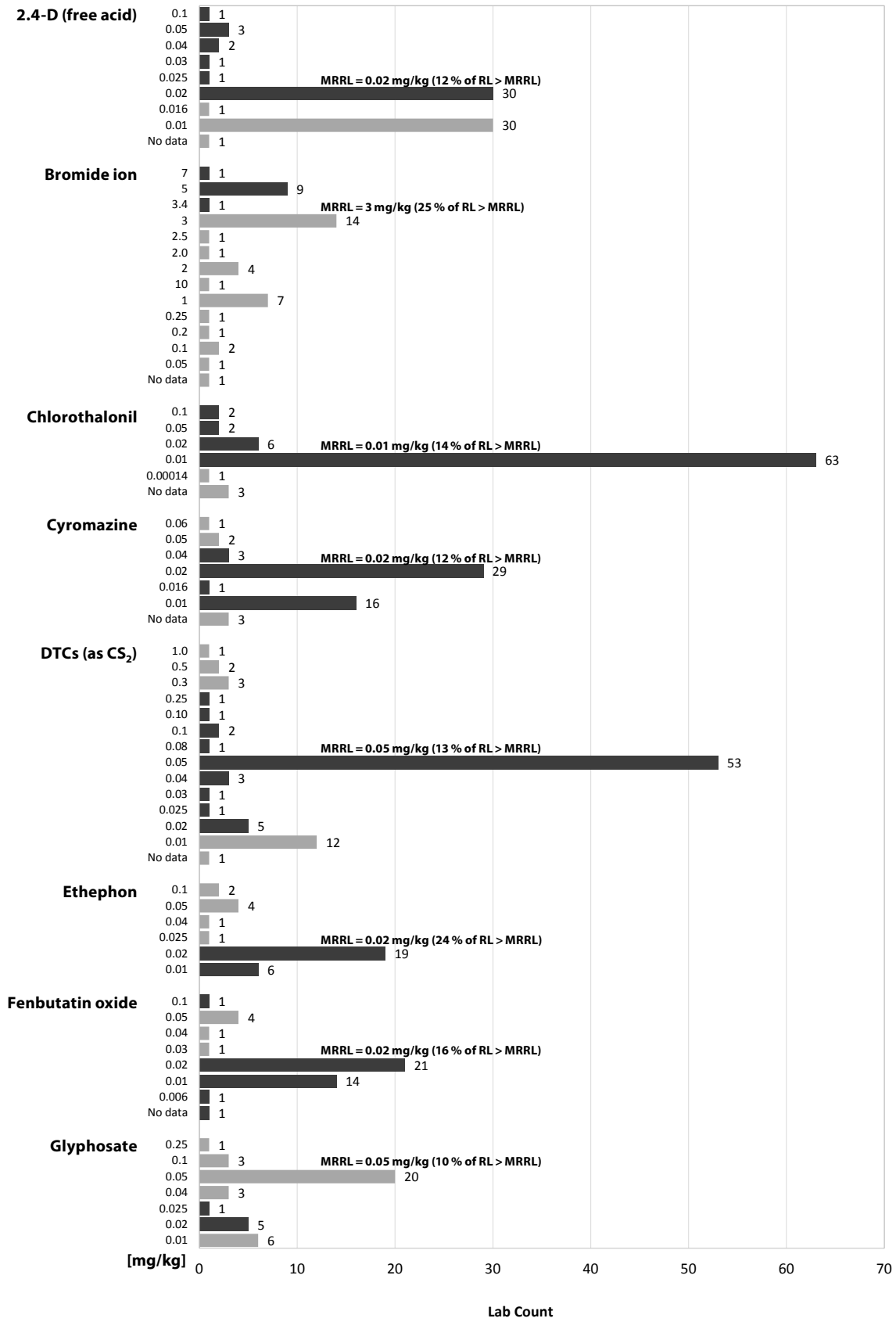

Figure 3-4: Labs' Reporting Limits [mg/kg] and comparison with the MRRLs set by the Organizers.

3.6 Complilation of advices to the participants

- Do not perform a hydolysis step (to hydrolyse esters and conjugates) , if "free acid" is stated in the residue definition within the Target Pesticides List.
- When analysing acidic pesticides (e.g. ***2,4-D***) dispersive SPE cleanup should be performed without amino-sorbents (e.g. PSA). Amino-sorbents tend to remove acidic pesticides from the extracts leading to low recoveries.
- When analysing base sensitive pesticides (e.g. ***chlorothalonil***) dispersive SPE cleanup with amino-sorbents (e.g. PSA) might lead to degradation. If performed, the extract should be re-acidified immediately to minimize losses.
- When analysing ***chlorothalonil*** in lentils the lentils should be wetted with acidified water to reduce losses (this might also apply to other dry commodities).
- When analysing organotin pesticides (e.g. ***fenbutatin oxide***) the samples should be acidified prior to or during extraction (this proved to be very important in the case of lentils).
- Wherever possible, use an appropriate isotopically labelled internal standard (IL-ISTD) to compensate for recovery and matrix effects. If an IL-ISTD is not available/affordable use other approaches to compensate for recovery and/or matrix effects such as the standard additions approach and the matrix-matched calibration.
- Avoid using very small analytical portions sizes (e.g. < 3 g) because sub-sampling variability increases as sample size is reduced. Keep in mind that the Organizers typically do not use analytical portions <5g in their homogeneity tests.
- Please fill-in the method information table comprehensively during results submission as this information is crucial for the detection of error sources and can be very helpfull in the interpretation of the results distribution profiles.
- Follow the advices in the Specific EUPT Protocol as regards the storage and further processing of Test Items
- Try to localise the reasons for results with questionable or unacceptable z-scores and/or false positive or negative results and take corrective measures where appropriate.

3.7 Summary, conclusions and prospects for the SRM pesticides

The EUPT-SRM7 was the 7th scheduled annual EUPT focusing on pesticides requiring the use of "single" residue methods and the first for which the Test Item was produced by the EURL-SRM.

In total 114 laboratories, representing 25 EU and 2 EFTA countries, registered for the EUPT-SRM7 and 110 thereof submitted results. Additionally, 4 of the 5 laboratories from the Third Countries that registered for participation also reported results. EU-member states from which no laboratory participated in EUPT-SRM7 were Romania and Malta. The Maltese NRL was, however, represented by the UK NRL-SRM acting as proxy-NRL for Malta.

As shown in **Table 3-17** the participation of labs in EUPT-SRMs has clearly increased over the years. The number of participants analyzing pesticides present in the Test Item in EUPT-SRM1 – 7 is shown in **Table 3-18**. The positive trend concerned not only the number of participants and submitted results, but also the scope of pesticides covered by many individual labs.

The positive trend as regards scope and participation is based upon many factors such as the increased use of LC-MS/MS instrumentation by the laboratories, the implementation of simple methodologies including those developed and distributed by the EURL-SRM, as well as the strengthening of the network of OfLs

Table 3-17: Comparison of EUPT-SRMs

EUPT-	SRM1 (2006)	SRM2 (2007)	SRM3 (2008)	SRM4 (2009)	SRM5 (2010)	SRM6 (2011)	SRM7 (2012)
Matrix	Strawberry homogenate	Wheat flour	Carrot homogenate	Oat flour	Apple purée	Rice flour	Lentil flour
Participants submitting results (EU/EFTA)	24	30	66	48	81	77	110
SRM pesticides in Target Pesticide List / in the Test Item	15 / 3 [1]	8 [3] / 5 [3]	8 / 5	21 [3] / 7 [3]	11 / 5 [4]	13 / 7	16 / 8 [5]
No. of results for SRM pesticides (without false positives)	38	73	193	138 [2]	239	291	439
No. of false negative results	0	7	0	5 [2]	5	5	11
Mean of no. of results per lab	1.58	2.50	2.92	2.88	2.95	3.79	4.12
Average of absolute z-scores	0.57	1.04	1.04	0.98	1.11	0.83	0.97 [7]
Acceptable z-scores	97 %	86 %	87 %	88 %	92 % [7]	91 %	90 % [7]
Questionable z-scores	–	7 %	7 %	6 %	3 % [7]	6 %	3 % [7]
Unacceptable z-scores (thereof false negatives) [3]	3 %	8 % [3] (1.3 %) [3]	6 %	7 % [3] (3.6 %) [3]	5 % [7] (0.6 %) [7]	4 % (1.7 %)	7 % [7] (2.1 %) [7]
Number of false positives	0	1	0	0	6	0	0
Category A laboratories [6]	–	–	–	31 %	19 %	25 %	28 %
Qn-RSD (average)	25 %	25 %	29 %	27 %	22 % [7]	23 %	27 % [7]

1) One compound was evaluate for information only due to insufficient number of participants.
2) Two compounds were excluded from evaluation due to insufficient number of participants.
3) Including optional analytes
4) One of the 5 compounds was not included in the evaluation due to uncertain assigned value.
5) 3 of the 8 pesticides were not included in the evaluation.
6) The criteria applied to define Category A and B in EUPT-SRM4 and -SRM5 were different from those in EUPT-SRM6 and -SRM7.
7) Pesticides that were evaluated for information only were excluded.
8) One compound was excluded due to insufficient number of results.

within the EU and the information flow within it. Another important factor contributing to this positive trend lies in the fact that participation in the EUPTs became compulsory for EU OfLs from 2009 onwards. Nevertheless, it should be noted that participation in EUPTs also largely depends on the pesticides included in the Target Pesticides List. The inclusion of ***dithiocarbamates*** in the Target Pesticides List for the EUPTs 5-7 positively impacted participation as ***dithiocarbamates*** analysis does not require sophisticated instrumentation and is routinely conducted by the majority of OfLs.

Table 3-18: Number of labs having analysed selected pesticides present in the Test Items of the EUPT-SRMs 1 – 7

EUPT	Acidic pesticides					Requiring individual methods		Polar pesticides			Other
	2,4-D	MCPA	MCPP	Haloxyfop	Fluazifop	Bromide	Dithiocarbamates	Chlormequat	Ethephon	Glyphosate	Fenbutatin Oxide
SRM1		10						23			10
SRM2		23	28					25			
SRM3		38			35		59		7	9	
SRM4	33							38			
SRM5					51		70		28	35	35
SRM6	57			49		34	64		29		
SRM7	70					44	83		32	39	44

The quality of the results as reflected by the average Qn-RSDs and the overall average of absolute z-scores (AAZ) remained at satisfactory levels for the majority of the compounds. ***Cyromazine***, ***chlorothalonil*** and ***fenbutatin oxide*** which are analytically difficult and were newly introduced in the EUPT-SRM scheme, had to be excluded from evaluation due to the broad and non-unimodal distribution of the received results, which did not allow the establishment of reliable assigned values (see **Table 3-5**).

The Target Pesticide List for EUPT-SRM7, distributed to the laboratories well in advance to the test, contained in total 16 SRM-compounds with 14 of them belonging to the EU co-ordinated control program. The Test Item itself contained 8 pesticides; namely, ***2,4-D***, ***bromide ion***, ***dithiocarbamates*** (thiram), ***ethephon***, ***glyphosate***, ***chlorothalonil***, ***cyromazine*** and ***fenbutatin oxide***. All pesticides but ***glyphosate*** were spiked by the Organizer.

For each laboratory/pesticide combination, z-scores based on the FFP-RSD of 25 % were calculated and classified into "acceptable", "questionable" and "unacceptable" according to the rules in the General EUPT Protocol. Overall, the quality of the results was good with 64 out of 70 laboratories (91 %) reporting results within the acceptable z-score-range for ***2,4-D***, 42 out of 45 (93 %) for ***bromide ion***, 76 out of 87 (87 %) for ***dithiocarbamates***, 30 out of 33 (91 %) for ***ethephon*** and 34 out of 39 labs (90 %) for ***glyphosate***. ***Chlorothalonil***, ***cyromazine*** and ***fenbutatin oxide*** showed a broad and non-unimodal and/or broad distribution of results and were thus only evaluated for informative purposes as it was not possible to establish a reliable assigned value with an acceptable certainty. Suggestions to improve the analysis of these compounds are given in **Section 3.5**.

The robust relative standard deviation (Qn-RSD), reflecting the result-distribution, was calculated for each pesticide. Excluding the 3 above-mentioned problematic compounds the Qn-RSD was 25.7 % on average and thus very close to the FFP-RSD of 25 %, which is used to calculate the z-scores. The Qn-RSD for ***2,4-D*** was 27.9 %, for ***bromide ion*** 18 %, for dithiocabamates (sum as CS_2) 23.1 %, for ***ethephon*** 25.2 % and for ***glyphosate*** 34.5 %. For ***chlorothalonil***, ***cyromazine*** and ***fenbutatin oxide*** the Qn-RSDs were 45.7 %, 45.3 % and 58.0 %, respectively. Overall dry lentils proved to be analytically a very challenging commodity for these 3 compounds. Both ***chlorothalonil*** and ***fenbutatin oxide*** were shown by the Organizers to give very low recoveries using the QuEChERS method if the samples were not acidified during the extraction and partitioning step. ***Chlorothalonil*** experiences losses during the cleanup step if PSA sorbent is used as well as during the GC-measurement from non-acidified QuEChERS extracts. ***Chlorothalonil*** additionally degrades rapidly during soaking of lentils with water if this is not acidified immediately. ***Fenbutatin oxide*** seems to behave differently in lentils compared to most other commodities and exhibits a very strong affinity towards lentil matrix. Simple correction of results for recovery via standard additions also proved to be problematic as aged ***fenbutatin oxide*** is more strongly retained on the matrix than a freshly spiked one. In the case of ***cyromazine***, a compound newly introduced to the EUPT-scheme, recoveries using the QuEChERS method are low ranging typically between 25 % and 45 %. Due to a lack of experience (47 % of the labs reporting results had less than one year of experience with the analysis of this compound) many labs were unable to properly deal with this compound and reported results uncorrected for recovery. This resulted in an overall median that was too low. The Organizers suggest a proper correction for recovery when using multiresidue approaches, such as QuEChERS, e.g., by the standard additions to sample portions or with the help of an appropriate isotopically labelled ISTD. The use of isotopically labelled ***cyromazine*** or standard addition to extract aliquots is also recommended when "dilute and shoot" (QuPPe type) methods are employed to compensate for matrix effects on LC-MS/MS measurements.

False negative results concerned ***dithiocarbamates*** (4×), ***ethephon*** (1×), ***bromide*** (1×), ***chlorothalonil*** (4×) and ***cyromazine*** (1×). In one case the result was reported as < RL but it was still judged as a false negative result in accordance with the rules in the General EUPT Protocol.

Laboratories were classified based on their scope according to the criteria in the General EUPT Protocol. Laboratories that had reported quantitative results for at least 7 of the 8 pesticides present in the Test Item were classified into Category A. In total 23 laboratories (21 %) were classified into Category A. The other 91 laboratories (79 %) were classified in Category B.

The 108 EU labs that participated in this EUPT represent only 47 % of all 228 labs that were considered as being obligated to participate in this exercise based on their status (NRL-SRM) or scope (routinely analyzing for pesticide residues in vegetables, cereals or feedingstuff). This figure needs to further increase in future EUPTs. Among the most frequent reasons given by labs to explain their non-participation were that "the pesticides in the SRM target list are out of the lab's scope" and that "there is a shortage of instruments and staff". To encourage laboratories to further expand their analytical scope and improve their reporting limits the EUPT-Scientific Committee strongly recommends laboratories to be equipped with LC-MS/MS. The EURL-SRM is pleased to assist the labs via bilateral discussions, exercises, workshops and training. The goal is that laboratories continue expanding their scope of analytes in order to be able to fully enforce EU legislation and to improve their overall performance, both in terms of correctly detecting the pesticides present in the samples, as well as in terms of being able to accurately quantify the residue levels. To promote the expansion of OfLs' scope of SRM analytes, the EURL-SRM will further continue developing, validating and distributing simple-to-use, fast and cost-efficient methodologies for compounds that are not amenable to multiresidue methods. In future EUPTs, the selection of pesticides will continue to focus on those included in the scope of the EU co-ordinated control programmes as well as on additional pesticides of high relevance. Labs' requests will also be taken into account.

The Organizers emphasize that any laboratories that received questionable or unacceptable z-scores in this PT should aim to find the reasons for this underperformance. Following the distribution of the preliminary results, all laboratories achieving questionable or unacceptable z-scores were asked to provide the reasons for this as far as possible. In many cases the reasons of poor performance could not be traced by the laboratories. The most prominent among the clarified sources of errors were the use of inappropriate procedures, the lack of experience with the analyte and/or matrix and the inappropriate or wrong correction for recovery.

4. ACKNOWLEDGEMENTS

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5. 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) 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.

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

[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

6. APPENDICES

Appendix 1 List of Laboratories registered to participate in the SRM7

(a): participating labs of EU and EFTA member states

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Austria	Austria	AGES (Austrian Agency for Health and Food Safety), Institute for Food Safety Innsbruck, Austria	Innsbruck	x	Yes
Belgium	Belgium	Scientific Institute of Public Health	Brussels	x	Yes
Belgium	Belgium	LOVAP (Laboratorium voor Onderzoek Van levensmiddelen en Aanverwante Produkten) NV	Geel		Yes
Belgium	Belgium	Fytolab	Gent - Zwijnaarde		Yes
Bulgaria	Bulgaria	Central Laboratory for Chemical Testing and Control, Sofia	Sofia	x	Yes
Cyprus	Cyprus	Laboratory of Pesticide Residues Analysis, State General Laboratory	Nicosia	x	Yes
Czech Republic	Czech Republic	Central Institute for Supervising and Testing in Agriculture	Brno		Yes
Czech Republic	Czech Republic	Czech Agriculture and Food Inspection Authority	Praha	x	Yes
Czech Republic	Czech Republic	Institute of Chemical Technology, Dept. of Food Chemistry and Analysis - Prague	Praha		Yes
Denmark	Denmark	Danish Veterinary and Food Administration, Region East	Ringsted		Yes
Denmark	Denmark	National Food Institute, Technical University of Denmark	Søborg	x	Yes
Estonia	Estonia	Agricultural Research Centre, Saku, Lab for Residues and Contaminants	Saku		Yes
Estonia	Estonia	Health Board - Tartu Laboratory	Tartu	x	Yes
Finland	Finland	Customs Laboratory	Espoo	x	Yes
Finland	Finland	Finnish Food Safety Authority	Helsinki		Yes
France	France	GIRPA - Groupement Interrégional Recherche Produits Agropharma	BEAUCOUZE		Yes
France	France	CERECO SUD	GARONS		Yes
France	France	ANSES Laboratoire de Maisons-Alfort	MAISONS-ALFORT	x	Yes
France	France	Service Commun des Laboratoires / Laboratoire Ile de France - Massy	Massy		Yes
France	France	Service Commun des Laboratoires / Laboratoire de Montpellier	Montpellier		Yes
France	France	Laboratoire Départemental d`Analyses des Cotes d`Armor	Ploufragan		Yes
France	France	Laboratoire Départemental d`Analyses du MORBIHAN	Saint Ave		No
Germany	Germany	Federal Office of Consumer Protection and Food Safety, NRL for Pesticide Residues	Berlin	x	Yes
Germany	Germany	Chemisches und Lebensmitteluntersuchungsamt Dortmund	Bochum		Yes
Germany	Germany	Chemisches und Veterinäruntersuchungsamt Rheinland, Standort Bonn	Bonn		Yes
Germany	Germany	State Investigation Institute of Health and Veterinary Saxony	Dresden		Yes
Germany	Germany	Bavarian Health and Food Safety Authority Office Erlangen	Erlangen		Yes
Germany	Germany	Bioanalytik/ZIEL	Freising		Yes
Germany	LT, LV, CY, EE	GALAB Laboratories GmbH	Geesthacht		Yes
Germany	Germany	Landesanstalt für Landwirtschaft, Forsten und Gartenbau, Halle	Halle/Saale		Yes
Germany	Germany	Landesamt für Verbraucherschutz - Sachsen-Anhalt	Halle/Saale		Yes
Germany	Germany	Institut für Hygiene und Umwelt Hamburg	Hamburg		Yes
Germany	MT, NL	Eurofins - Dr. Specht Laboratorien GmbH	Hamburg		Yes
Germany	Germany	Thuringian Institute of Agriculture	Jena		Yes
Germany	Germany	Landwirtschaftliches Technologiezentrum Augustenberg, Karlsruhe	Karlsruhe		Yes
Germany	Germany	Landesbetrieb Hessisches Landeslabor, Kassel	Kassel		Yes
Germany	Belgium	LUFA-ITL GmbH	Kiel		Yes

* only for EU-member states

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

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Germany	Germany	Chemical and Veterinary Analytical Institute Rhine-Ruhr-Wupper	Krefeld		Yes
Germany	Germany	State Department of Environmental and Agricultural Operations in Saxony	Leipzig		Yes
Germany	Germany	Chemical and Veterinary Analytical Institute Muensterland-Emscher Lippe	Münster		Yes
Germany	Germany	State Laboratory Schleswig-Holstein	Neumünster		Yes
Germany	Germany	Food and Veterinary Institute Oldenburg	Oldenburg		Yes
Germany	Germany	Berlin-Brandenburg State Laboratory, Potsdam	Potsdam		Yes
Germany	Germany	Berlin-Brandenburg State Laboratory, Berlin	Potsdam		Yes
Germany	Germany	Landesamt für Landwirtschaft, Lebensmittelsicherheit und Fischerei Mecklenburg-Vorpommern	Rostock		Yes
Germany	Germany	Landwirtschaftliche Untersuchungs- und Forschungsanstalt Speyer	Speyer		Yes
Germany	Germany	Landesuntersuchungsamt Institut für Lebensmittelchemie Speyer	Speyer		Yes
Greece	Greece	General Chemical State Laboratory, D Division, Pesticide Residues Laboratory	Athens	x	Yes
Greece	Greece	Regional Center of Plant Protection and Quality Control of Iraklion, Pesticide Residues Laboratory	Iraklion Crete		Yes
Greece	Greece	Benaki Phytopathological Institute, Pesticide Residues Laboratory	Kifissia	x	Yes
Greece	Greece	Regional Center of Plant Protection and Quality Control of Achaia, Pesticide Residues Laboratory	Patra		Yes
Hungary	Hungary	Agricultural Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Hódmezovásárhely	Hódmezovásárhely		Yes
Hungary	Hungary	Agricultural Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Miskolc	Miskolc	x	Yes
Hungary	Hungary	Agricultural Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Velence	Velence		Yes
Ireland	Ireland	Pesticide Control Laboratory, Department of Agriculture, Fisheries and Food	Co. Kildare	x	Yes
Italy	Italy	ARPA Puglia - Dipartimento di Bari	Bari		Yes
Italy	Italy	Laboratorio di Sanità Pubblica ASL BERGAMO	Beragmo		Yes
Italy	Italy	APPA Bolzano	Bolzano		Yes
Italy	Italy	ARPA Ferrara Eccellenza Fitofarmaci	Ferrara		Yes
Italy	Italy	ARPALAZIO SEZIONE P.LE DI LATINA - SERVIZIO LABORATORIO AMBIENTE E SALUTE, UNITA` DI CHIMICA INORGAN	Latina		Yes
Italy	Italy	ASL di Milano - Laboratorio Prevenzione	Milano		No
Italy	Italy	ARPAC-Dipartimento Provinciale di Napoli-L.S. Fitofarmaci	Napoli		No
Italy	Italy	ARPA LAZIO Servizio Ambiente e Salute Sez. di Roma	Roma		Yes
Italy	Italy	Istituto Superiore di Sanità, Pesticide Section	Roma	x	No
Italy	Italy	Istituto Zooprofilattico Sperimentale Abruzzo e Molise	Teramo		Yes
Italy	Italy	APPA Trento Settore Laboratorio e Controlli	Trento		Yes
Italy	Italy	ARPA VENETO DIP.REG.LAB. S.L. VERONA	Verona		Yes
Latvia	Latvia	Institute of Food Safety, Animal Health and Environment (BIOR) - Riga	Riga	x	Yes
Lithuania	Lithuania	National Food and Veterinary Risk Assessment Institute (Lithuania, Vilnius)	Vilnius	x	Yes
Luxembourg	Luxembourg	National Health Laboratory Luxembourg (Food Laboratory)	Luxembourg	x	Yes
Netherlands	Belgium	Groen Agrocontrol	Delfgauw		Yes
Netherlands	BE, NL	Grond-, Gewas- en Milieulaboratorium Zeeuws-Vlaanderen b.v.	Graauw		Yes
Netherlands	Netherlands	NVWA - Netherlands Food and Consumer Product Safety Authority	Wageningen	x	Yes
Netherlands	Netherlands	RIKILT Institute of Food Safety (Natural Toxins & Pesticides)	Wageningen		Yes

* only for EU-member states

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

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Norway	Norway	Norwegian Institute for Agricultural and Environmental Research, Plant Health and Plant Protection Division	Aas	x	Yes
Poland	Poland	Institute of Plant Protection Pesticide Residue Laboratory, Bialystok	Bialystok		Yes
Poland	Poland	Wojewódzka Stacja Sanitarno-Epidemiologiczna w Opolu, Oddzial Laboratoryjny w Kluczborku	Kluczbork		Yes
Poland	Poland	Voievodship Sanitary - Epidemiological Station in Lodz	Lodz		Yes
Poland	Poland	Voievodship Sanitary - Epidemiological Station in Opole	Opole		Yes
Poland	Poland	Institute of Plant Protection, Department of Pesticide Residue Research - Poznan	Poznan		Yes
Poland	Poland	Voievodship Sanitary - Epidemiological Station in Rzeszow, Oddzial Laboratoryjny w Przemyslu	Przemysl		Yes
Poland	Poland	Institute of Plant Protection - National Research Institute, Regional Experimental Station in Rzeszo	Rzeszow		Yes
Poland	Poland	Institute of Horticulture, Food Safety Laboratory (Skierniewice)	Skierniewice		Yes
Poland	Poland	Institute of Plant Protection - National Research Institute, Branch Sosnicowice	Sosnicowice		Yes
Poland	Poland	Main Inspectorate of Plant Health And Seed Inspection, Central Laboratory	Torun		Yes
Poland	Poland	Voievodship Sanitary - Epidemiological Station in Warszaw	Warszaw	x	Yes
Poland	Poland	Voievodship Sanitary - Epidemiological Station in Wroclaw	Wroclaw		Yes
Portugal	Portugal	Regional Laboratory of Veterinary and Food Safety - Madeira Island	Funchal - Madeira Island		Yes
Portugal	Portugal	Direcção Regional de Agricultura e Pescas do Norte- DEQAL	Matosinhos		Yes
Portugal	Portugal	INIA - Pesticides Residues Laboratory	Oeiras	x	Yes
Slovakia	Slovakia	State Veterinary and Food Institute Bratislava	Bratislava	x	Yes
Slovakia	Slovakia	State Veterinary and Food Institute Kosice	Kosice		Yes
Slovenia	Slovenia	Institute of Public Health, Ljubljana	Ljubljana		Yes
Slovenia	Slovenia	Kmetijski inštitut Slovenije	Ljubljana		Yes
Slovenia	Slovenia	Institute of Public Health, Maribor	Maribor	x	Yes
Spain	Spain	Agricultural and Phytopathological Laboratory of Galicia	Abegondo. A Coruña		Yes
Spain	Spain	Instituto Tecnologico de Canarias, División de Investigación y Desarrollo Tecnológico	Agüimes, Gran Canaria		Yes
Spain	Spain	Laboratorio Agrario Regional de Castilla La Mancha	Albacete		Yes
Spain	Spain	Laboratory of Barcelona Public Health Agency	Barcelona		Yes
Spain	Spain	Laboratorio Agrario Regional - Junta de Castilla y Leon	Burgos		Yes
Spain	Spain	Agrofood Laboratory of the Comunidad Valenciana	Burjassot-Valencia		Yes
Spain	Spain	Laboratorio de Salud Pública de Cuenca	Cuenca		Yes
Spain	Spain	Laboratorio de Producción y Sanidad Vegetal de Jaén	Jaen		Yes
Spain	Spain	Laboratorio Arbitral Agroalimentario, Madrid	Madrid	x	Yes
Spain	Spain	National Centre for Food - Spain, Majadahonda	Majadahonda		Yes
Spain	Spain	Navarra de Servicios y Tecnologias, S.A.	Villava		Yes
Spain	Spain	Laboratorio Agroalimentario de Zaragoza	Zaragoza		Yes
Sweden	Sweden	Eurofins - Food & Agro Sweden, Lidköping	Lidköping		Yes
Sweden	Sweden	National Food Agency, Uppsala, Sweden	Uppsala	x	Yes
Switzerland	Switzerland	Kantonales Laboratorium Zürich	Zürich		Yes
United Kingdom	United Kingdom	Science and Advice for Scottish Agriculture	Edinburgh		Yes
United Kingdom	United Kingdom	Laboratory of the Government Chemist - Teddington	Teddington		Yes
United Kingdom	United Kingdom	Eurofins - United Kingdom, Wolverhampton	Wolverhampton		Yes
United Kingdom	UK, MT	The Food and Environment Research Agency - York	York	x	Yes

* only for EU-member states

(b): participating labs from Third Countries

Country	Institution	City	Reported results
Australia	National Measurement Institute	Melbourne	Yes
Egypt	Central Laboratory of Residue analysis of Pesticides and Heavy Metals in Foods	Giza	Yes
Singapore	Veterinary Public Health Laboratory	Singapore	Yes
USA	Eurofins Central Analytical Laboratories	Metairie, LA	Yes
Zambia	Central Veterinary Reseach Institute	Lusaka	No

Appendix 2 Data of homogeneity test

2.4-D (free acid) [mg/kg]			Bromide ion [mg/kg]			Chlorothalonil [mg/kg]		
Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2
6	0.289	0.289	6	32.1	28.6	6	0.172	0.190
23	0.308	0.281	23	39.5	34.3	23	0.179	0.177
45	0.293	0.291	45	37.3	36.5	45	0.191	0.169
51	0.293	0.293	51	29.4	36.4	51	0.179	0.158
79	0.289	0.271	79	37.0	35.5	79	0.171	0.175
83	0.306	0.305	83	35.4	29.4	83	0.165	0.172
106	0.290	0.289	106	35.9	30.8	106	0.172	0.172
118	0.299	0.301	118	33.9	34.1	118	0.173	0.197
140	0.287	0.281	140	33.0	35.5	140	0.177	0.177
144	0.305	0.310	144	32.7	26.6	144	0.173	0.152

Cyromazine [mg/kg]			Dihtiocarbamates [mg/kg]			Ethephon [mg/kg]		
Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2
6	0.352	0.373	6a	0.813	0.862	6	0.220	0.225
23	0.339	0.358	23a	0.727	0.738	23	0.210	0.229
45	0.342	0.344	45a	0.783	0.828	45	0.210	0.219
51	0.351	0.344	51a	0.810	0.843	51	0.212	0.230
79	0.356	0.374	79a	0.909	1.013	79	0.229	0.248
83	0.364	0.350	83a	0.753	0.711	83	0.253	0.213
106	0.359	0.358	106a	0.810	0.884	106	0.270	0.234
118	0.340	0.383	114a	0.879	0.858	118	0.254	0.216
140	0.349	0.360	118	0.853	0.748	140	0.207	0.251
144	0.367	0.361	140	0.844	0.837	144	0.208	0.203

Fenbutatin oxide [mg/kg]			Glyphosate [mg/kg]		
Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2
6	0.242	0.228	6	0.800	0.941
23	0.236	0.230	23	0.792	0.793
45	0.244	0.242	45	0.767	0.822
51	0.234	0.238	51	0.790	0.877
79	0.240	0.226	79	0.794	0.849
83	0.236	0.224	83	0.764	0.870
106	0.224	0.238	106	0.835	0.862
118	0.234	0.224	118	0.914	0.933
140	0.248	0.226	140	0.902	0.888
144	0.236	0.232	144	0.923	0.991

Sample number with suffix „a" were samples after the 2. mixing procedure.

Appendix 3 Data of stability test

	2.4-D (free acid)						Bromide ion					
	12.04.2012		08.05.2012		30.05.2012		12.04.2012		—		30.05.2012	
	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]
	6	0.289	6a	0.303	6a	0.309	6	30.3	—		6a	33.1
	45	0.292	45a	0.291	45a	0.304	45	36.9	—		45a	26.2
	79	0.280	79a	0.299	79a	0.296	79	36.3	—		79a	33.0
	118	0.300	118a	0.307	118a	0.325	118	34.0	—		118a	31.4
	144	0.307	144a	0.293	144a	0.300	144	29.7	—		144a	37.0
Mean [mg/kg]	**0.294**		**0.299**		**0.307**		**33.4**		**—**		**32.1**	
RSD* [%]	**3.54 %**		**2.19 %**		**3.72 %**		**9.94 %**		**—**		**12.17 %**	
Diviation [%] (ref. 1. Anaylsis)	**—**		**1.16 %**		**4.48 %**		**—**		**—**		**-3.88 %**	

	Chlorothalonile						Cyromazine					
	25.04.2012		08.05.2012		30.05.2012		12.04.2012		08.05.2012		30.05.2012	
	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]
	6a	0.115	6a	0.116	6a	0.119	6	0.350	6a	0.344	6a	0.380
	45a	0.108	45a	0.114	45a	0.118	45	0.355	45a	0.370	45a	0.365
	79a	0.124	79a	0.117	79a	0.117	79	0.386	79a	0.364	79a	0.374
	118a	0.097	118a	0.121	118a	0.125	118	0.377	118a	0.383	118a	0.371
	144a	0.118	144a	0.127	144a	0.116	144	0.380	144a	0.368	144a	0.395
Mean [mg/kg]	**0.112**		**0.119**		**0.119**		**0.370**		**0.366**		**0.377**	
RSD* [%]	**9.22 %**		**4.23 %**		**3.03 %**		**4.34 %**		**3.86 %**		**3.03 %**	
Diviation [%] (ref. 1. Anaylsis)	**—**		**5.98 %**		**5.78 %**		**—**		**-1.03 %**		**2.00 %**	

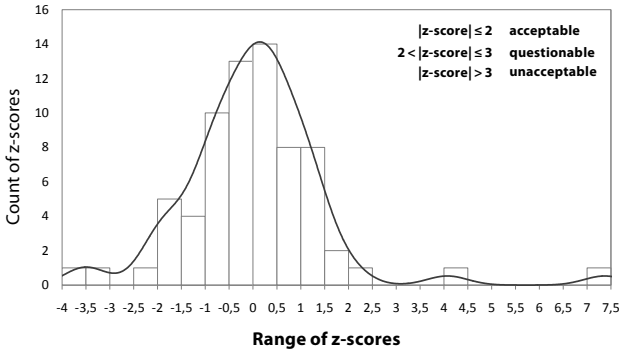
	Ethephon						Fenbutatin oxide					
	12.04.2012		08.05.2012		30.05.2012		12.04.2012		08.05.2012		30.05.2012	
	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]
	6	0.222	6a	0.246	6a	0.239	6	0.235	6a	0.221	6a	0.241
	45	0.215	45a	0.232	45a	0.240	45	0.243	45a	0.222	45a	0.229
	79	0.239	79a	0.222	79a	0.239	79	0.233	79a	0.224	79a	0.247
	118	0.235	118a	0.244	118a	0.221	118	0.229	118a	0.231	118a	0.227
	144	0.206	144a	0.229	144a	0.224	144	0.234	144a	0.234	144a	0.238
Mean [mg/kg]	**0.223**		**0.235**		**0.233**		**0.235**		**0.226**		**0.236**	
RSD* [%]	**6.19 %**		**4.36 %**		**3.99 %**		**2.18 %**		**2.63 %**		**3.55 %**	
Diviation [%] (ref. 1. Anaylsis)	**—**		**5.11 %**		**4.26 %**		**—**		**-3.62 %**		**0.71 %**	

***** RSD = relative standard diviation
Sample number with suffix „a" were samples after the 2. mixing procedure.

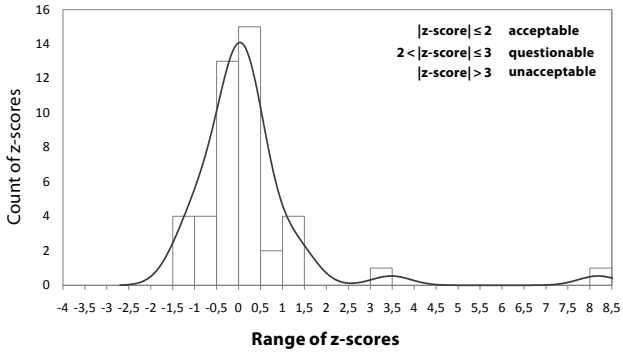
	Glyphosate						Dithiocarbamates					
	18.04.2012		08.05.2012		30.05.2012		18.04.2012		08.05.2012		14.06.2012	
	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]	Sample	[mg/kg]
	6	0.870	6a	0.879	6a	0.882	114a-1	0.820	114a-1	0.873	114a-1	0.605
	45	0.795	45a	0.833	45a	0.897	114a-2	—	114a-2	0.758	114a-2	0.641
	79	0.821	79a	0.797	79a	0.852	114a-3	0.683	114a-3	0.663	114a-3	0.816
	118	0.923	118a	0.919	118a	0.864	114a-4	0.840	114a-4	0.871	114a-4	0.719
	144	0.957	144a	0.880	144a	0.820	114a-5	0.910	114a-5	0.703	114a-5	0.621
Mean [mg/kg]	**0.873**		**0.861**		**0.863**		**0.813**		**0.774**		**0.680**	
RSD* [%]	**7.77 %**		**5.46 %**		**3.42 %**		**11.69 %**		**12.42 %**		**12.88 %**	
Diviation [%] (ref. 1. Anaylsis)	**—**		**-1.35 %**		**-1.14 %**		**—**		**-4.87 %**		**-16,35 %**	

Appendix 4 Histograms and kernel density estimates of z-scores distribution

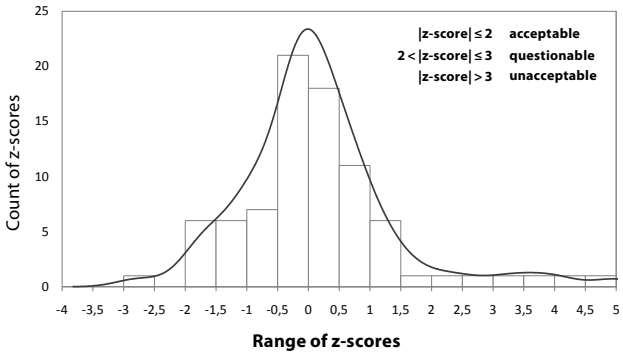
2,4-D (free acid)



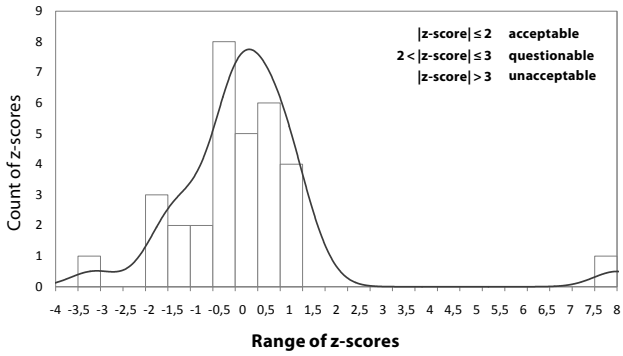
Bromide ion



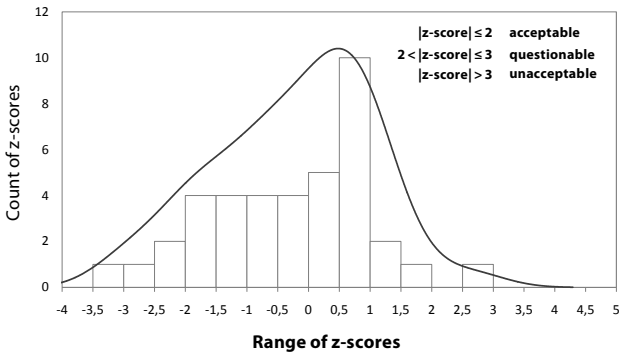
Dithiocarbamates (sum) expr. as CS_2



Ethephon

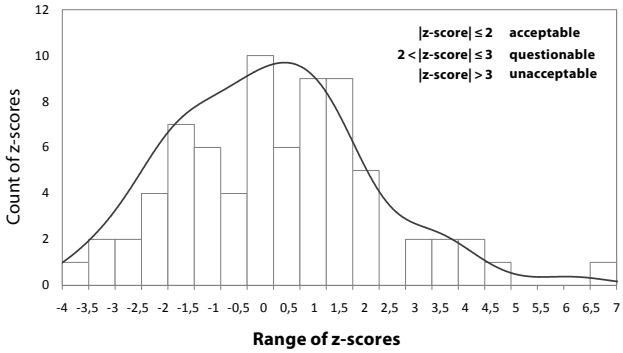


Glyphosate

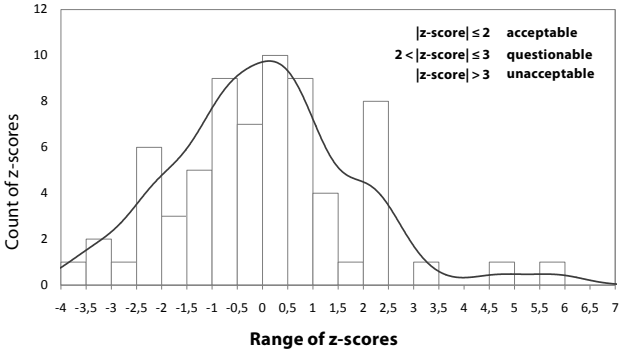


Appendix 4 (cont.) Histograms and kernel density estimates of z-scores distribution

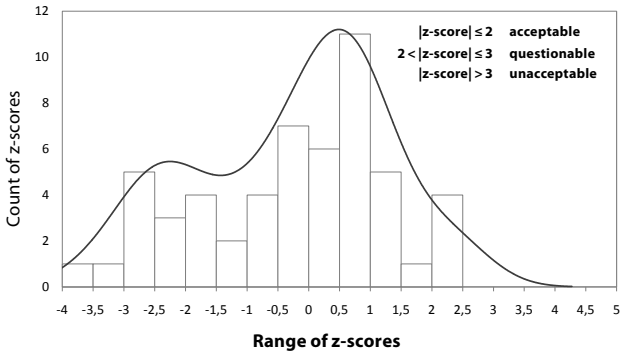
Chlorothalonil
all results



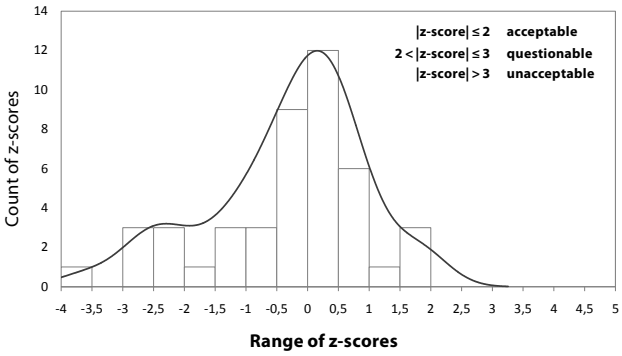
Chlorothalonil
only results recovery corrected
(originally corrected + corrected by Organizer)



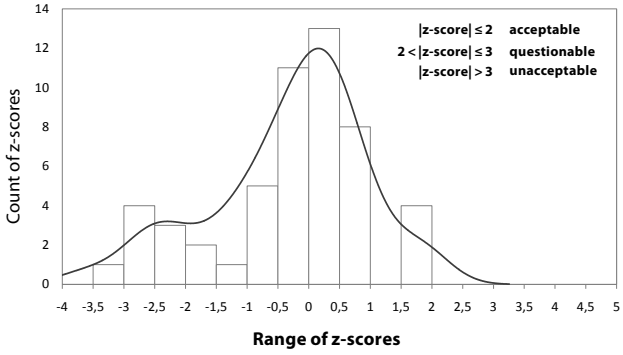
Cyromazine
all results



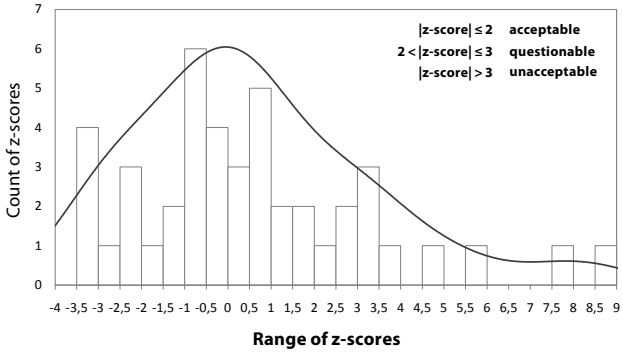
Cyromazine
excluding results
obtained using QuEChERS without correction of results for recovery



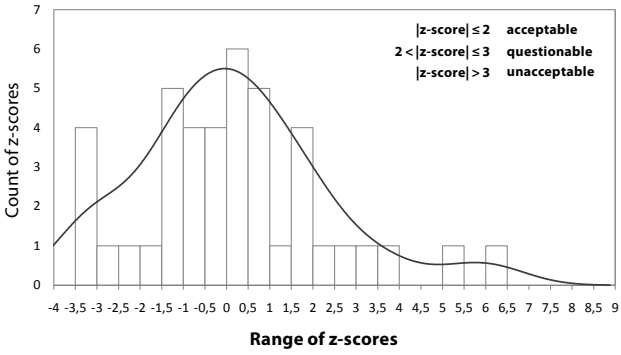
Cyromazine
only results recovery corrected
(originally corrected + corrected by Organizer)



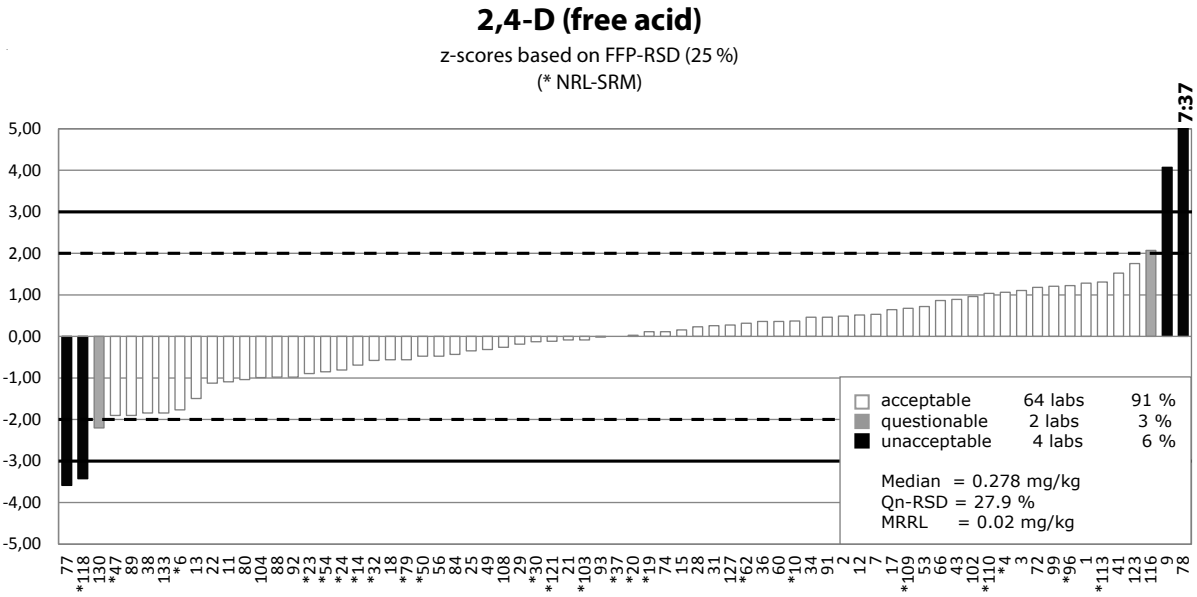
Fenbutatin oxide
all results

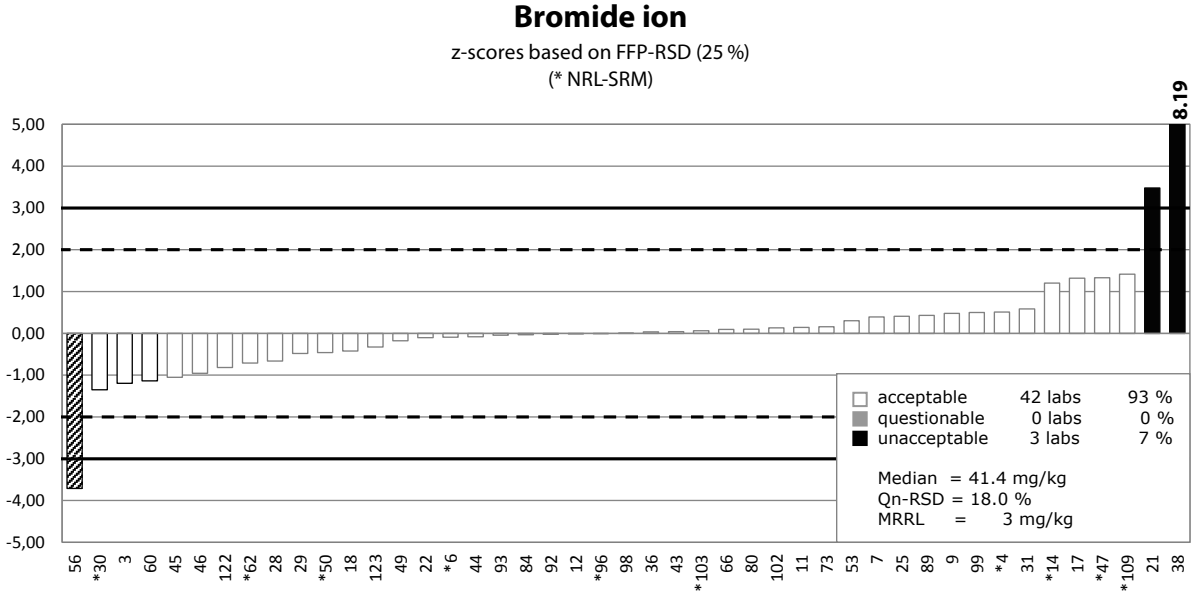


Fenbutatin oxide
only results recovery corrected
(originally corrected + corrected by Organizer)



Appendix 5 Graphic presentation of z-scores

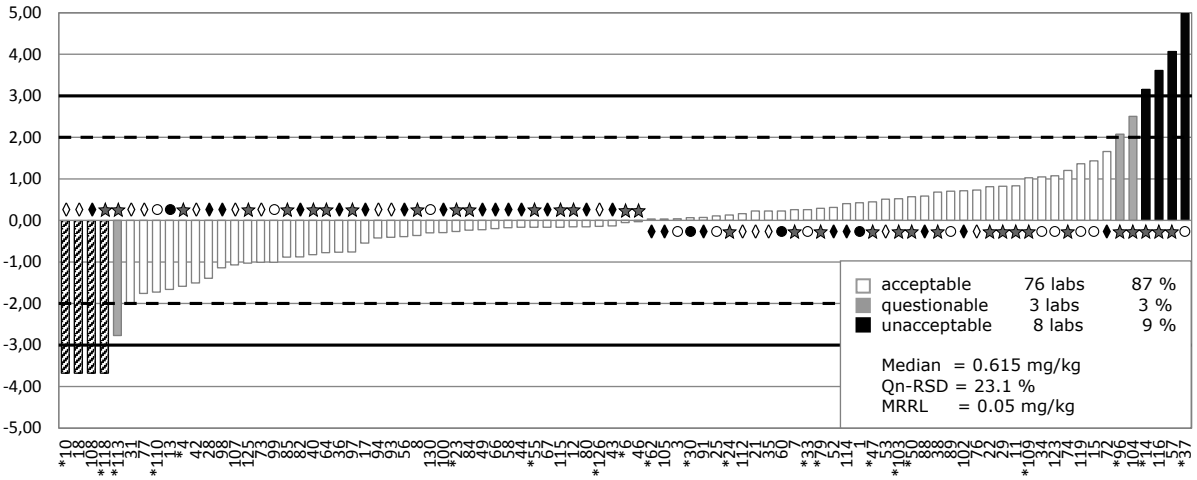




Appendix 5 (cont.) Graphic presentation of z-scores

Dithiocarbamates (as CS_2)

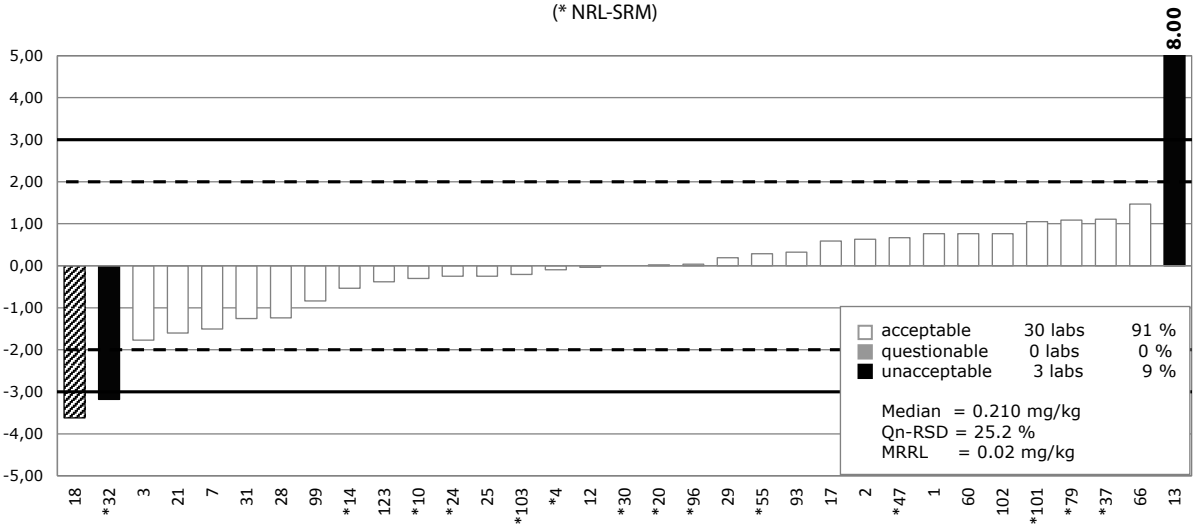
z-scores based on FFP-RSD (25 %)
(* NRL-SRM)



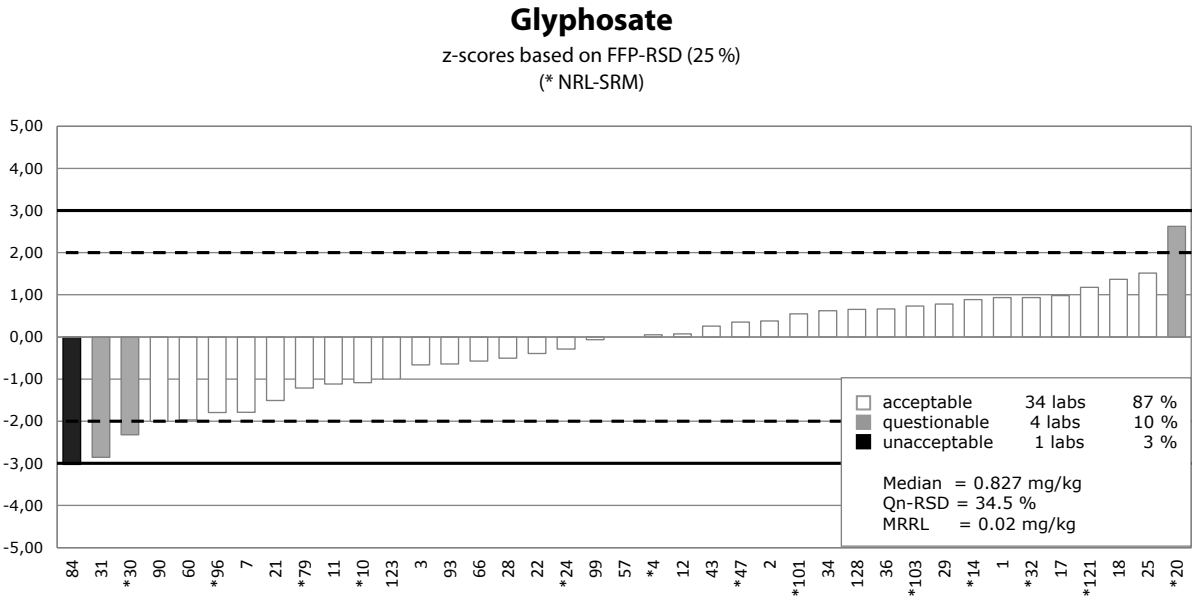
Methode used:
- ○ Headspace/GC
- ● Headspace-SPME/GC
- ★ Liquid-liquid Partitioning/GC
- ◊ Photometric Cu (II)/DEA
- ♦ Photometric Xanthogenate

Ethephon

z-scores based on FFP-RSD (25 %)
(* NRL-SRM)



Appendix 5 (cont.) Graphic presentation of z-scores

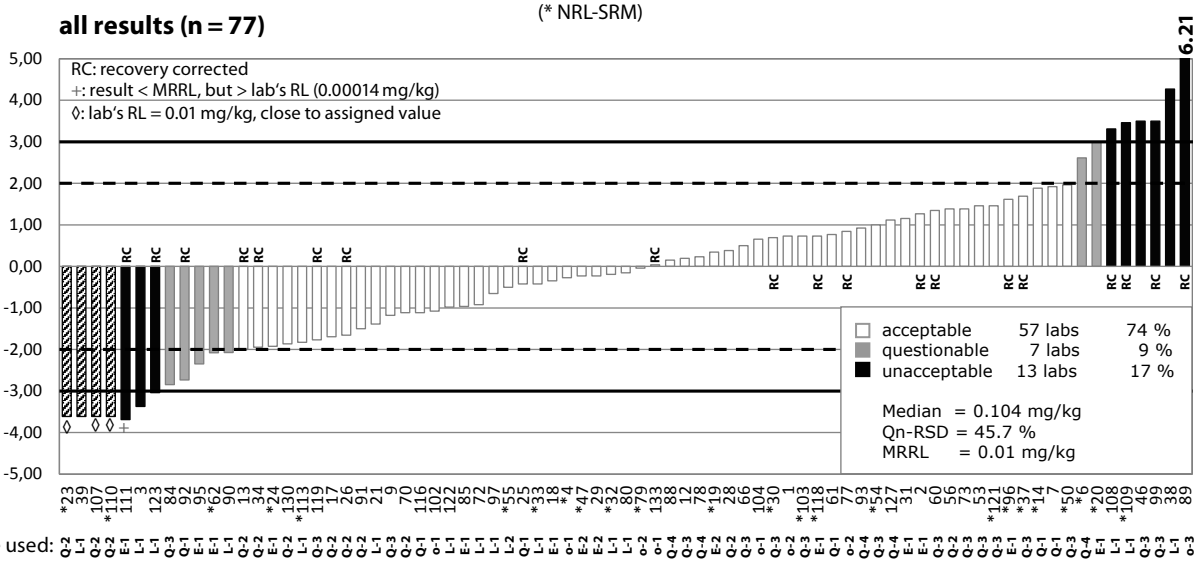


Appendix 5 (cont.) Graphic presentation of z-scores

Chlorothalonil (FOR INFORMATION ONLY)

z-scores based on FFP-RSD (25 %)
(* NRL-SRM)

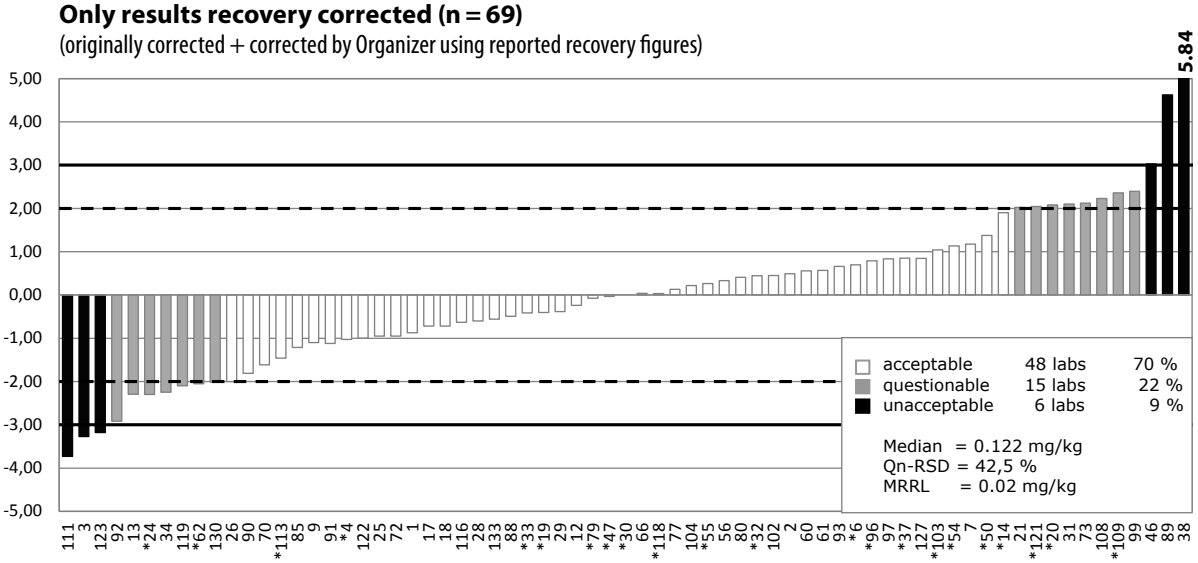
all results (n = 77)



Methode used:

E-1) Ethylacetate based
E-2) Ethylacetate based, acidified during extraction/partitioning
L-1) Luke/S19-Type
L-2) Luke/S19-Type + acidified during extraction
Q-1) QuEChERS (original, acetate buffered, citrate buffered, other) without dSPE
Q-2) QuEChERS + dSPE with PSA
Q-3) QuEChERS for chlorothalonil (acidified during extraction/partitioning)
Q-4) QuEChERS for chlorothalonil (acidified during extraction/partitioning) + dSPE with PSA
o-1) Other
o-2) Other, acidified during extraction/partitioning
o-3) Dilute and shoot

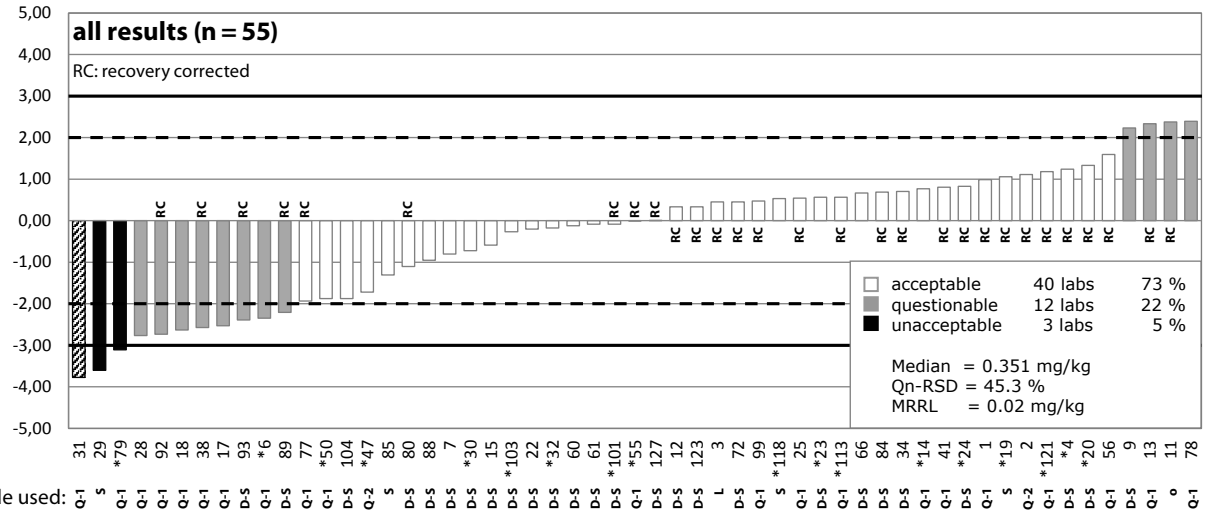
Only results recovery corrected (n = 69)
(originally corrected + corrected by Organizer using reported recovery figures)



Appendix 5 (cont.) Graphic presentation of z-scores

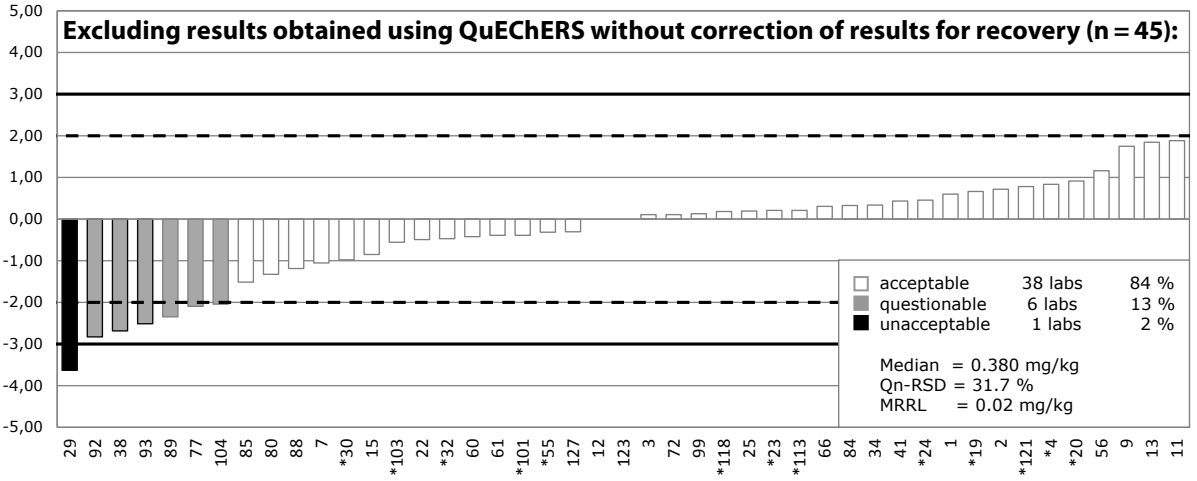
Cyromazine (FOR INFORMATION ONLY)

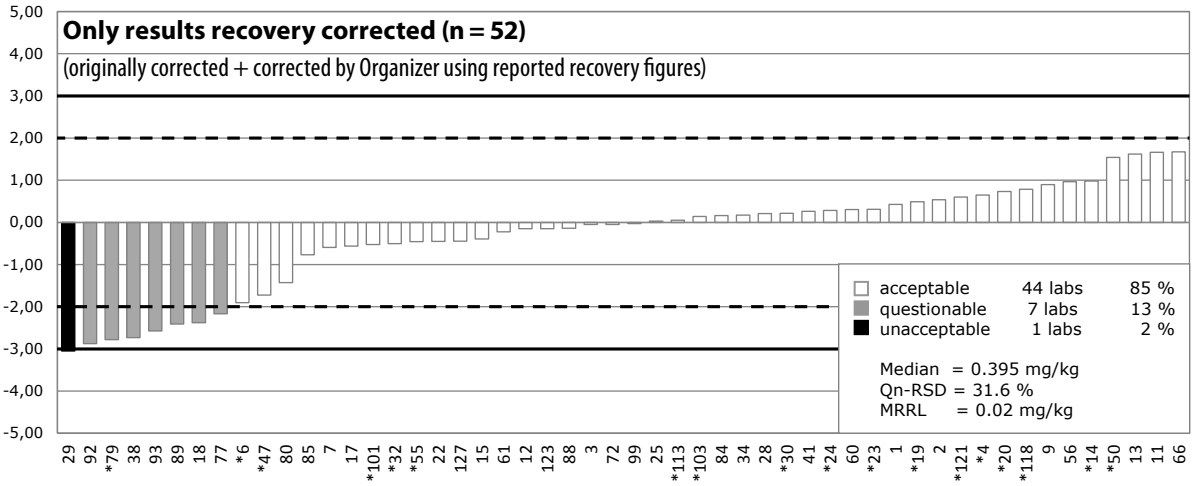
z-scores based on FFP-RSD (25 %)
(* NRL-SRM)



Methode used:

D-S) Dilute and Shoot (QuPPe-Type)
Q-1) QuEChERS
Q-2) QuEChERS (acetate buffered)
S) Sweet
L) Luke Type
o) Solid liquid extraction or other

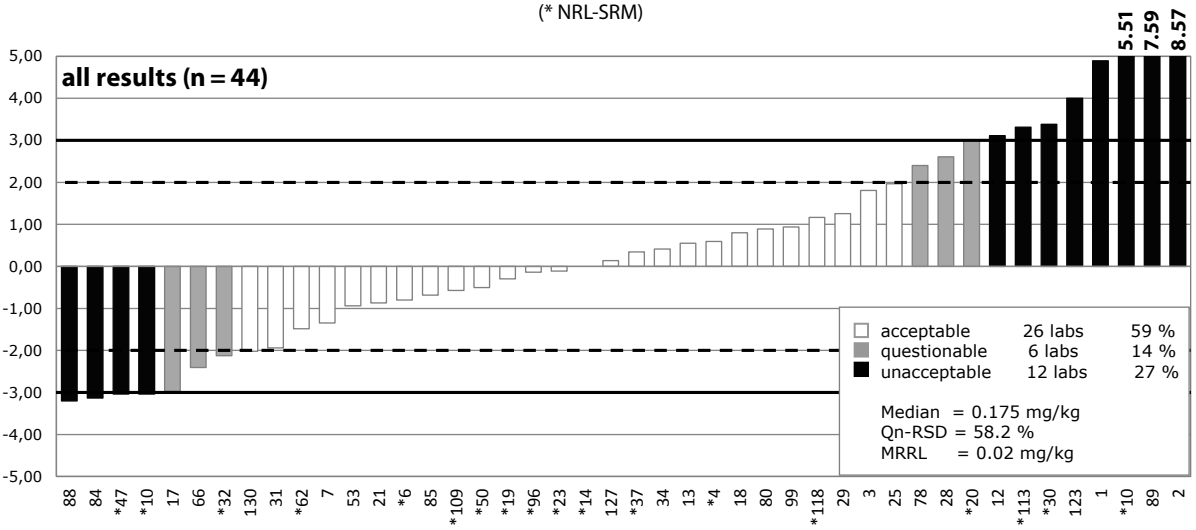


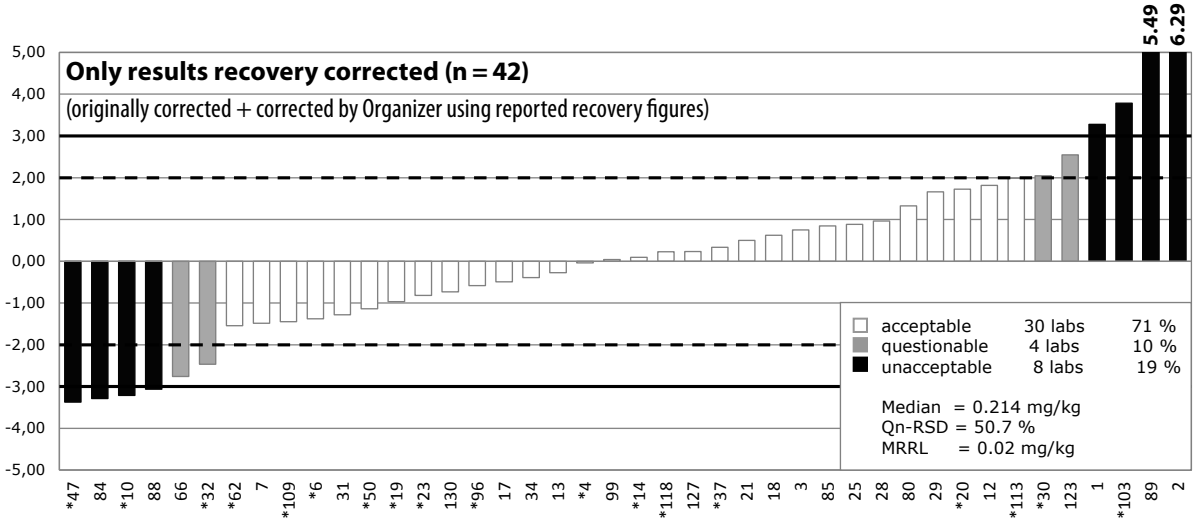


Appendix 5 (cont.) Graphic presentation of z-scores

Fentutatin oxide (FOR INFORMATION ONLY)

z-scores based on FFP-RSD (25 %)
(* NRL-SRM)





Appendix 6 Special evaluation for chlorothalonil, cyromazine, and fenbutatin oxide FOR INFORMATION ONLY

Compound		Chlorothalonil			Cyromazine				Fenbutatin Oxide		
Assigned Value* [mg/kg]			0.104	0.122		0.351	0.380	0.395		0.175	0.214
Qn-RSD			45.7%	42.5%		45.3%	31.7%	31.6%		58.0%	50.7%
Lab code SRM7-	NRL-SRM	Conc. [mg/kg]	z-scores	z-scores	Conc. [mg/kg]	z-scores	z-scores	z-scores	Conc. [mg/kg]	z-scores	z-scores
1		0.123	0.73	0.03	0.437	0.98	0.60	0.43	0.389	4.89	3.27
2		0.137	1.27	0.49	0.448	1.11	0.72	0.54	0.550	8.57	6.28
3		0.016	-3.37	-3.46	0.390	0.44	0.11	-0.05	0.254	1.81	0.75
4	*	0.097	-0.27	-0.82	0.459	1.23	0.83	0.65	0.201	0.59	-0.24
6	*	0.172	2.62	1.64	0.145	-2.35	-2.47	-2.53	0.140	-0.80	-1.38
7		0.154	1.92	1.05	0.280	-0.81	-1.05	-1.16	0.116	-1.35	-1.83
9		0.073	-1.18	-1.59	0.546	2.22	1.75	1.53			
10	*								0.042	-3.04	-3.21
11					0.559	2.37	1.88	1.66			
12		0.109	0.19	-0.43	0.380	0.33	0.00	-0.15	0.311	3.11	1.81
13		0.052	-2.00	-2.30	0.555	2.32	1.84	1.62	0.199	0.55	-0.28
14	*	0.153	1.88	1.02	0.418	0.76	0.40	0.23	0.175	0.00	-0.73
15					0.299	-0.59	-0.85	-0.97			
17		0.060	-1.69	-2.03	0.129	-2.53	-2.64	-2.69	0.045	-2.97	-3.16
18		0.095	-0.35	-0.89	0.120	-2.63	-2.74	-2.78	0.210	0.80	-0.07
19	*	0.113	0.35	-0.30	0.443	1.05	0.66	0.49	0.162	-0.30	-0.97
20	*	0.182	3.00	1.97	0.467	1.32	0.92	0.73	0.306	2.99	1.72
21		0.068	-1.38	-1.77					0.137	-0.87	-1.44
22					0.333	-0.21	-0.49	-0.63			
23	*	FN	-3.62	-3.67	0.400	0.56	0.21	0.05	0.170	-0.11	-0.82
24	*	0.054	-1.92	-2.23	0.423	0.82	0.45	0.28			
25		0.093	-0.42	-0.95	0.398	0.54	0.19	0.03	0.261	1.97	0.88
26		0.061	-1.65	-2.00							
28		0.114	0.38	-0.26	0.108	-2.77	-2.86	-2.91	0.289	2.61	1.40
29		0.098	-0.23	-0.78	0.035	-3.60	-3.63	-3.65	0.230	1.26	0.30
30	*	0.122	0.69	0.00	0.287	-0.73	-0.98	-1.09	0.323	3.38	2.04
31		0.134	1.15	0.39	FN	-3.77	-3.79	-3.80	0.090	-1.94	-2.32
32	*	0.099	-0.19	-0.75	0.335	-0.18	-0.47	-0.61	0.082	-2.13	-2.47
33	*	0.093	-0.42	-0.95							
34		0.054	-1.94	-2.25	0.412	0.70	0.34	0.17	0.193	0.41	-0.39
37	*	0.148	1.69	0.85					0.190	0.34	-0.45
38		0.215	4.27	3.05	0.125	-2.58	-2.68	-2.73			
39		FN	-3.62	-3.67							
41					0.421	0.80	0.43	0.26			
46		0.195	3.50	2.39							
47	*	0.098	-0.23	-0.79	0.200	-1.72	-1.89	-1.97	0.042	-3.04	-3.21
50	*	0.155	1.96	1.08	0.186	-1.88	-2.04	-2.12	0.153	-0.50	-1.14
53		0.142	1.46	0.66					0.134	-0.94	-1.50
54	*	0.130	1.00	0.26							
55	*	0.091	-0.50	-1.02	0.350	-0.01	-0.32	-0.46			
56		0.140	1.38	0.59	0.490	1.58	1.16	0.96			
60		0.139	1.35	0.56	0.340	-0.13	-0.42	-0.56			

* details about establishment of the hypothetical Assigned Values of each sub-population please see Section 3.5.4 and Appendix 5.

Appendix 6 (cont.) Special evaluation for chlorothalonil, cyromazine, and fenbutatin oxide FOR INFORMATION ONLY

Compound		Chlorothalonil			Cyromazine				Fenbutatin Oxide		
Assigned Value* [mg/kg]			0.104	0.122		0.351	0.380	0.395		0.175	0.214
Qn-RSD			45.7%	42.5%		45.3%	31.7%	31.6%		58.0%	50.7%
Lab code SRM7-	NRL-SRM	Conc. [mg/kg]	z-scores	z-scores	Conc. [mg/kg]	z-scores	z-scores	z-scores	Conc. [mg/kg]	z-scores	z-scores
61		0.124	0.77	0.07	0.343	-0.09	-0.39	-0.53			
62	*	0.050	-2.08	-2.36					0.110	-1.49	-1.94
66		0.117	0.50	-0.16	0.409	0.66	0.31	0.14	0.070	-2.41	-2.70
70		0.075	-1.12	-1.54							
72		0.080	-0.92	-1.38	0.390	0.44	0.11	-0.05			
73		0.140	1.38	0.59							
77		0.126	0.85	0.13	0.181	-1.94	-2.09	-2.17			
78		0.110	0.23	-0.39	0.560	2.38	1.89	1.67	0.280	2.40	1.23
79	*	0.103	-0.04	-0.62	0.078	-3.11	-3.18	-3.21			
80		0.100	-0.15	-0.72	0.254	-1.11	-1.33	-1.43	0.214	0.89	0.00
84		0.030	-2.85	-3.02	0.411	0.68	0.33	0.16	0.038	-3.13	-3.29
85		0.079	-0.96	-1.41	0.236	-1.31	-1.52	-1.61	0.145	-0.69	-1.29
88		0.108	0.15	-0.46	0.267	-0.96	-1.19	-1.30	0.035	-3.20	-3.35
89		0.263	6.12	4.62	0.157	-2.21	-2.35	-2.41	0.507	7.59	5.48
90		0.050	-2.07	-2.36							
91		0.065	-1.50	-1.87							
92		0.033	-2.73	-2.92	0.111	-2.74	-2.83	-2.88			
93		0.128	0.92	0.20	0.141	-2.39	-2.52	-2.57			
95		0.043	-2.35	-2.59							
96	*	0.146	1.62	0.79					0.169	-0.14	-0.84
97		0.087	-0.65	-1.15							
99		0.195	3.50	2.39	0.392	0.47	0.13	-0.03	0.216	0.94	0.04
101	*				0.343	-0.09	-0.39	-0.53			
102		0.076	-1.08	-1.51							
103	*	0.123	0.73	0.03	0.327	-0.27	-0.56	-0.69	0.416	5.51	3.78
104		0.121	0.65	-0.03	0.186	-1.88	-2.04	-2.12			
107		FN	-3.62	-3.67							
108		0.190	3.31	2.23							
109	*	0.194	3.46	2.36					0.150	-0.57	-1.20
110		FN	-3.62	-3.67							
111		0.008	-3.68	-3.73							
113	*	0.057	-1.83	-2.15	0.400	0.56	0.21	0.05	0.320	3.31	1.98
116		0.075	-1.12	-1.54							
118	*	0.123	0.73	0.03	0.397	0.52	0.18	0.02	0.226	1.17	0.22
119		0.058	-1.77	-2.10							
121	*	0.142	1.46	0.66	0.454	1.17	0.78	0.60			
122		0.079	-0.98	-1.43							
123		0.025	-3.04	-3.18	0.380	0.33	0.00	-0.15	0.350	4.00	2.54
127		0.133	1.12	0.36	0.351	0.00	-0.31	-0.45	0.181	0.14	-0.62
130		0.056	-1.87	-2.18					0.087	-2.02	-2.38
133		0.105	0.04	-0.56							
137		FN	-3.62	-3.67	0.330	-0.24	-0.53	-0.66	0.067	-2.47	-2.75
138		0.170	2.54	1.57	0.440	1.01	0.63	0.46			

* details about establishment of the hypothetical Assigned Values of each sub-population please see Section 3.5.4 and Appendix 5.

Appendix 7 Methods used by the participating laboratories (ordered by z-scores)

2,4-D (free acid)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation
77		No	1 – 2 y	0.029	-3.58	0.01	5	10 mL	No	ACN	No	Centrifugation	No
118	x	Yes	> 2 y	0.04	-3.42	0.02	5	No	No	ACN	No		No
130		Yes	> 2 y	0.125	-2.20	0.01	5	10 mL	No	acidified ACN 5 g sample +10 g H_20 +10 mL (ACN + 0.1 % HAc)	1) 0.1 % HAc in ACN during extraction; 2) citrate buffer during separation		No
47	x	Yes	> 2 y	0.146	-1.90	0.02	5	10 ml	No	ACN	Acetate Buffer	Centrifugation (2×), 150 mg $MgSO_4$ added before 2nd centrifugation	No
89		Yes	> 2 y	0.146	-1.90	0.02	1	No	No	ACN	No	Centrifugation, solvent exchange	No
38		Yes	> 2 y	0.15	-1.84	0.01	1	10 ml	No	ACN	Citrate Buffer	None	No
133		Yes	> 2 y	0.15	-1.84	0.01	1	No	No	ACN	No		No
6	x	Yes	1 – 2 y	0.155	-1.77	0.02	5	Yes	No	ACN	Citrate Buffer	None	No
13		No	> 2 y	0.174	-1.50	0.01	5	10 ml	No	ACN	No	dSPE (PSA/ $MgSO_4$)	No
22		Yes	> 2 y	0.2	-1.12	0.03	1	Yes	No	MeOH, Water	No	Filtration, Centrifugation	No
11		Yes	None	0.202	-1.09	0.01	5	9 ml	No	9 ml Water/ 20 ml MeOH	6-7	SPE-column, diatomaceous earth	No
80		Yes	> 2 y	0.206	-1.04	0.04	5	10 g	No	MeOH, DCM	pH 4.5	LLP, ChemElut pH 4.5	No
104		No	None	0.209	-0.99	0.02	1	Yes	No	MeOH/Water	pH over 8 before clean up 1, pH about 1 after clean up 1		No

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 3 trasitions	Std add. to extract aliquots	No	No	85 % (0.2 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer), No PSA clean-up
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	Yes-1	58 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to Extract	No	No	100.1 % (0.04 mg/kg)	SB-EUPT	3	EN 151662 (QuEChERS - Citrate Buffer) modified, Acetonitrilie used with 0.1 % HAc
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	TPP	No	77 % (0.02 mg/kg)	SB-Other	1	AOAC Official Method 2007.01 (QuEChERS - Acetate Buffer)
	LC-MS/MS (QQQ)	No	Std add. to sample portions (Std add. with A-Spikes, strong Signalinhibition approx. factor 3 cp. with extern Standard)	No	Yes-2		SB-EUPT	4	other, ACN extraction
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No Info	No	63 % (0.010 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer), Without SPC with PSA
	LC-MS/MS (QQQ)	No	PS-ML	Cloprop	Yes-1	No Info	SB-EUPT	2	other, Extraction w. ACN dosage LC-MS/MS
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	79 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer), modified
	LC-MS/MS (QQQ)	No	MM-ML	unspecified	Yes-1	27 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	MM-ML	No	No	100 % (0.02 and 0.1 mg/kg)	SB-EUPT	2	other, methanolic method Kit Granby et al
	LC-MS/MS (QQQ)	No	Std add. to sample portions	No	Yes-2	68 % (blank spiked,; different conc. levels)	SB-EUPT	4	Klein, Alder, J. AOAC 86/1015/2003
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Bentazone-D6	No	85.7 % (0.2 mg/kg)	SB-EUPT	1	Klein, Alder, J. AOAC 86/1015/2003, ChemElut pH 4.5
	LC-MS/MS (QQQ)	No	MM-SL	No	No	99 % (0.02 mg/kg)	SB-EUPT	1	other, confidential method

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

2,4-D (free acid)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
88		Yes	> 2 y	0.21	-0.98	0.02	5	10 ml, waiting for 10 min	Add. 5N NaOH	ACN	pH ca. 12	Centrifugation	No	
92		Yes	> 2 y	0.21	-0.98	0.02	5	Yes	No	ACN	No	w/o PSA	No	
23	x	Yes	> 2 y	0.216	-0.89	0.01	5	10 ml	No	ACN	No	Freeze-out, Centrifugation, Filtration	No	
54	x	Yes	> 2 y	0.219	-0.85	0.02	5	10 ml	No	ACN	No	None	No	
24	x	Yes	> 2 y	0.222	-0.81	0.02	15	15 ml	No	ACN	Acetate Buffer QuEChERS	dSPE (PSA/ $MgSO_4$)	No	
14	x	Yes	> 2 y	0.23	-0.69	0.016	5	10 ml before extraction	No	ACN	No	only desiccation with $mgSO_4$	No	
32	x	No	> 2 y	0.238	-0.58	0.02	5	5 ml	No	MeOH ammonium acetate 20mM	No	None	No	
18		Yes	1 – 2 y	0.239	-0.56	0.01	5	Yes	Yes	ACN	No	None	No	
79	x	Yes	< 1 y	0.239	-0.56	0.01	5	10 ml	No	ACN	No	None	No	
50	x	Yes	> 2 y	0.245	-0.47	0.01	5	10 ml	No	ACN	No	Freeze-out	No	
56		No	> 2 y	0.245	-0.47	0.010	5	10 g	No	ACN	No	None	No	
84		Yes	> 2 y	0.248	-0.43	0.01	5	prior to extraktion	No	ACN	No	dSPE (w/o PSA)		
25		Yes	> 2 y	0.254	-0.35	0.01	1	Yes	No	ACN, Water	No	LLP	No	
49		Yes	> 2 y	0.256	-0.32	0.01	5	10 g	No	ACN	No	None	No	
108		No	< 1 y	0.26	-0.26	0.02	5	10 ml	No	ACN	No		No	
29		Yes	> 2 y	0.265	-0.19	0.01	5	Yes	No	EtAc	HAc 1 %	Filtration	No	
30	x	Yes	> 2 y	0.269	-0.13	0.01	5	10 ml	No	ACN	No	None	No	
121	x	No	1 – 2 y	0.27	-0.12	0.02	5	Yes	No	ACN 20 ml ACN instead of 10 ml	No	Freeze-Out	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	(but NO recov. corr.)	No	71 %	SB-EUPT	3	QuEChERS (EURL-SRM mth for acidic pesticides, with alkaline hydrolysis)
	LC-MS/MS (QQQ)	No	Std add. to extract aliquots	Nicarbazin	Yes-2		SB-EUPT		EN 151662 (QuEChERS - Citrate Buffer), without PSA
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	66.4 % (0.02 mg/kg)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer), without PSA/C18
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2nd transition	MM-ML	No	No	70 % (0.020 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	TPP	Yes-1	10.2 % (0.1 mg/kg)	SB-EUPT	1	AOAC Official Method 2007.01 (QuEChERS - Acetate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	TPP	No	88 % (0.05 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer), QuEChERS without PSA
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Oxfendazole	No	113 % (200 mg/kg)	SB-EUPT	1	other, MeOH extraction
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	102 %	SB-EUPT	5	QuEChERS (EURL-SRM mth for acidic pesticides, with alkaline hydrolysis)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	MM-ML	No	No	79 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), relevant ions	MM-ML	No	No	92 % (0.2 mg/kg)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	MM-SL	No	No	80.1 % (0.150 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	Nicarbazin	No	90 % (0.02 mg/kg)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	Std add. to sample portions	Isoproturon	Yes-2	77 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Nicarbazin	No	71.9 % (0.2 mg/kg)	SB-EUPT	4	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	None	No	89 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer),
	LC-MS/MS (QQQ)	No	MM-SL	Pirimicarb-D6	No	77 %	SB-EUPT	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, EtAc with 1 % HAc, National Food Administration, Sweden
	LC-MS/MS (QQQ)	No	MM-ML	TPP	No	87.9 % (0.5 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer), w/o dSPE
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Carbaryl-C13	No	84 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

2,4-D (free acid)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
21		Yes	> 2 y	0.272	-0.09	0.01	1	No	No	MeOH	No	Na_2SO_4	No	
103	x	Yes	> 2 y	0.272	-0.09	0.02	5	Yes	No	ACN	Citrate Buffer		No	
93		Yes	1 – 2 y	0.277	-0.01	0.020	8	15 ml	No	ACN	Citrate Buffer	None	No	
37	x	Yes	> 2 y	0.278	0.00	0.01	5	Yes	No	ACN	No	None	No	
20	x	Yes	> 2 y	0.28	0.03	0.02	5	10 ml	No	ACN	Citrate Buffer	Centrifugation	No	
19	x	Yes	> 2 y	0.286	0.12	0.01	5	Yes	No	EtAc	1 % HAc in EtAc	Centrifugation, Filtration	No	
74		No	None	0.286	0.12	0.01	5	5 mL, soak for 30 min. prior to extraction	No	MeOH	No	None	No	
15		Yes	> 2 y	0.289	0.16	0.010	5	Yes	No	ACN	Citrate Buffer	Filtration	No	
28		Yes	> 2 y	0.294	0.23	0.01	1	80 mL	alkaline with NaOH	Acetone, C_6H_{12}, EtAc	first NaOH for hydrolysis then acid/ base wash with H_2SO_4/ NaOH for extraction and cleanup	GPC, Gel-Permeation Chr/phy, Clean-up 2 acid/base distribution	Yes, Methylation with tetrabutylammonium-hydroxide/ iodomethane	
31		Yes	> 2 y	0.296	0.26	0.010	5	10 ml	No	ACN	No	None	No	
127		No	None	0.297	0.27	0.02	5	10 ml	No	ACN	No		No	
62	x	No	1 – 2 y	0.3	0.32	0.04	5	Yes	Yes	ACN	No	None	No	
36		Yes	1 – 2 y	0.303	0.36	0.05	5	10 mL water	No	ACN	No	None	No	
60		Yes	> 2 y	0.303	0.36	0.02	5	Yes	No	10 ml ACN	No	Freeze-out, Centrifugation	No	
10	x	Yes	> 2 y	0.304	0.37	0.02	5	10 ml	alkaline hydrolysis	ACN	first alkaline then neutralizedand citrate Buffer	SPE-column (specify under details), Freeze-out	No	
34		Yes	> 2 y	0.31	0.46	0.01	5	10 ml	No	ACN, Citrate Buffer	Citrate Buffer	Centrifugation	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	nicarbazin	No	109 %	SB-EUPT	1	other, in house method
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	102 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	No	No	92 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer), without PSA
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	90 %	QC	>5	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Nicarbazin	No	91.7 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	76 % (0.2 mg/kg)	SB-EUPT	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, 5 g sample,10 ml water+10 ml EtAC+1 %HAc
	LC-MS/MS (QQQ)	No	MM-ML	No	No	92 % (0.1 mg/kg)	SB-EUPT	1	other, 15 mL MeOH extraction, centrifuge, decant, make up to 20 mL, dilute× 5 with H_2O and analyse
	LC-MS/MS (QQQ)	No	MM-ML	No	No	86 %	SB-EUPT	4	EN 151662 (QuEChERS - Citrate Buffer)
	GC-MSD	GC-MSD, via second m/z	PS-SL	Mercopro-D3, No calculation, only to check extr. e	No	117 %	SB-EUPT	1	other, alkaline hydrolysis,extraction, GPC, acid/base distrubution, methylation, GC-MSD detection
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	89.5 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	(4-Chloro-2,5-dimethylpheNoxy)-HAc	No	102 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-SL	No	No	72.8 %	SB-EUPT	2	QuEChERS (EURL-SRM mth for acidic pesticides, with alkaline hydrolysis)
	LC-MS/MS (QQQ)	No	MM-ML	No	No	81 % (0.2 mg/kg)	SB-Other	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	PS-ML	No	No	105.5 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	Nicarbazin	No	103 % (spiked blank)	SB-EUPT	1	QuEChERS (EURL-SRM mth for acidic pesticides, with alkaline hydrolysis), Alkaline hydrolysis, neutralized, Citrate Buffer QuEChERS,No cleanup
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	93.1 % (0.315 mg/kg)	SB-EUPT	3	EN 151662 (QuEChERS - Citrate Buffer)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

2,4-D (free acid)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
91		Yes	1 – 2 y	0.31	0.46	0.025	1	20 ml	No	ACN, Acetone	No	None	No	
2		Yes	> 2 y	0.312	0.49	0.01	3	7.5 mL	No	ACN	Acetate Buffer QuEChERS	LLP	No	
12		Yes	> 2 y	0.314	0.52	0.02	2	Yes	No	ACN	No	Centrifugation	No	
7		Yes	> 2 y	0.315	0.53	0.02	5	Yes	No	ACN	No	None	No	
17		Yes	> 2 y	0.323	0.65	0.02	5	Yes	No	ACN	Citrate Buffer	None	No	
109	x	Yes	> 2 y	0.325	0.68	0.05	5	10 ml	hydrolysis with 5N NaOH ,neutralized with 5N H_2SO_4	ACN	300 µl 5N NaOH-pH=12, 300 µl 5 N H_2SO_4		Yes, Trimethylsulfonium hydroxide	
53		No	> 2 y	0.328	0.72	0.02	2	10 ml	No	ACN	100µl 1 %HCOOH at the end	None	No	
66		Yes	> 2 y	0.338	0.86	0.02	5	10 ml	No	ACN	No	Freeze-out	No	
43		Yes	> 2 y	0.34	0.89	0.05	2	10 g	No	ACN	extraction	dSPE, dispersive SPE w/o PSA, and w/o $mgSO_4$	No	
102		Yes	> 2 y	0.345	0.96	0.02	2	8 ml	No	ACN	No		No	
110	x	Yes	1 – 2 y	0.35	1.04	0.1	6	12 g	No	ACN	No		No	
4	x	Yes	> 2 y	0.352	1.06	0.02	5	Yes	No	ACN	No	None	No	
3		Yes	> 2 y	0.355	1.11	0.01	5	10 ml	No	Acetone, DCM, PE	No	Filtration, Centrifugation	No	
72		Yes	< 1 y	0.36	1.18	0.020	2	10 ml	Addition NaOH	ACN	neutralized with H_2SO_4	None	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS	LC-MS	MM-SL	No	No	94 %	SB-EUPT	4	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	Std add. to sample portions	No	Yes-2	55 % (0.05 mg/kg)	SB-EUPT	1	AOAC Official Method 2007.01 (QuEChERS - Acetate Buffer), in-house version
	LC-Ion Trap	LC-Ion Trap	MM-ML	Nicarbazin	Yes-2	95 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	86,2 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	MCPA-D6	No	95 % (0.15 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	GC-MSD	GC-MSD, SIM	MM-ML	No	No	105 % (0.1 mg/kg)	SB-EUPT	2	QuEChERS (EURL-SRM mth involving alkaline hydrolysis) modif., In-house modification, involving derivatization and GC-MS
	LC-MS/MS (QQQ)	No	Std add. to extract aliquots	No	No	None			EN 151662 (QuEChERS - Citrate Buffer) modif., QuEChERS 1 step
	LC-MS/MS (QQQ)	additional standard addition to extract aliquots	MM-ML	No	No	84 %	QC	>5	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	Nicarbazin	No	None			EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-SL	No	Yes-2	76,5 % (Recovery-corr by cal over the whole procedure)	SB-EUPT	3	QuEChERS (original version) J. AOAC 86 (2003)
	LC-MS/MS (QQQ)	No	MM-ML	Trimethyl-pheNoxy-acetic-acid	No	87 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	No	No	100 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-Ion Trap	PS-ML	No	Yes-1	66,8 %	SB-EUPT	2	Mini-Luke-Type (acetone/DCM-PE), The sample is wetted in water at least 2 hours, than aceton is added, turrax, add PE and DCM, turrax
	LC-MS/MS (QQQ)	No	MM-ML	No	No	93 % (0.020 and 0.2 mg/kg)	SB-EUPT	3	QuEChERS (EURL-SRM mth involving alkaline hydrolysis), after extraction and centrifugation deep frozen over night

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

2,4-D (free acid)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
99		Yes	> 2 y	0.362	1.21	0.01	5	10 g	pH 12, 60 min, RT	Water, 10 mL	pH 1		Yes, PFBBr, 60 min 90°C	
96	x	Yes	1 – 2 y	0.363	1.22	0.02	1	Yes	No	EtAc	No		No	
1		Yes	> 2 y	0.367	1.28	0.02	3	7.5 mL 1 % HCOOH in water	No	ACN	with 1 % HCOOH	None	No	
113	x	Yes	> 2 y	0.369	1.31	0.01	5	5 mL	No	ACN	No		No	
41		Yes	> 2 y	0.384	1.53	0.02	25	Yes	NaOH addition, 30min	ACN	H_2SO_4 addition pH=2	None	No	
123		Yes	> 2 y	0.4	1.76	0.01	15	15 ml	No	Acetone, DCM, PE	No		No	
116		Yes	1 – 2 y	0.422	2.07	0.010	5	Yes	No	ACN	No		No	
9		Yes	< 1 y	0.561	4.07	0.02	5	Yes	5N NaOH	ACN	neutralized with 5N H_2SO_4	None	No	
78		No	None	0.79	7.37	0.79	5	8 ml	No	ACN	No	None	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-MSD	LC-MS/MS (QQQ), LC-MS-MS confirmation in QuEChERS extracts	MM-ML	2,4-D-D3	Yes-4	95 %	SB-EUPT	4	Solid supported liquid/liquid Extraction , SLE, Derivatization PFBBr, GC-NCI-MSD
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	Yes-1	62 %	SB-EUPT	3	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789
	LC-MS/MS (QQQ)	No	MM-ML	TPP	No	112 % (0.2 mg/kg)	SB-EUPT	2	QuEChERS (original version) J. AOAC 86 (2003), acidified water addition
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), Ion ratio	MM-ML	No	Yes-1	58 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS-OTHER, partitioning w. mgSO_4 only
	LC-MS/MS (QQQ)	No	MM-ML	MCPA-D3	No	96 %	SB-EUPT	2	QuEChERS (EURL-SRM mth for acidic pesticides, with alkaline hydrolysis)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	TPP	Yes-2	100 %	SB-EUPT	4	Mini-Luke-Type (acetone/DCM-PE)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	TPP	No	70 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	No	No	99 %	SB-Other	2	QuEChERS (EURL-SRM mth for acidic pesticides, with alkaline hydrolysis)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	No	No	None			EN 151662 (QuEChERS - Citrate Buffer)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Bromide ion

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
56		No		FN	-3.71	7	2	100 mL	No	Water	No	None	No	
30	x	Yes	1 – 2 y	27.4	-1.35	5	1	Yes 8 ml	No	Water/H_2SO_4, EtAc	H_2SO_4	None	Yes, w. 1,2 propylene oxide/H_2SO_4 (60 min)	
3		Yes	1 – 2 y	29	-1.19	5	5	45 ml	No	Water	No	Filtration, Centrifugation	No	
60		Yes	< 1 y	29.6	-1.14	3	1	8 ml	No	Water/H_2SO_4, EtAc, 50 ml of EtAc and 4 g of $(NH_4)_2SO_4$	H_2SO_4	LLP, Na_2SO_4	Yes, w. 1,2 propylene oxide (5 mL = 4 g / 100 mL water)/ H_2SO_4 1 ml (3 mol / l), 60 min	
45		No	None	30.5	-1.05	1	5	No	No	Water	No	SPE-column (specify under details), C-18	No	
46		No	< 1 y	31.5	-0.95	1	1	No	No	Water	No	SPE-column (specify under details), SPE C18	No	
122		Yes	1 – 2 y	32.9	-0.82	5.0	1	Yes	No	Water/H_2SO_4, EtAc, Ethylene oxide/ Diisopropyl ethyl	H_2SO_4		Yes, w. ethyleneoxide/ H_2SO_4 to 2-bromoethaNol	
62	x	Yes	> 2 y	34	-0.71	5	1	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4	LLP, Na_2SO_4	Yes, w. 1,2 propylene oxide (5mL) / H_2SO_4	
28		Yes	> 2 y	34.5	-0.66	1	1	Yes	No	Water/H_2SO_4, EtAc, solvent A watery ethylene oxide, solvent B H_2SO_4	H_2SO_4	LLP, with EtAc	Yes, w. ethyleneoxide/ H_2SO_4 to 2-bromoethaNol	
29		Yes	> 2 y	36.4	-0.48	5	15	Yes	No	Water	No	Filtration	No	
50	x	Yes	1 – 2 y	36.6	-0.46	3	1	8 ml	No	Water/H_2SO_4, EtAc	H_2SO_4	LLP, EtAc	Yes, w. 1,2 propylene oxide/H_2SO_4	
18		No	> 2 y	37	-0.42	5	25	No	No	Water	No	None	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	IC-Conductivity	No	PS-ML	No	No	94 % (0.009 mg/kg)	SB-other	1,00	other, IC using conductivity detector
	GC- (μ) ECD	No	PS-ML	3-Bromo-1-propaNol	No	102,7 % (25 mg/kg)	SB-EUPT	>5	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), homogen. sample+water+derivat. with propylene oxid+H_2SO_4, partit. with EtAc and (NH4)2SO_4, decant.
	IC-Conductivity	No	PS-ML	No	No	73 %	QC	2	other, extraction with water, add carrez reagens and measure with ion chromatografie
	GC- (μ) ECD	No	PS-ML	3-Bromo-1-propaNol	No	88,3 %	SB-EUPT	1	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide
	IC-Conductivity	No	PS-ML	No	No	None			other
	IC-Conductivity	No	MM-ML	No	No	95 %	SB-EUPT	5	other, Water extraction, purif. W. SPE C18 , analysis w. IC-Conductivity
	GC- (μ) ECD	No	MM-ML	No	No	110.8 %	SB-EUPT	2	Bromide: deriv. w. ethyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 /DFG-S18 type), EN 13191-2:2000
	GC- (μ) ECD	No	MM-ML	No	No	84,6 %	SB-EUPT	2	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide
	GC- (μ) ECD	Different Column	PS-SL	No	No	85 % (KBr used)	SB-EUPT	2	Bromide: deriv. w. ethyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 /DFG-S18 type), extraction with ethylene oxide, derivatisation, determination with GC-ECD
	ICP-MS	No	PS-ML	No	No	94 %	SB-EUPT	1	other, Water extraction and ICP-MS determination of Bromide Ion, National Food Administration Sweden, M010
	GC- (μ) ECD	GC-ECD	PS-ML	3-Bromo-1-propaNol	No	106 % (25 mg/kg)	SB-EUPT	3	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type)
	IC-Conductivity	No	PS-ML	No	No	88 %	SB-EUPT	5	other

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Bromide ion

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
123		Yes	> 2 y	38	-0.32	5	2	198 ml	15 min	Water	No		No	
49		Yes	> 2 y	39.5	-0.18	3.4	5	10 g	No	Water/H_2SO_4, EtAc	H_2SO_4	None	Yes, w. ethyleneoxide/H_2SO_4 to 2-bromoethaNol	
22		Yes	1 – 2 y	40.3	-0.10	2.5	1	8 ml	No	Water/H_2SO_4, EtAc	H_2SO_4	LLP, Na_2SO_4	Yes, w. 1,2 propylene oxide/H_2SO_4	
6	x	Yes	1 – 2 y	40.4	-0.09	3	1	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4	LLP, Na_2SO_4	Yes, w. 1,2 propylene oxide/H_2SO_4	
44		Yes	1 – 2 y	40.5	-0.08	1	2	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4 (1 ml 3 M)	Na_2SO_4	Yes, w. 1,2 propylene oxide/H_2SO_4 (3M)	
93		Yes	> 2 y	40.9	-0.04	2	1	9 ml	No	Water/H_2SO_4, EtAc	H_2SO_4	None	Yes, w. 1,2 propylene oxide/H_2SO_4	
84		Yes	> 2 y	41	-0.03	0.2	1	prior to extraktion	No	Water/H_2SO_4, EtAc	H_2SO_4	None	Yes, w. 1,2 propylene oxide/H_2SO_4	
92		Yes	> 2 y	41.1	-0.02	2	1	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4	LLP	Yes, w. 1,2 propylene oxide/H_2SO_4	
12		Yes	> 2 y	41.2	-0.01	3	1	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4	None	Yes, w. 1,2 propylene oxide/H_2SO_4	
96	x	Yes	1 – 2 y	41.3	0.00	3	1	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4		Yes, w. 1,2 propylene oxide/H_2SO_4 (3M)	
98		Yes	> 2 y	41.4	0.00	1	1	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4		Yes, w. 1,2 propylene oxide/H_2SO_4	
36		Yes	> 2 y	41.7	0.03	3.00	1	10 mL	No	Water/H_2SO_4, EtAc, extraction after derivatization	H_2SO_4	None	Yes, w. 1,2 propylene oxide/H_2SO_4	
43		Yes	> 2 y	41.8	0.04	0.1	2	10 g	No	Water/H_2SO_4, EtAc	H_2SO_4	LLP, EtAc	Yes, w. ethyleneoxide/H_2SO_4 to 2-bromoethaNol	
103	x	Yes	> 2 y	42	0.06	2	1	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4		Yes, w. ethyleneoxide/H_2SO_4 to 2-bromoethaNol	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	IC-Conductivity	Different Method, spike to blank sample	MM-ML	No	No	95 %	SB-EUPT	4	based on NEN12014-2
	GC-MSD	GC-MSD	PS-ML	No	No	81,4 % (20 and 50 mg/kg)	SB-EUPT	2	Bromide: deriv. w. ethyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 /DFG-S18 type), DFG S-18 modified
	GC-MSD	GC-MSD	PS-ML	3-Bromo-1-propaNol	No	90 %	SB-EUPT	1	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide
	GC- (µ) ECD	derivatization	MM-ML	3-Bromo-1-propaNol	No	80 %	SB-EUPT	1	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide
	GC- (µ) ECD	GC-ECD	PS-ML	3-Bromo-1-propaNol	No	101 %	SB-EUPT	1	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), § 64 LFGB L 00.00-36/2
	GC- (µ) ECD	No	PS-ML	No	No	93 %	SB-EUPT	2	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), § 64 LFGB L 00.00-36/2
	GC- (µ) ECD	No	PS-ML	No	No	97 % (sample with kown amount)	SB-Other	1	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type)
	GC- (µ) ECD	No	PS-ML	No	No	None			Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), § 64 LFGB L 00.00-36/2
	GC- (µ) ECD	GC-ECD	PS-ML	No	No	99 %	SB-EUPT	1	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), § 64 LFGB L 00.00-36/2
	GC- (µ) ECD	No	PS-ML	3-Bromo-1-propaNol	No	98,3 %	SB-EUPT	3	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide
	GC- (µ) ECD	No	PS-ML	No	No	99 % (50 mg/kg)	SB-EUPT	2	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), modified
	GC- (µ) ECD	No	MM-ML	No	No	99 % (KBr at 40 mg Bromide ion/kg)	SB-EUPT	4	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), § 64 LFGB L 00.00-36/2 modified
	GC- (µ) ECD	No	PS-ML	No	No	None			Bromide: deriv. w. ethyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 /DFG-S18 type), DFG S-18
	GC- (µ) ECD	Different Method, x-RAY fluorescence	MM-ML	No	No	108 %	SB-Other	1	Bromide: deriv. w. ethyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 /DFG-S18 type), EN 13191-2:2000

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Bromide ion

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
66		Yes	> 2 y	42.3	0.09	0.25	1	Yes	No	Water/H_2SO_4, EtAc, extraction after derivation	H_2SO_4	None	Yes, w. 1,2 propylene oxide/H_2SO_4	
80		Yes	> 2 y	42.4	0.10	2.0	1	10 g	No	Water/H_2SO_4, n-Hexane, n-Hexane	H_2SO_4	LLP, n-Hexan	Yes, w. 1,2 propylene oxide/H_2SO_4	
102		Yes	> 2 y	42.7	0.13	2	1	10 mL	No	Water/H_2SO_4, EtAc	H_2SO_4		Yes, w. 1,2 propylene oxide/H_2SO_4	
11		Yes	1 – 2 y	42.8	0.14	3	1	7 ml	No	Water/H_2SO_4, EtAc	H_2SO_4	LLP, Na_2SO_4	Yes, w. 1,2 propylene oxide/H_2SO_4	
73		No	None	43	0.16	1	1	No	No	Water	No	SPE-column	No	
53		No	None	44.5	0.30	3	1	8 ml	No	Water/H_2SO_4, EtAc	H_2SO_4 (1 ml 3 M)	LLP, Na_2SO_4	Yes, w. 1,2 propylene oxide (5mL)/ H_2SO_4	
7		Yes	< 1 y	45.4	0.39	3	1	Yes	No	Water/H_2SO_4, EtAc, EtAc/extraction after derivation	No	None	Yes, w. 1,2 propylene oxide/H_2SO_4	
25		Yes	> 2 y	45.6	0.41	5	1	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4	None	Yes, w. 1,2 propylene oxide/H_2SO_4	
89		Yes	> 2 y	45.8	0.43	3	5	No	No	Water	No	Centrifugation, Filtration	No	
9		No	< 1 y	46.3	0.48	3	1	Yes	No	Water/H_2SO_4, EtAc, acidified aqueous soln. of propylene oxide	H_2SO_4	LLP, Na_2SO_4	Yes, w. 1,2 propylene oxide/H_2SO_4	
99		Yes	> 2 y	46.49	0.50	1	5	10 g	No	Water/H_2SO_4, EtAc, 10 mL	H_2SO_4		Yes, w. 1,2 propylene oxide/H_2SO_4 (16 h, RT)	
4	x	Yes	> 2 y	46.6	0.51	5	1	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4	None	Yes, w. 1,2 propylene oxide/H_2SO_4	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC- (μ) ECD	No	PS-ML	1,2-Dibromethan	No	95 %	SB-Other	5	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), § 64 LFGB L 00.00-36/2; derivation to propyleNoxid
	GC- (μ) ECD	No	PS-ML	No	No	105 % (10.0 mg/kg)	SB-EUPT	1	§64 LFBG L 00.00-36/1, Bestimmung von aNorganischem Bromid
	GC- (μ) ECD	GC-MSD	PS-ML	No	No	105,4 %	SB-EUPT	3	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), § 64LFGB L00.00-36/1 DIN EN 13191-1
	GC- (μ) ECD	Different Column	PS-ML	3-Bromo-1-propaNol	No	100.8 % (10 and 50 mg/kg)	SB-EUPT	>5	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide
	IC-Conductivity	No	PS-ML	No	No	80 %	SB-EUPT	5	other, water extraction purification w. SPE C18 analysis IC Condcttivity
	GC- (μ) ECD	No	PS-ML	3-Bromo-1-propaNol	No	None			Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide
	GC- (μ) ECD	GC-ECD	MM-ML	No	No	97 %	SB-EUPT	2	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide
	GC-MSD	No	Std add. to sample portions	No	Yes-2	94 %	SB-EUPT		Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), GC-MSD after derivatisation with PropyleNoxid
	IC-Conductivity	No	Std add. to sample portions	No	Yes-2	% (Standardaddition mit A-Spikes, nichts auffälliges)	SB-EUPT	3	other, Water extraction
	GC-MSD	No	MM-ML	No	No	107 %	SB-Other	2	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide
	GC-MSD	No	MM-ML	No	Yes-2	95 %	SB-EUPT	4	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), SLE, derivatization propylene oxide, GC-MSD
	GC- (μ) ECD	No	MM-ML	3-Bromo-1-propaNol	No	100 %	SB-EUPT	1	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Bromide ion

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
31		Yes		47.4	0.59		1	100	No	Water Hot water	No	None	No	
14	x	Yes	> 2 y	53.8	1.20	3	1	10 ml before extraction	No	Water/H_2SO_4, EtAc	H_2SO_4	None	Yes, w. 1,2 propylene oxide/H_2SO_4	
17		Yes	> 2 y	55.02	1.32	0.1	1	Yes	No	Water/H_2SO_4, EtAc	H_2SO_4	None	Yes, w. 1,2 propylene oxide/H_2SO_4	
47	x	Yes	> 2 y	55.1	1.33	10	1	partition with EtAc with $(NH_4)_2SO_4$	No	Water/H_2SO_4, EtAc	H_2SO_4 (3M)	partition with EtAc with ammonium sulphate, dry organic phase with sodium sulphate	Yes, w. ethyleneoxide/ H_2SO_4 to 2-bromoethaNol	
109	x	No	1 – 2 y	56	1.42	3	1	8 ml	No	Water/H_2SO_4, EtAc	H_2SO_4		Yes, w. 1,2 propylene oxide/H_2SO_4 (3 M/l)	
21		Yes	> 2 y	77.3	3.48	3	5	No	No	MeOH, Water,	No	Filtration	No	
38		No	> 2 y	126	8.19	0.05	1	Yes	No	Water	No	Centrifugation, Filtration	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	IC-Conductivity	No	PS-ML	No	No	87,8 %	From on going performance verification		other, internal method adapted from NF EN 12014-2
	GC- (μ) ECD	No	MM-ML	No	No	95 % (50 mg/kg)	SB-EUPT	1	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EN 13191-2:2000
	GC- (μ) ECD	No	PS-ML	No	No	119 % (matrix with known content of 100 mg/kg bromide)	SB-Other	1	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), derivatisation with propyleNoxide
	GC-MSD	GC-MSD	MM-ML	No	No	102 % (KBr at 5 mg/kg)	SB-Other	1	Bromide: deriv. w. ethyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 /DFG-S18 type), in house
	GC- (μ) ECD	No	PS-ML	No	No	98 % (50 mg/kg)	SB-EUPT	2	Deriv. w. propyleneoxide (EN 13191-2 / §64 LFGB L00.36-2 / EURL-SRM Mth type), EURL-SRM-Method for bromide
	LC-UV or DAD	LC-UV or DAD	PS-ML	No	No	92 %	SB-EUPT	1	other, ion pair chromatography
	LC-UV or DAD	No	PS-ML	No	No	92 % (100 mg/Kg)	SB-EUPT	1	other

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Chlorothalonil

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
111		Yes	None	0.0082	-3.68	1.4×10^{-4}	4	No	No	EtAc	No		No	
23	x	Yes		FN	-3.62	0.05	5	10 mL	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$), Centrifugation	No	
39		Yes		FN	-3.62	0.01	1	10 ml	No	Acetone, DCM/PE (1:1)	No	Centrifugation	No	
107		Yes		FN	-3.62	0.1	5	Yes	No	ACN	No	dSPE with PSA	No	
110	x	Yes		FN	-3.62	0.1	6	12 mL	No	ACN	Citrate Buffer	dSPE with PSA	No	
3		Yes	> 2 y	0.0164	-3.37	0.01	5	10 ml	No	Acetone, DCM, PE	No	Filtration, Centrifugation	No	
123		Yes	> 2 y	0.025	-3.04	0.01	15	15 ml	No	Acetone, DCM, PE	No		No	
84		Yes	> 2 y	0.03	-2.85	0.01	1	prior to extraktion	No	ACN	pH 1 with H_2SO_4	None		
92		Yes	> 2 y	0.033	-2.73	0.01	5	Yes	No	ACN	Citrate Buffer	dSPE without PSA	No	
95		Yes	> 2 y	0.043	-2.35	0.043	1	No	No	EtAc	No		No	
62	x	Yes	> 2 y	0.05	-2.08	0.01	5	Yes	No	EtAc	No	None	No	
90		Yes	> 2 y	0.0501	-2.07	0.01	1	No	No	CH, EtAc	No	GPC, Gel-Permeation Chr/phy	No	
13		No	> 2 y	0.052	-2.00	0.01	5	10 mL	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$)	No	
34		Yes	> 2 y	0.0535	-1.94	0.01	5	No	No	ACN, Other, B: Citrate Buffer	Citrate Buffer	dSPE (PSA/ $MgSO_4$), 1: Centrifugation and Freeze-out	No	
24	x	Yes	> 2 y	0.054	-1.92	0.01	2	20 mL	No	EtAc	No	GPC, Gel-Permeation Chr/phy	No	
130		Yes	> 2 y	0.0555	-1.87	0.01	5	10 mL	No	acidified ACN 5 g sample +10 g H_20 +10 mL(CH_3CN + 0.1 % HAc)	1) 0.1 % HAC in ACN during extraction; 2) citrate buffer during separation		No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC- (μ) ECD	No	PS-ML	No	Yes-2	85 %	SB-EUPT	2	EtAc based, other, Pesticide Analytical Manual vol.1, Multiresidual methods, Section 302, 3rd Edition, 1994
	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	TPP					EN 151662 (QuEChERS - Citrate Buffer)
	GC-Ion Trap	GC-MSD	MM-ML	No					Mini-Luke-Type (acetone/DCM-PE)
	GC-Ion Trap	GC-Ion Trap	MM-ML	No	No	None			QuEChERS (original version) J. AOAC 86 (2003)
	GC-MSD	No		No		None			EN 151662 (QuEChERS - Citrate Buffer)
	GC-MS/MS (QQQ)	GC-Ion Trap	MM-SL	PCB-153	No	74 %	SB-EUPT	2	Mini-Luke-Type (acetone/DCM-PE), The sample is wetted in water at least 2 hours, than aceton is added, turrax, add PE and DCM, turrax
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	TPP	Yes-2	95 %	QC	>5	Mini-Luke-Type (acetone/DCM-PE)
	GC-MSD	No	MM-ML	TPP	No	None			QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MS/MS (QQQ)	No	Std add. to extract aliquots	TPP	Yes-2		SB-EUPT		EN 151662 (QuEChERS - Citrate Buffer), without PSA
	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	TPP	No	None			EtAc based, other
	GC- (μ) ECD	GC-Ion Trap	MM-ML	No	No	84,1 %	SB-EUPT	2	EtAc based, other, EN 12393
	GC-MS/MS (QQQ)	GC-ECD, 2 different polar columns	MM-ML	No	No	75 % (of all processsteps)	SB-Other	1	S-19 (§ 64 LFGB L00.00-34), ASE
	GC-MS/MS (QQQ)	No	MM-ML	Yes, other (unspecifies)	Yes-1	87,5 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	GC-MSD	GC-MSD	MM-ML	No	Yes-1	68,1 % (0.030, 0.060, 0.089 mg/kg)	SB-EUPT	3	EN 151662 (QuEChERS - Citrate Buffer)
	GC-MS/MS (QQQ)	No	MM-ML	TPP	No	104 % (0.1 mg/kg)	SB-EUPT	1	EtAc based, other, Dutch EtAc extraction
	GC- (μ) ECD	Different Column, SPB-1	Std add. to Extract	No ISTD used	No	91,8 % (0.04 mg/kg)	SB-EUPT	3	EN 151662 (QuEChERS - Citrate Buffer) modified, Acetonitrilie used with 0.1 % HAc

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Chlorothalonil

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation
113	x	Yes	> 2 y	0.0565	-1.83	0.01	5	10 mL	No	Acetone, DCM, +PE	No		No
119		Yes	> 2 y	0.058	-1.77	0.01	15	No	No	ACN	H_2SO_4		No
17		Yes	> 2 y	0.06	-1.69	0.01	5	Yes	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$)	No
26		No	None	0.061	-1.65		5	10 mL	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$)	No
91		Yes	> 2 y	0.065	-1.50	0.01	1	20 mL	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$)	No
21		Yes	> 2 y	0.068	-1.38	0.01	1	Yes	No	Acetone, DCM, PE	No	Na_2SO_4	No
9		Yes	< 1 y	0.0734	-1.18	0.02	1	No	No	ACN	H_2SO_4, pH 1	None	No
70		Yes	> 2 y	0.075	-1.12	0.01	1	milliQ water at low temperature (4°C)	No	ACN, EtAc	Citrate Buffer	dSPE (PSA/ $MgSO_4$), Na_2SO_4	No
116		Yes	> 2 y	0.075	-1.12	0.010	5	Yes	No	ACN	No		No
102		Yes	> 2 y	0.076	-1.08	0.01	1	No	No	EtAc, C_6H_{12}	No		No
122		Yes	> 2 y	0.0785	-0.98	0.01	5	Yes	No	Acetone, DCM, EtAc	No		No
85		No	> 2 y	0.079	-0.96	0.01	1	10 mL	No	EtAc	sodium hydrogen carbonate	SPE-column (specify under details), SampliQ Carbon SPE	No
72		Yes	> 2 y	0.08	-0.92	0.010	6	No	No	Acetone, DCM	No	GPC, Gel-Permeation Chr/phy, Silica Column, Silica Column 1.5 %	No
97		Yes	> 2 y	0.087	-0.65	0.02	5	10 g	No	Acetone, DCM, Other	No		No
55	x	Yes	> 2 y	0.091	-0.50	0.01	5	H_2SO_4 is added to water	No	Acetone, DCM, Hexane	No	None	No

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-MSD	GC-Ion Trap, Rel. intensity spec. ions	MM-ML	Bromophos-ethyl	No	73 % (0.2 mg/kg)	SB-EUPT	2	Mini-Luke-Type (acetone/DCM-PE)
	GC- (μ) ECD	Different Column	PS-ML	No	Yes-1	82 %	SB-EUPT	2	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MSD	No	MM-ML	Tris-(1,3-dichlorisopropyl)-phosphat	No	60 % (0.08 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	GC-MSD	GC-Ion Trap	MM-ML	No	Yes-1	100 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	GC- (μ) ECD	GC-Ion Trap	MM-SL	No	No	74 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	TPP	No	37 %	SB-EUPT	1	Mini-Luke-Type (acetone/DCM-PE)
	GC-MSD	No	MM-ML	No	No	83 %	SB-Other	2	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC- (μ) ECD	GC-MSD	MM-ML	Fenchlorphos	No	103 % (spiked in matrix)	QC	>5	EN 151662 (QuEChERS - Citrate Buffer), -
	GC-Ion Trap	GC-Ion Trap	MM-ML	TPP	No	73 %	SB-EUPT	2	QuEChERS for Chlorothalonil (EURL-SRM mth), Modified QuEChERS-Method
	GC-TOF	GC-TOF	MM-ML	No	No	56 %	SB-EUPT	3	S-19 (§ 64 LFGB L00.00-34)
	GC- (μ) ECD	No	MM-ML	No	No	85,7 %	SB-EUPT	1	other, PN-EN 12393-1,2,3:2009
	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), 2nd MSMS transition	MM-ML	Trifluralin D14	No	93 % (0.02 mg/kg)	SB-EUPT	2	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, EtOAc extraction
	GC- (μ) ECD	Different Column, DB5, DB1	PS-ML	No	No	86 % (0.010 and 0.10mg/kg)	SB-EUPT	2	S-19 (§ 64 LFGB L00.00-34), ASE, 80°C, GPC, silicagel 1,5 %, elution with toluene
	GC-Ion Trap	GC-Ion Trap	MM-ML	TPP	No	59 % (0.06 mg/kg)	SB-EUPT	1	Mini-Luke-Type (acetone/DCM-PE)
	GC- (μ) ECD	GC-MS/MS (QQQ)	MM-ML	No	No	70 %	SB-EUPT	>5	Luke, M.A. J.A.O.A.C. 64, 1981

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Chlorothalonil

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation
25		Yes	> 2 y	0.093	-0.42	0.01	1	Yes	No	ACN, Water	Citrate Buffer	LLP	No
33	x	Yes	> 2 y	0.093	-0.42	0.01	5	Yes	No	Acetone, DCM	between 6-7	Florisil Column	No
18		Yes	> 2 y	0.095	-0.35	0.01	5	Yes	No	EtAc	No	None	No
4	x	Yes	> 2 y	0.097	-0.27	0.01	5	Yes	No	EtAc	No	None	No
47	x	Yes	> 2 y	0.098	-0.23	0.01	1	30 mL added to sample	No	EtAc	acidic extraction addition of H_2SO_4	GPC, Gel-Permeation Chr/phy	No
29		Yes	> 2 y	0.0981	-0.23	0.05	5	Yes	No	EtAc	1 % HAc in EtAc	Filtration	No
32	x	No	1 – 2 y	0.099	-0.19	0.01	25	5 ml	No	Other isopropyl ether	No	LLP	No
80		Yes	> 2 y	0.1	-0.15	0.01	5	10 g water	No	Acetone, C_6H_{12}, EtAc	No	GPC, Gel-Permeation Chr/phy, Silica Column,	No
79	x	Yes	> 2 y	0.103	-0.04	0.01	5	10 ml of deionized water	No	ACN	pH 2	SPE-column (specify under details), DEA column	No
133		Yes	> 2 y	0.105	0.04	0.01	1	No	No	ACN, DCM	No		No
88		Yes	> 2 y	0.108	0.15	0.02	5	10 ml water, waiting for 10 min	No	ACN	H_2SO_4 to pH ca. 1	Centrifugation	No
12		Yes	< 1 y	0.109	0.19	0.01	5	Yes	No	ACN	H_2SO_4	Centrifugation	No
78		Yes	< 1 y	0.11	0.23	0.11	5	10 ml	No	ACN	pH = 1	dSPE (PSA/$MgSO_4$)	No
19	x	Yes	> 2 y	0.113	0.35	0.01	5	10mL	No	EtAc	1 % HAc in EtAc	Centrifugation	No
28		Yes	> 2 y	0.114	0.38	0.01	5	10 mL	No	ACN	Citrate Buffer	dSPE (PSA/$MgSO_4$)	No
66		Yes	> 2 y	0.117	0.50	0.01	5	10 ml to 5 g sample weight	No	ACN after the half shaking-time addition of $mgSO_4$/NaCl	acidified with 100 µl H_2SO_4 (conc.) before extraction with ACN	None	No

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-MSD	No	Std add. to sample portions	PCB 20	Yes-2	75 %	SB-EUPT		EN 151662 (QuEChERS - Citrate Buffer)
	GC- (µ) ECD	GC-MSD	MM-ML	No	No	85 %	SB-EUPT	2	Mini-Luke-Type (acetone/DCM-PE)
	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	95 %	SB-EUPT	5	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789
	GC- (µ) ECD	No	MM-ML	PCB 97	No	107 %	SB-EUPT	1	other, modified QuEChERS with EtAc
	GC-MSD	GC-MSD	MM-ML	Tetraphenylethylene	No	81 % (0.02 mg/kg)	SB-Other	1	EtAc based, other, in house
	GC-MS/MS (QQQ)	No	MM-SL	Pirimicarb-D6	No	89 %	SB-EUPT	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, EtAc with 1 % HAc, National Food Administration, Sweden
	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	73 % (100 mg/kg)	SB-EUPT	1	Mini-Luke-Type (acetone/DCM-PE), acetone
	GC- (µ) ECD	GC-Ion Trap	MM-ML	No	No	74,4 % (0.04 mg/kg)	SB-EUPT	1	S-19 (§ 64 LFGB L00.00-34), E2, GPC, C1, D5
	GC-MSD	GC-MSD, 3 SIM ions	MM-ML	Phenanthrene-D10	No	86 %	SB-EUPT	1	other, In-house method
	GC-MS/MS (QQQ)	No	MM-ML	PCB	Yes-2		SB-EUPT	5,00	other: Extraction w. ACN, partitioning into DCM, SPE Cleanup
	GC-MSD	GC-MS/MS (QQQ)	MM-ML	Pirimicarb-D6	No	101 %	SB-EUPT	2	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MSD	GC-MSD	MM-ML	Chlorpyriphos-D10	No	95 %	SB-EUPT	1	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-SL	No	No	None			QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	103 % (0.124 mg/kg)	SB-EUPT	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, 5 g sample,10 ml water+10 ml EtAC+1 %HAc
	GC-MSD	GC-MSD, via second m/z	MM-SL	No	No	110 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	GC-MS/MS (QQQ)	GC-TOF, additional standard addition to extract aliquots	MM-ML	TPP	No	95 %	SB-Other	4	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Chlorothalonil

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation
104		No	< 1 y	0.121	0.65	0.010	1	No	No	acetone/H_2SO_4	No		No
30	x	Yes	> 2 y	0.122	0.69	0.01	5	10 ml water	No	ACN	before extraction step to pH=1	None	No
1		Yes	> 2 y	0.123	0.73	0.01	3	10 mL 1 % HCOOH in water	No	ACN	with 1 % HCOOH	dSPE (PSA/$MgSO_4$)	No
103	x	Yes	> 2 y	0.123	0.73	0.01	5	Yes	No	ACN, Water	H_2SO_4	freeze-out	No
118	x	Yes	> 2 y	0.123	0.73	0.01	1	prior to extraction	No	EtAc	No		No
61		Yes	> 2 y	0.124	0.77	0.01	1	5 ml	No	ACN	No	Centrifugation	No
77		Yes	> 2 y	0.126	0.85	0.01	5	10 mL	No	DCM	citric acid	None	No
93		Yes	> 2 y	0.128	0.92	0.01	8	15 ml	No	ACN	first acidified then Citrate Buffer?	dSPE (PSA/$MgSO_4$)	No
54	x	Yes	1 – 2 y	0.13	1.00	0.01	5	10 ml	No	ACN	H_2SO_4	None	No
127		Yes	> 2 y	0.133	1.12	0.01	5	5 ml	No	ACN	pH=1		No
31		Yes	> 2 y	0.134	1.15	0.010	5	10 mL	No	EtAc, DCM	No	None	No
2		Yes	> 2 y	0.137	1.27	0.01	3	7.5 mL	No	EtAc	No	LLP	No
60		Yes	> 2 y	0.139	1.35	0.01	5	No	No	10 ml ACN	pH=1	Centrifugation, 4 g $mgSO_4$ anhydrous 1 g NaCl	No
56		No	> 2 y	0.14	1.38	0.010	5	10 mL	No	ACN	Citrate Buffer	dSPE (PSA/C18/$MgSO_4$)	No
73		No	None	0.14	1.38	0.01	1	No	No	ACN	100 µL H_2SO_4 (conc.) to pH of ~1	None	No

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-MS/MS (QQQ)	No	MM-SL	No	No	94 % (0.02 mg/kg)	SB-EUPT	1	other, confidential method
	GC-MS/MS (QQQ)	No	Std add. to sample portions	TPP	Yes-2	122 % (0.05 mg/kg (st. addition))	SB-EUPT	1	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MS/MS (QQQ)	No	MM-ML	TPP	No	129 % (0.2 mg/kg)	SB-EUPT	2	QuEChERS (original version) J. AOAC 86 (2003), modified by addition of acidified water
	GC-MS/MS (QQQ)	GC-ECD	MM-ML	TPP	No	80 %	SB-EUPT	1	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MSD	GC-MSD	MM-ML	for GC stability only	Yes-1	53 %	SB-EUPT	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789
	GC-MSD	GC-MSD	MM-ML	No	No	89 %	SB-EUPT	>5	QuEChERS for Chlorothalonil (EURL-SRM mth), Modified QuEChERS-Method
	GC-MSD	GC-MSD, 3 sim ions	PS-ML	Bromophos	Yes-1	35 % (0.1 mg/kg)	SB-EUPT	2	Solid supported liquid/liquid Extraction , CH_2Cl_2+ diatomaceous earths
	GC-MSD	No	MM-ML	No	No	90 %	SB-EUPT	1	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-Ion Trap	GC-Ion Trap, product scan spectrum	MM-ML	No	No	83 % (0.020 mg/kg)	SB-EUPT	1	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MSD	GC-MSD	MM-ML	TPP	No	90 %	SB-EUPT	2	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-Ion Trap	GC-MS/MS (QQQ)	PS-ML	Bromophos	No	72 %	SB-EUPT	1	EtAc based, other, internal method adapted from NF EN 12393
	GC-MSD	GC-MSD, 3 ions	Std add. to sample portions	PCB198	Yes-2	100 % (0.05 mg/kg)	SB-EUPT	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, in-house version
	GC-Ion Trap	LC-MS/MS (QQQ)	MM-ML	No	Yes-1	61 %	SB-EUPT	1	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MSD	GC-MSD, 3 ions	MM-SL	TDCPP	No	106 % (0.150 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	GC- (μ) ECD	GC-MSD	PS-SL	Ethion	No	75 %	SB-EUPT	5	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Chlorothalonil

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
53		No	1 – 2 y	0.142	1.46	0.01	5	10 ml	No	ACN 4 g $mgSO_4$+1 g NaCl	100µl H_2SO_4	None	No	
121	x	No	< 1 y	0.142	1.46	0.01	5	100 µl H_2SO_4 added to 10 ml water	No	20 ml ACN (instead of 10 ml)	100 µl H_2SO_4 added to 10 ml water		No	
96	x	Yes	> 2 y	0.146	1.62	0.01	1	Yes	No	EtAc	No		No	
37	x	Yes	> 2 y	0.148	1.69	0.01	5	Yes	No	ACN	H_2SO_4	None	No	
14	x	Yes	> 2 y	0.153	1.88	0.01	5	10 mL	No	ACN	Citrate Buffer	only desiccation with $mgSO_4$	No	
7		Yes	> 2 y	0.154	1.92	0.01	5	Yes	No	ACN	Citrate Buffer	None	No	
50	x	Yes	< 1 y	0.155	1.96	0.01	5	10 ml	No	ACN	100µl conc. H_2SO_4	Freeze-out	No	
6	x	Yes	> 2 y	0.172	2.62	0.01	5	10 ml	No	ACN	100µL H_2SO_4 (pH = 1)	dSPE (PSA/ $MgSO_4$)	No	
20	x	Yes	> 2 y	0.182	3.00	0.02	5	10mL	No	EtAc	No	Freeze-out: 6 hours at -18 °C	No	
108		Yes	> 2 y	0.19	3.31	0.01	25	98 ml	No	Acetone, CH, EtAc (2/1/1)	No		No	
109	x	Yes	> 2 y	0.194	3.46	0.02	1	15 ml	No	Acetone, DCM/PE	No		No	
46		Yes	> 2 y	0.195	3.50	0.01	5	10 ml	No	ACN	H_2SO_4 addition	None	No	
99		Yes	> 2 y	0.195	3.50	0.01	5	10 g	No	ACN, Water, 10 mL	pH 1 (1 mL 10 % H_2SO_4)		No	
38		No	> 2 y	0.215	4.27	0.02	15	No	No	Acetone, DCM, PE	No	None	No	
89		Yes	> 2 y	0.263	6.12	0.01	1	No	No	ACN	No	Centrifugation, solvent exchange	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-MSD	No	Std add. to extract aliquots	No	No	None			QuEChERS for Chlorothalonil (EURL-SRM mth), EURL-SRM modif QuEChERS
	GC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	77 %	SB-EUPT	1	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-Ion Trap	GC-Ion Trap	MM-ML	No	Yes-1	59 %	SB-EUPT	3	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789
	GC-MSD	GC-MSD	MM-ML	No	Yes-2	76 %	SB-Other	>5	QuEChERS for Chlorothalonil (EURL-SRM mth), add H_2SO_4 before extraction,H_2O,ACN and salts
	GC-MS/MS (QQQ)	No	MM-ML	TPP	No	85 % (0.05 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer), QuEChERS without PSA
	GC-NPD	GC-MSD	MM-ML	No	No	97,6 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	GC- (μ) ECD	GC-MSD, GC MS NCI	MM-ML	No	No	94,5 % (0.2 mg/kg)	SB-EUPT	3	QuEChERS (original version) J. AOAC 86 (2003)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	120 %	SB-EUPT	1	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MSD	GC-MSD	MM-ML	PCB 209	No	98,1 %	SB-Other	3	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, extraction salts sodium chlorid and magnesium sulfate
	GC- (μ) ECD	GC-ECD	MM-ML	None	Yes-1	40 %	SB-EUPT	1	S-19 (§ 64 LFGB L00.00-34),
	GC-MSD	GC-MSD, SIM	MM-ML	TRIS	Yes-1	25 % (0.1 mg/kg)	SB-EUPT	3	Mini-Luke-Type (acetone/DCM-PE)
	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	TPP	No	91 %	SB-EUPT	5	QuEChERS for Chlorothalonil (EURL-SRM method, acidified (pH~1) at the begining of procedure
	GC-MSD	GC-MS/MS (QQQ)	MM-ML	PCB 108	Yes-2	95 %	SB-EUPT	4	QuEChERS (original version) J. AOAC 86 (2003)
	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No Info	No	72 % (0.02 mg/kg)	SB-EUPT	1	Mini-Luke-Type (acetone/DCM-PE)
	GC-MS/MS (QQQ)	No	Std add. to sample portions	No	Yes-2	% (Standardaddition with A-Spikes, strong Signalinhibition approx. factor 3 cp.with extern Standard)	SB-EUPT	4	other, ACN extraction

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Cyromazine

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
31		Yes		FN	-3.77		5	10 ml	No	ACN	No	dSPE (PSA/ $MgSO_4$)	No	
29		No	None	0.0348	-3.60	0.02	1	No	No	EtAc	Na_2CO_3	Filtration	No	
79	x	Yes	1 – 2 y	0.0783	-3.11	0.01	5	10 ml water	No	ACN	Citrate Buffer	None	No	
28		Yes	> 2 y	0.108	-2.77	0.02	5	10 g	No	ACN	No	dSPE (PSA/ $MgSO_4$)	No	
92		Yes	> 2 y	0.111	-2.73	0.02	5	Yes	No	ACN	No	without PSA	No	
18		Yes	> 2 y	0.12	-2.63	0.01	5	Yes	No	ACN	No	dSPE (ODS/ $MgSO_4$)	No	
38		Yes	1 – 2 y	0.125	-2.57	0.01	1	10 ml	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$)	No	
17		Yes	> 2 y	0.129	-2.53	0.02	5	Yes	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$)	No	
93		No	None	0.141	-2.39	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	None	No	
6	x	Yes	> 2 y	0.145	-2.35	0.02	5	Yes	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$)	No	
89		Yes	> 2 y	0.157	-2.21	0.02	1	No	No	ACN	No	Centrifugation, solvent exchange	No	
77		Yes	> 2 y	0.181	-1.93	0.01	5	10 mL	No	ACN	No	dSPE (PSA/ $MgSO_4$), dSPE, PSA + C18	No	
50	x	No	None	0.186	-1.88	0.02	5	10 ml	No	ACN	No	Freeze-out, Filtration, solvent exchange	No	
104		No	None	0.186	-1.88	0.050	1	Yes	No	Water, MeOH	No		No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No				EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-SL	Pirimicarb-D6	No	37 %	SB-EUPT	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, EtAc with 1 % HAc, National Food Administration, Sweden
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	MM-ML	No	No	65 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), via second mass transition, MRM ratio	PS-ML	No	No	26 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	Std add. to extract aliquots	Nicarbazin	Yes-2		SB-EUPT		EN 151662 (QuEChERS - Citrate Buffer), without PSA
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	TPP	No	75 %	SB-EUPT	5	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	No Info	Yes-2			1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	Linuron-D6	No	38 % (0.1 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	IL-Cyromazine	Yes-3	95 %			QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	70 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	Std add. to sample portions	No	Yes-2	Standard-addition with A-Spikes, strong Signalinhibition approx. factor 2 cp.with extern Standard)	SB-EUPT	4	other, ACN extraction
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 3 transitions	PS-ML	TPP	Yes-1	13 % (0.1 mg/kg)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), relevant ions	MM-ML	No	No	34 % (0.2 mg/kg)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-SL	No	No	None, (No recovery obtained at LOQ level)			other, confidential method

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Cyromazine

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
47	x	Yes	> 2 y	0.2	-1.72	0.02	5	10 ml	No	ACN	Acetate Buffer	Centrifugation (2×), 150 mg $MgSO_4$ added before 2nd centrifugation	No	
85		No	1 – 2 y	0.236	-1.31	0.01	1	10 ml	No	EtAc	sodium hydrogen carbonate	None	No	
80		No	< 1 y	0.254	-1.10	0.06	1	20 g	No	MeOH	No	None	No	
88		Yes	< 1 y	0.267	-0.95	0.04	5	10 ml (10 min soaking before extraction)	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation	No	
7		Yes	< 1 y	0.28	-0.80	0.02	5	10 ml	No	MeOH, Water, HCOOH	1 % HCOOH in MeOH	None	No	
30	x	No	None	0.287	-0.72	0.02	5	8.5 ml water	No	MeOH, Water	1 % HCOOH in MeOH	None	No	
15		No	None	0.299	-0.59	0.020	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Freeze-out, Filtration	No	
103	x	No	None	0.327	-0.27	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH		No	
22		Yes	> 2 y	0.333	-0.20	0.04	1	Yes	No	MeOH, Water	No	Filtration, Centrifugation	No	
32	x	No	> 2 y	0.335	-0.18	0.02	5	5 ml	No	MeOH ammonium acetate 20mM	No	None	No	
60		No	< 1 y	0.34	-0.12	0.02	5	10 ml	No	MeOH, Water, 10 ml MeOH (1 % HCOOH)	1 % HCOOH in MeOH	Centrifugation	No	
61		Yes	> 2 y	0.343	-0.09	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation	No	
101	x	Yes	None	0.343	-0.09	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH		No	
55	x	Yes	> 2 y	0.35	-0.01	0.02	5	Yes	No	ACN	No	dSPE (PSA/ $MgSO_4$)	No	
127		No	None	0.351	0.01	0.01	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH		No	
12		Yes	None	0.38	0.34	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	None	No	
123		Yes	> 2 y	0.38	0.34	0.01	10	10 ml	No	MeOH, Water	No		No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	TPP	No	89 % (0.02 mg/kg)	SB-Other	1	AOAC Official Method 2007.01 (QuEChERS - Acetate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2nd MSMS transition	MM-ML	Carbendazim-D4	No	74 % (0.02 mg/kg)	SB-EUPT	2	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, EtOAc extraction, solvent exchange into MeOH
	GC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	IL-Cyromazine	Yes-3	83,2 % (0.20 mg/kg)	SB-EUPT	1	other, § 64 LFGB, L00.00-76, Method for Chlormequat/Mepiquat (LC-MS/MS)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Pirimicarb-D6	No	70 %	SB-EUPT	2	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	83,2 %	SB-EUPT	2	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	No	No	69 % (0.5 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	No	No	84 %	SB-EUPT	5	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-SL	No	No	80 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	MM-ML	No	No	95 % (0.02 and 0.1 mg/kg)	SB-EUPT	2	other, methanolic method Kit Granby et al
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Oxfendazole	No	97 % (200 mg/kg)	SB-EUPT	1	other, MeOH extraction
	LC-MS/MS (QQQ)	No	MM-ML	No	No	80 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	92 %	SB-EUPT	>5	QuPPe-Method (EURL-SRM method for polar pesticides), version 6
	LC-MS/MS (QQQ)	No	Std add. to sample portions	IL-Cyromazine	Yes-4	88 % (0.5 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides), QuPPe EURL-SRM method for polar pesticides v.6
	LC-MS/MS (QQQ)	No	MM-ML	No	Yes-1	40 %	SB-EUPT	4	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	IL-Cyromazine	No	100 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to extract aliquots	IL-Cyromazine	Yes-4	101 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	TPP	Yes-2	70 %	SB-EUPT	4	QuPPe-Method (EURL-SRM method for polar pesticides), modified

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Cyromazine

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
3		Yes	> 2 y	0.39	0.45	0.01	5	10 ml	No	Acetone, DCM, PE	No	Filtration, Centrifugation	No	
72		No	None	0.39	0.45	0.020	5	No	No	MeOH	+ 100 µl HCOOH	None	No	
99		Yes	> 2 y	0.392	0.47	0.01	5	10 g	No	ACN, Water, 10 mL	No		No	
118	x	Yes	> 2 y	0.397	0.53	0.01	1	prior to extraction	No	EtAc	No		No	
25		Yes	> 2 y	0.398	0.54	0.01	1	Yes	No	ACN, Water	No	LLP	No	
23	x	Yes	> 2 y	0.4	0.56	0.02	5	8.5 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No	
113	x	Yes	1 – 2 y	0.4	0.56	0.02	5	5 mL	No	ACN	No		No	
66		Yes	1 – 2 y	0.409	0.67	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Freeze-out	No	
84		No	< 1 y	0.411	0.69		5	10 ml prior to extraction	No	MeOH, Water	1 % HCOOH in MeOH	None		
34		Yes	None	0.412	0.70	0.02	5	10 ml	No	acidified MeOH	No	Centrifugation, Filtration, 2: Polyester filters 0.45 µm pore size	No	
14	x	Yes	> 2 y	0.418	0.77	0.016	5	10 ml before extraction	No	ACN	No	Other, specify under clean up details, only desiccation with $mgSO_4$	No	
41		No	None	0.421	0.80	0.05	25	Yes	No	ACN	Citrate Buffer	None	No	
24	x	Yes	< 1 y	0.423	0.83	0.04	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	None	No	
1		No	< 1 y	0.437	0.99	0.02	3	7.5 mL 1 % HCOOH in water	No	ACN	with 1 % HCOOH	None	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	No	Yes-1	39 %	SB-EUPT	2	Mini-Luke-Type (acetone/DCM-PE), The sample is wetted in water at least 2 hours, than aceton is added, turrax, add pe and dcm, turrax
	LC-MS/MS (QQQ)	No	MM-ML	No	Yes-1	71 % (0.020 and 0.20 mg/kg)	SB-EUPT	3	QuPPe-Method (EURL-SRM method for polar pesticides), QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	IL-Cyromazine	Yes-4	95 %	SB-EUPT	4	QuEChERS (original version) J. AOAC 86 (2003)
	GC-MSD	GC-MSD	MM-ML	for GC stability only	No	84 %	SB-EUPT	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789
	LC-MS/MS (QQQ)	No	Std add. to sample portions	Isoproturon	Yes-2	36 %	SB-EUPT		EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	94 % (0.2 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), Ion ratio	MM-ML	No	Yes-1	47 % (0.05 mg/kg)	SB-EUPT	1	other, $mgSO_4$ only
	LC-MS/MS (QQQ)	additional standard addition to extract aliquots	MM-ML	No	No	73 %	SB-EUPT	2	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	Cyromazine-D4	Yes-3				QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	Yes-1	72,1 % (0.028, 0.196, 0.420 mg/kg)	SB-EUPT	3	QuPPe-Method (EURL-SRM method for polar pesticides) Version 6, LC-house-method, EURL QuPPe, Version 6
	LC-MS/MS (QQQ)	No	MM-ML	TPP	No	85 % (0.05 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer), QuEChERS without PSA
	LC-MS/MS (QQQ)	No	MM-ML	Pirimicarb-D6	Yes-1	26 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	IL-Cyromazine	No	104 % (0.1 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	TPP	Yes-1	40 % (0.2 mg/kg)	SB-EUPT	2	QuEChERS (original version) J. AOAC 86 (2003), acidified water addition

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Cyromazine

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
19	x	No	< 1 y	0.443	1.06	0.01	5	10 ml prior to extraction	No	EtAc	3 g $NaHCO_3$	Centrifugation, Filtration	No	
2		Yes	> 2 y	0.448	1.11	0.01	3	7.5 mL	No	ACN	Acetate Buffer QuEChERS	LLP	No	
121	x	No	None	0.454	1,18	0.02	5	Yes	No	ACN 20 ml ACN instead of 10 ml	No		No	
4	x	Yes	> 2 y	0.459	1,24	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	None	No	
20	x	No	None	0.467	1,33	0.02	2	10 ml prior to extraction	No	MeOH, Water, acidified MeOH	via extraction using 1 % HCOOH in MeOH	Centrifugation, Filtration	No	
56		No	> 2 y	0.49	1,59	0.010	5	10 g	No	ACN	No	None	No	
9		No	< 1 y	0.546	2,23	0.02	1	Yes	No	MeOH, Water, MeOH/Water	No	None	No	
13		Yes	> 2 y	0.555	2,33	0.01	5	10 ml	No	ACN	No	dSPE (PSA/$MgSO_4$)	No	
11		Yes	< 1 y	0.559	2,38	0.01	5	9 ml water	No	MeOH, Water, 9 ml water/20 ml MeOH	6-7	SPE-column (specify under details), diatomaceous earth	No	
78		No	None	0.56	2,39	0.56	5	8 ml	No	ACN	No	dSPE (PSA/$MgSO_4$)	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	No	Yes-2	28,4 % (0.05 mg/kg)	QC	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, 5 g sample,10 ml water+10 ml EtAC
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	Std add. to sample portions	No	Yes-2	Not available			AOAC Official Method 2007.01 (QuEChERS - Acetate Buffer), in-house version
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Carbaryl-C13	Yes-1	30 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	No	Yes-2	100 %	SB-EUPT		QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	TPP	Yes-2	173,5 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	MM-SL	No	Yes-1	31 % (0.150 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	No	No	113 %	SB-Other	2	QuPPe-Method (EURL-SRM method for polar pesticides), Chlormequat and Mepiquat (provided by EURL - Single Residue Methods)
	LC-MS/MS (QQQ)	No	MM-ML	Yes, other (unspecifies)	Yes-1	21 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	Std add. to sample portions	No	Yes-2	60 % (blank spiked at different conc. levels)	SB-EUPT	4	Klein, Alder, J. AOAC 86/1015/2003
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-SL	No	No	None			EN 151662 (QuEChERS - Citrate Buffer)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dithiocarbamates (as CS_2)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
10	x	Yes		FN	-3.67	0.05	200	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	None	Yes, with Cu(II) acetate-diethanolamine sln	
18		Yes		FN	-3.67	0.5	5	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	pass through NaOH and $Zn(AcO)_2$	Yes, with Cu(II) acetate-diethanolamine sln	
108		Yes		FN	-3.67	1.0	50	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl		Yes, to potassium-×anthogenate	
118	x	Yes		FN	-3.67	0.05	25	prior to extraction	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl		No	
113	x	Yes	> 2 y	0.189	-2.77	0.05	25	25 mL	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl		No	
31		Yes	> 2 y	0.31	-1.98	0.300	5	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH, $Zn(CH_3COO)_2$	Yes, with Cu(II) acetate-diethanolamine sln	
77		Yes	> 2 y	0.345	-1.76	0.5	5	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH, $Zn(CH_3COO)_2$, passing thru NaOH	Yes, with Cu(II) acetate-diethanolamine sln	
110	x	No	> 2 y	0.35	-1.72	0.01	6	12 g	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl		No	
13		Yes	> 2 y	0.36	-1.66	0.01	5	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl SPME fibre	HCl	Enrichment on SPME fibre	No	
4	x	Yes	> 2 y	0.371	-1.59	0.05	25	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl	LLP	No	
42		Yes	> 2 y	0.384	-1.50	0.05	50	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	None	Yes, with Cu(II) acetate-diethanolamine sln	
28		Yes	> 2 y	0.401	-1.39	0.01	1	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×anthogenate	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	55 %			$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer	No	PS-SL	No					$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer	No	PS-ML	No	No	None			$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type), DFG S-15
	GC-MSD	GC-MSD	MM-ML	No		None			$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC-Ion Trap	GC-FPD, Rel. intensity spec. ions	MM-ML	No	No	78 % (0.2 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	No	PS-ML	No	No	120 %	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer	None	PS-ML	No	No	90 % (Thiram at 0.5 mg/kg)	QC	2	$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	GC-MSD	No	PS-ML	No	No	86 %	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, headspace sampling, GC-analysis of CS_2
	GC-MSD	No	MM-ML	Chloroform	No	77,8 %	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, headspace SPME, GC-Analysis of CS_2 (EN 12396-2 type)
	GC-MSD	No	MM-ML	DCM	No	95 %	SB-EUPT	1	$SnCl_2$/HCl-cleavage, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	No	PS-ML	No	No	85 % (0.05 mg/kg)	SB-EUPT		$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	72 % (Mancozeb used)	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated); Yes-5: Yes, using procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dithiocarbamates (as CS_2)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
98		Yes	> 2 y	0.44	-1.14	0.01	15	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl		Yes, to potassium-×anthogenate	
107		Yes	> 2 y	0.45	-1.07	0.3	75	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl		Yes, with Cu(II) acetate-diethanolamine sln	
125		No	< 1 y	0.457	-1.03	0.457	2	20 mL	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$ (80°C,2h)	$H_2O/SnCl_2$/ HCl, Isooctane	HCl		No	
73		No	> 2 y	0.46	-1.01	0.1	1	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH, $Zn(CH_3COO)_2$	Yes, with Cu(II) acetate-diethanolamine sln	
99		Yes	> 2 y	0.46	-1.01	0.01	5	5 g	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl 10 mL	HCl		No	
85		No	> 2 y	0.479	-0.88	0.05	5	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl	LLP	No	
82		Yes	> 2 y	0.48	-0.88	0.05	1	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×anthogenate	
40		Yes	> 2 y	0.488	-0.83	0.05	4	(1:1) (w:v)	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$ (1:2.5) (weight:volume)	$H_2O/SnCl_2$/ HCl, Isooctane	HCl	LLP	No	
64		Yes	> 2 y	0.496	-0.77	0.05	5	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl	LLP	No	
36		Yes	> 2 y	0.497	-0.77	0.05	2	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×anthogenate	
97		Yes	> 2 y	0.498	-0.76	0.05	1	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl		No	
17		Yes	> 2 y	0.531	-0.55	0.02	25	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×anthogenate	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	Spectrophotometer	GC-MS/MS (QQQ)	PS-ML	No	No	74 % (Matrix Rice)	QC	1	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type), § 64 L 00.00-49/3
	Spectrophotometer	No	PS-ML	No	No	None			$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	GC-MSD	GC-MSD, SIM	PS-ML	No	No	77,5 % (Recovery at LoQ)	SB-EUPT	3	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	No	PS-ML	No	No	90 %	SB-EUPT	5	$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type), Chemical Reduction of Ditiocarbamates into CS_2, developing yellow color with Cu2Ac in EtOH
	GC-MSD	No	MM-ML	No	Yes-2	95 %	SB-EUPT	4	$SnCl_2$/HCl-cleavage/reduction, headspace sampling, GC-analysis of CS_2
	GC-MSD	GC-MSD, repeat sample, std, spike	MM-ML	No	No	122 % (Ziram at 0.1 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	No	PS-ML	No	No	70 % (0.5 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	GC- (P) FPD	No	PS-ML	No	No	93 % (Thiram at 0.05 mg/kg)	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2, GC liquid injection
	GC-MSD	No	PS-SL	No	No	92 %	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2, EN 12396-2 type + Internal Precedure
	Spectrophotometer	No	PS-ML	No	No	59 % (Thiram at 0.698 mg CS_2/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	GC- (P) FPD	No	PS-ML	No	No	86 % (Thiram at 0.1 mg/kg)	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	No	PS-ML	No	No	84 % (Thiram at 0.25 mg/kg CS_2)	SB-Other	1	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated); Yes-5: Yes, using procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dithiocarbamates (as CS_2)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation
94		Yes	> 2 y	0.55	-0.42	0.05	1	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/HCl	HCl		Yes, with Cu(II) acetate-diethanol-amine sln
93		Yes	> 2 y	0.553	-0.40	0.04	25	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/HCl	HCl	Distillation passing through NaOH, $Zn(CH_3COO)_2$	Yes, with Cu(II) acetate-diethanol-amine sln
56		No	> 2 y	0.555	-0.39	0.04	5	150 mL	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate
8		Yes	> 2 y	0.559	-0.36	0.05	1	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	H_2O/ $SnCl_2$/HCl, Isooctane, CS_2 released dissolved in isooctane	HCl	LLP	No
130		Yes	> 2 y	0.569	-0.30	0.01	25	25 ml	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl 25 g sample + 25 ml Water	HCl		No
100		Yes	> 2 y	0.57	-0.29	0.05	2	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/HCl	HCl		Yes, to potassium-×antho-genate
23	x	Yes	> 2 y	0.574	-0.27	0.01	1	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl	LLP	No
84		Yes	1 – 2 y	0.579	-0.23	0.05	1	prior to extraktion	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl	LLP	No
49		Yes	> 2 y	0.581	-0.22	0.08	5	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate
66		Yes	> 2 y	0.585	-0.20	0.05	1	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate
58		Yes	> 2 y	0.588	-0.18	0.01	5	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate
44		Yes	> 2 y	0.59	-0.16	0.01	5	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	Spectrophotometer	No	PS-ML	No	No	95 %	QC	2	$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer	No	PS-ML	No	No	None			$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	80 % (0.050 and 2.0 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type), And EN 12396-1 type
	GC-MSD	GC-MSD, fragment 76 m/z	PS-ML	No	No	99,3 % (Thiram used)	SB-EUPT	2	$SnCl_2$/HCl-cleavage, LLP w. Non-polar solvent, GC-analysis of CS_2, No IS used
	GC-MSD	No	PS-ML	No	Yes-1	53,8 % (0.5 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, headspace sampling, GC-analysis of CS_2
	Spectrophotometer	Spectrophotometer	MM-ML	No	Yes-1	83,6 %	SB-EUPT	5	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	GC-MSD	GC-MSD	PS-ML	No	No	79 % (0.1 and 1 mg/kg)	SB-EUPT	4	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC- (μ) ECD	No	MM-ML	No	No	104 % (0.411 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2, method provided by EURL for SRM
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	105,3 % (0.102 mg/kg)	SB-Other	2	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	Spectrophotometer	No	PS-ML	No	No	91 %	SB-Other	3	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	Spectrophotometer	Spectrophotometer, EN 12396-1 type	PS-ML	No	No	88 % (Thiram at 0.600 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	82 %	SB-EUPT	3	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated); Yes-5: Yes, using procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dithiocarbamates (as CS_2)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
55	x	Yes	> 2 y	0.59	-0.16	0.10	3	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Toluene	HCl	LLP	No	
67		Yes	> 2 y	0.59	-0.16	0.05	1	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate	
115		Yes	> 2 y	0.59	-0.16	0.05	1	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl		No	
12		Yes	> 2 y	0.591	-0.16	0.05	1	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl	LLP	No	
80		Yes	> 2 y	0.591	-0.16	0.05	2	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate	
126	x	Yes	> 2 y	0.593	-0.14	0.05	1	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl		Yes, with Cu(II) acetate-diethanol-amine sln	
43		Yes	> 2 y	0.595	-0.13	0.02	5	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate	
6	x	Yes	1 – 2 y	0.607	-0.05	0.05	5	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl	LLP	No	
46		No	> 2 y	0.61	-0.03	0.05	25	Yes	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, Isooctane	HCl	LLP	No	
62	x	Yes	> 2 y	0.62	0.03	0.05	5	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate	
105		Yes	> 2 y	0.62	0.03	0.1	10	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl		Yes, to potassium-×antho-genate	
3		Yes	> 2 y	0.621	0.04	0.05	5	8 ml	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl	HCl	Headspace sampling	No	
30	x	Yes	> 2 y	0.625	0.07	0.02	1	No	Cleavage/reduction to CS_2 w. $HCl/SnCl_2$	$H_2O/SnCl_2$/ HCl, SPME fibre	HCl	Enrichment on SPME fibre	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC- (P) FPD	GC-MSD	MM-ML	No	No	65 %	SB-EUPT	>5	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	No	MM-ML	No	No	109 % (0.05 mg/kg)	QC	5	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	GC-MSD	GC-MSD	MM-ML	PCB	No	75 %	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC-MSD	No	PS-ML	No	No	105 %	SB-EUPT	1	$SnCl_2$/HCl-cleavage, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	74,9 % (0.25 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	Spectrophotometer	Spectrophotometer, Spectrum comparation	PS-ML	No	No	79 %	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer	second derivation	PS-ML	No	No	None			$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	GC- (P) FPD	No	PS-ML	No	No	91 %			$SnCl_2$/HCl-cleavage, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC- (μ) ECD	GC-ECD	MM-ML	Chloroform	No	103 %	SB-EUPT	5	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	No	MM-ML	No	No	106,6 %	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	Spectrophotometer	No	PS-ML	No	No	77,6 %	SB-EUPT	5	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	GC-MSD	GC-MSD	PS-ML	No	Yes-1	45 %	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, headspace sampling, GC-analysis of CS_2, wet the sample, add $snCl_2$/hcl measue with headspace GC-MS
	GC- (P) FPD	No	PS-ML	No	No	71 % (0.1 mg/kg)	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, headspace SPME, GC-Analysis of CS_2 (EN 12396-2 type)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated); Yes-5: Yes, using procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dithiocarbamates (as CS_2)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
91		Yes	1 – 2 y	0.626	0.07	0.01	5	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×anthogenate	
25		Yes	> 2 y	0.632	0.11	0.01	2	Yes (+acid $SnCl_2$ HCl)	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	Water	HCl	Headspace sampling	No	
24	x	Yes	> 2 y	0.635	0.13	0.05	5	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl	LLP	No	
112		Yes	> 2 y	0.64	0.16	0.3	1	Yes	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl		Yes, with Cu(II) acetate-diethanolamine sln	
21		Yes	> 2 y	0.65	0.23	0.05	4	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Distillation passing through NaOH, $Zn(CH_3COO)_2$	Yes, with Cu(II) acetate-diethanolamine sln	
35		Yes	> 2 y	0.65	0.23	0.05	1	Yes	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Distillation passing through NaOH, $Zn(CH_3COO)_2$	Yes, with Cu(II) acetate-diethanolamine sln	
60		Yes	> 2 y	0.65	0.23	0.05	10	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl SPME fibre	HCl	Enrichment on SPME fibre	No	
7		Yes	> 2 y	0.655	0.26	0.05	5	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl	LLP	No	
33	x	No	> 2 y	0.655	0.26	0.05	2	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Headspace sampling	No	
79	x	Yes	> 2 y	0.66	0.29	0.05	1	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl	LLP	No	
52		Yes	> 2 y	0.663	0.31	0.05	5	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×anthogenate	
114		Yes	> 2 y	0.677	0.40	0.02	50 g	50 g, H_2O/$SnCl_2$/HCl	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl		Yes, to potassium-×anthogenate	
1		Yes	> 2 y	0.68	0.42	0.05	1	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$; 5 M HCl addition	SPME-fibre	HCl	Enrichment on SPME fibre, Enrichment on SPME fibre	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	Spectrophotometer	Spectrophotometer	PS-ML	No	Yes-1	83 %	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	GC-MSD	Headspace	Std add. to sample portions	No	Yes-2	101 %	SB-EUPT		$SnCl_2$/HCl-cleavage/reduction, headspace sampling, GC-analysis of CS_2
	GC-MSD	GC-MSD	MM-ML	No	No	89 % (Thiram at 1.8 mg/kg)	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	Spectrophotometer, spectrum	PS-ML	No	No	94 % (0.6 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	110 %	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer	No	PS-ML	No	No	87 % (0.30 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type), EN 12396-1
	GC- (P) FPD	No	Std add. to sample portions	No	No	94,2 %	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, headspace SPME, GC-Analysis of CS_2 (EN 12396-2 type)
	GC- (μ) ECD	GC-MSD	MM-ML	No	No	92 %	SB-EUPT	2	$SnCl_2$/HCl-cleavage, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC- (P) FPD	No	PS-ML	No	No	None (qualitative recovery)	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, headspace sampling, GC-analysis of CS_2
	GC- (P) FPD	No	PS-ML	Thiophene	No	89 %	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	No	PS-ML	No	No	86 %	QC	>5	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	Spectrophotometer	No	PS-ML	No	No	90 % (Thiram at 10 & 30 µg / 50 g sample)	SB-EUPT	3	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	GC-Ion Trap	No	MM-ML	No	Yes-2	100 % (0.3 mg/kg)		>5	$SnCl_2$/HCl-cleavage/reduction, headspace SPME, GC-Analysis of CS_2 (EN 12396-2 type)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated); Yes-5: Yes, using procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dithiocarbamates (as CS_2)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
47	x	Yes	> 2 y	0.684	0.45	0.05	1	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane, 2,2,4-trimethyl pentane added	HCl	LLP, 1) 2,2,4-trimethyl pentane layer partitioned	No	
53		Yes	> 2 y	0.694	0.51	0.05	25	10 ml	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Distillation passing through NaOH, $Zn(CH_3COO)_2$	Yes, with Cu(II) acetate-diethanol-amine sln	
103	x	Yes	> 2 y	0.695	0.52	0.05	1	Yes	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl		No	
50	x	Yes	> 2 y	0.703	0.57	0.05	25	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$ (2h at 80°C)	H_2O/$SnCl_2$/HCl, Isooctane	HCl	LLP, Na_2SO_4	No	
88		Yes	> 2 y	0.705	0.59	0.05	30	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate	
38		Yes	> 2 y	0.72	0.68	0.05	2	1 ml	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl	LLP	No	
89		Yes	> 2 y	0.723	0.70	0.05	1	4 ml water added	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Headspace sampling	No	
102		Yes	> 2 y	0.725	0.72	0.05	25	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl		Yes, to potassium-×antho-genate	
76		Yes	> 2 y	0.727	0.73	0.25	1	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Distillation passing through NaOH, $Zn(CH_3COO)_2$	Yes, with Cu(II) acetate-diethanol-amine sln	
22		Yes	> 2 y	0.74	0.81	0.04	5	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl	LLP	No	
29		Yes	> 2 y	0.741	0.82	0.025	25	Yes	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl	LLP	No	
11		Yes	> 2 y	0.743	0.83	0.050	2	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl	LLP	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC- (P) FPD	GC-MSD	MM-ML	No	No	108 % (Thiram at 0.08 mg/kg)	SB-Other	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2, in house
	Spectrophotometer	No	PS-ML	No	No	None			$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	GC-MSD	GC-MSD	PS-ML	$13CS_2$	No	113 %	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC- (μ) ECD	GC-ECD	MM-ML	No	No	90 % (0.37 mg/kg CS_2)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	115 %	SB-EUPT	3	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	GC-NPD	No	PS-ML	No Info	No	68,6 % (0.05 mg/kg)	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC-MSD	No	Std add. to sample portions	Thiophene	Yes-2	% (Standardaddition mit A-Spikes, nichts auffälliges)	SB-EUPT	3	$SnCl_2$/HCl-cleavage/reduction, headspace sampling, GC-analysis of CS_2
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	85 %	SB-EUPT	3	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type)
	Spectrophotometer	Spectrophotometer, Spectrum	PS-ML	No	No	91,7 % (Thiram at 0.65 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, Cu(II) acetate & diethaNolamine, spectroph. analysis (EN 12396-1 type)
	GC-MSD	GC-MSD	PS-ML	No	No	97 %	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2, Combination of methods from EURL SRM, Treland and Norway
	GC- (P) FPD	No	MM-ML	No	No	79 %	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC-MSD	No	PS-ML	No	No	85 % (0.8 mg/kg)	SB-EUPT	>5	$SnCl_2$/HCl-cleavage, LLP w. Non-polar solvent, GC-analysis of CS_2

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated); Yes-5: Yes, using procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dithiocarbamates (as CS_2)

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation
109	x	Yes	> 2 y	0.773	1.03	0.05	25	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl		No
34		Yes	> 2 y	0.776	1.05	0.05	1	40 ml water	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Headspace sampling	No
123		Yes	> 2 y	0.78	1.07	0.05	20	Yes	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl		No
74		No	None	0.8	1.20	0.05	25	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl	LLP	No
119		Yes	> 2 y	0.825	1.37	0.05	5	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl		No
15		No	< 1 y	0.835	1.43	0.020	1	Yes	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Headspace sampling	No
72		Yes	> 2 y	0.87	1.66	0.050	25	200 ml	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Distillation passing through NaOH and H_2SO_4 (for DTCs)	Yes, to potassium-×antho-genate
96	x	Yes	> 2 y	0.934	2.07	0.05	25	Yes	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl		No
104		No	> 2 y	1	2.50	0.050	1	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl		No
14	x	Yes	> 2 y	1.1	3.15	0.03	3	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl	LLP	No
116		Yes	> 2 y	1.17	3.61	0.010	5	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl, Isooctane	HCl		No
57		Yes	> 2 y	1.24	4.07	0.05	1	No	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$ (2 hours, 80°C, multiple shaking)	H_2O/$SnCl_2$/HCl, Isooctane, 100 ml A / 10 ml B	HCl	LLP, Centrifugation, 5 minutes, 3000 rpm	No
37	x	Yes	> 2 y	1.38	4.98	0.05	5	Yes	Cleavage/reduction to CS_2 w. HCl/$SnCl_2$	H_2O/$SnCl_2$/HCl	HCl	Headspace sampling	No

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC- (μ) ECD	No	PS-ML	No	No	92 % (0.8 mg/kg)	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC- (μ) ECD	GC-ECD	MM-ML	No	Yes-5	None	SB-EUPT	None	$SnCl_2$/HCl-cleavage/reduction, head-space sampling, GC-analysis of CS_2
	GC-MSD	GC-MSD	MM-ML	Iodo ethane	No	95 %	SB-EUPT	4	$SnCl_2$/HCl-cleavage/reduction, head-space sampling, GC-analysis of CS_2
	GC-MSD	No	MM-ML	No	No	104 % (Thiram at 0.1 mg/kg)	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC- (P) FPD	No	Std add. to sample portions	Thiophene	Yes-2		SB-EUPT	4	$SnCl_2$/HCl-cleavage/reduction, head-space sampling, GC-analysis of CS_2
	GC-MSD	No	Std add. to sample portions	No	Yes-2	82 % (Thiram at 3 levels)	SB-EUPT	3,00	$SnCl_2$/HCl-cleavage/reduction, head-space sampling, GC-analysis of CS_2
	Spectrophotometer	No	PS-ML	No	No	109 % (1.0 mg/kg)	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, KOH/MeOH, spectroph. analysis (Xanthogenate mth., EN 12396-3 /DFG-S15-type), §64 LFGB, Methode L00.00-35
	GC- (P) FPD	No	MM-ML	No	Yes-1	51 %	SB-EUPT	3	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC- (μ) ECD	No	MM-ML	No	No	None			other, in-house
	GC-MSD	No	MM-ML	No	No	90 % (0.5 mg/kg)	SB-EUPT	1	$SnCl_2$/HCl-cleavage, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC- (P) FPD	GC-FPD	MM-ML	No	No	90 %	SB-EUPT	2	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC-MSD	GC-MSD, target 76, qualifier 78	PS-ML	No	No	78 % (1 mg/kg)	SB-EUPT	1	$SnCl_2$/HCl-cleavage/reduction, LLP w. Non-polar solvent, GC-analysis of CS_2
	GC- (μ) ECD	GC-ECD	MM-ML	No	No	85 %	SB-Other	>5	$SnCl_2$/HCl-cleavage/reduction, head-space sampling, GC-analysis of CS_2

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated); Yes-5: Yes, using procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Ethephon

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation
18		Yes		FN	-3.62	0.05	5	Yes	No	Water	Yes	None	No
32	x	No	None	0.043	-3.18	0.02	1	5 ml	No	MeOH (w. 1 % HCOOH)	before injection, basic medium	None	No
3		Yes	1 – 2 y	0.117	-1.77	0.05	1	5 ml	NaOH	Other NaOH	NaOH	None	No
21		Yes	> 2 y	0.126	-1.60	0.01	5	No	No	EtAc	No	None	Yes, diazomethane
7		Yes	1 – 2 y	0.131	-1.50	0.02	5	Yes	No	MeOH, DCM, HCOOH	No	None	No
31		Yes	< 1 y	0.144	-1.26	0.020	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No
28		Yes	> 2 y	0.145	-1.24	0.01	5	Yes	No	MeOH, additional 1 % HAc	No	Centrifugation, Filtration	No
99		Yes	> 2 y	0.166	-0.84	0.01	5	5 g	pH 14, 30 min, 90°C	Ethylene liberation by H_2O Aqueous KOH	Yes, pH 14		No
14	x	Yes	> 2 y	0.182	-0.53	0.02	5	10 ml prior to extraction	No	MeOH, Water	1 % HCOOH	Centrifugation, Filtration	No
123		Yes	1 – 2 y	0.19	-0.38	0.05	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH		No
10	x	Yes	> 2 y	0.194	-0.30	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No
24	x	Yes	< 1 y	0.197	-0.25	0.04	5	No	No	Other Water acidified with HCOOH	No	None	No
25		Yes	> 2 y	0.197	-0.25	0.01	1	Yes	No	MeOH, Water	No	LLP	No
103	x	Yes	1 – 2 y	0.199	-0.21	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH		No
4	x	Yes	> 2 y	0.205	-0.10	0.025	5	Yes	No	MeOH, Water	1 % HCOOH	Centrifugation, Filtration	No

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No					Dilute withWater/HCOOH, LC-MS/MS
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	IL-Eth-ephon	Yes-4	(50 & 100 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM method for polar pesticides), modified
	GC-FID	GC-FID	PS-ML	No	No	85 %	SB-EUPT	2	Ethylene-release type method (for ethephon), The sample is wetted with water, NaOH is added, boiled, the ethylen is measured.
	GC- (P) FPD	GC-FPD	Std add. to sample portions	No	Yes-2		SB-EUPT		Water/NaOH, diazomethane derivatisation
	LC-MS	LC-MS	MM-ML	No	No	88,2 %	SB-EUPT	2	Dilute with MeOH/Water/HCOOH, cleanup w. DCM, LC-MS, PA 048, EPRW 2010, Use of Ion Chromatography-Electrospray Mass Spectrometry for the Determination of
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	99 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), via second mass transition, MRM ratio	PS-ML	IL-Eth-ephon	Yes-3	80 %	SB-EUPT	1	other, Extraction with MeOH, detection with LC-MS/MS
	GC-MSD	LC-MS/MS (QQQ), LC-MS-MS confirmation in QuPPe extract	MM-ML	IL-Eth-ephon	Yes-4	95 %	SB-EUPT	4	Ethylene-release type method (for ethephon)
	LC-MS/MS (QQQ)	No	PS-ML	IL-Eth-ephon	Yes-3	85 % (1 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides), M. Anastassiades:Method for Analysis of Residues of Highly Polar Pesticides in Foods of Plant Origin
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	IL-Eth-ephon	Yes-4	85 % (using Labeled IS)	QC	>5	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	IL-Eth-ephon	Yes-3	98 % (spiked blank)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	IL-Eth-ephon	Yes-3	83,6 % (0.05 mg/kg)	SB-EUPT	1	other, Journal of chromatography A, 1218 (2011) 3675, 2 % HCOOH in water (20 mls), Obelisc N column.
	LC-MS/MS (QQQ)	No	Std add. to sample portions	IL-Eth-ephon	Yes-4	90 %	SB-EUPT		QuPPe-Method (EURL-SRM method for polar pesticides), modified
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	IL-Eth-ephon	Yes-1		SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	No	No	92 %	SB-EUPT	2	QuPPe-Method (EURL-SRM method for polar pesticides), QuPPe V5 , however different Chromatography

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Ethephon

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
12		Yes	> 2 y	0.208	-0.04	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No	
30	x	No	1 – 2 y	0.21	0.00	0.02	5	8.5 ml water	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No	
20	x	Yes	1 – 2 y	0.211	0.02	0.02	2	10 ml prior to extraction	No	MeOH, Water, acidified MeOH	via extraction using 1 % HCOOH in MeOH	Centrifugation, Filtration	No	
96	x	No	< 1 y	0.212	0.04	0.1	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH		No	
29		No	< 1 y	0.22	0.19	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No	
55	x	No	> 2 y	0.225	0.29	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No	
93		Yes	1 – 2 y	0.227	0.32	0.05	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No	
17		Yes	1 – 2 y	0.241	0.59	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No	
2		Yes	> 2 y	0.243	0.63	0.01	3	10 mL in extraction solvent	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No	
47	x	Yes	> 2 y	0.245	0.67	0.02	5	Yes	No	Water, MeOH, Other, conc HCl	Acidified water/MeOH	Centrifugation, LLP, 2) partition with DCM, centrifuge & filter	No	
1		Yes	1 – 2 y	0.25	0.76	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No	
60		No	> 2 y	0.25	0.76	0.02	5	10 ml	No	MeOH, Water, 10 ml MeOH (1 % HCOOH)	1 % HCOOH in MeOH	Centrifugation, Filtration	No	
102		Yes	> 2 y	0.25	0.76	0.02	1	7 ml	KOH	Other KOH/ Aceton	KOH		No	
101	x	Yes	None	0.265	1.05	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH		No	
79	x	Yes	> 2 y	0.267	1.09	0.01	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifugation, Filtration	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	IL-Eth-ephon	Yes-4	93 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	13C-N15-Glyphosate	Yes-1	20.7 % (0.5 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	IL-Eth-ephon	Yes-4	88,9 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	IL-Eth-ephon	Yes-3	91,1 %	SB-EUPT	3	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	PS-ML	IL-Eth-ephon	Yes-3	85 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	IL-Eth-ephon	Yes-3	92 %	SB-EUPT	4	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	IL-Eth-ephon	Yes-3	102 %	SB-EUPT	2,00	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	IL-Eth-ephon	Yes-3	101 % (0.2 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	Std add. to sample portions	IL-Eth-ephon	Yes-4	94 % (0.25 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	IL-Eth-ephon	Yes-2				other, in house
	LC-MS/MS (QQQ)	No	MM-ML	IL-Eth-ephon	Yes-3	112 % (0.4 mg/kg)	SB-EUPT	3	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	MM-ML	No	No	73,8 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	GC-FID	No	MM-ML	No	Yes-2	98 % (Recovery-corr by cal over the whole procedure)	SB-EUPT	3	Ethylene-release type method (for ethephon)
	LC-MS/MS (QQQ)	No	Std add. to sample portions	IL-Eth-ephon	Yes-4	98 % (0.5 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides), QuPPe EURL-SRM method for polar pesticides v.6
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	PS-ML	IL-Eth-ephon	Yes-3	76 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Ethephon

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
37	x	Yes	< 1 y	0.268	1.10	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Centrifuga-tion, Filtration	No	
66		Yes	> 2 y	0.287	1.47	0.02	2	Yes	alkaline hydrol-ysis to ethylen	Other No ex-traction/hydrol. takes place in headspace-via	Yes	None	No	
13		Yes	> 2 y	0.63	8.00	0.1	6	Yes	KOH	Water	KOH	None	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	91 %	QC	>5	QuPPe-Method (EURL-SRM method for polar pesticides)
	GC-FID	No	MM-ML	No	No	98 %	SB-EUPT	3	Ethylene-release type method (for ethephon), § 64LFGB 00.00-47 alkaline cleavage to ethen
	GC-FID	No	MM-ML	No	No	36,4 %	SB-EUPT	1	Ethylene-release type method (for ethephon)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fenbutatin Oxide

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
88		Yes	1 – 2 y	0.035	-3.20	0.02	5	10 ml water, waiting for 10 min	No	ACN	No	dSPE (PSA/ $MgSO_4$), Centrifugation,	No	
84		Yes	> 2 y	0.038	-3.13	0.01	5	prior to extraktion	No	ACN	No	dSPE (PSA/ $MgSO_4$)	No	
47	x	Yes	> 2 y	0.0421	-3.04	0.02	5	10 ml water added to sample	No	ACN	Acetate Buffer	Centrifugation (2×), 150 mg $MgSO_4$ added before 2nd centrifugation	No	
10	x	Yes	> 2 y	0.0422	-3.04	0.02	5	10 ml	No	ACN	No	dSPE (PSA/ $MgSO_4$), Centrifugation,	No	
17		Yes	> 2 y	0.045	-2.97	0.02	5	Yes	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$)	No	
66		Yes	> 2 y	0.0697	-2.41	0.02	5	10 ml to 5 g sample weight	No	ACN	No	Freeze-out	No	
32	x	No	None	0.082	-2.13	0.05	5	5 ml	No	MeOH ammonium acetate 20mM	No	None	No	
130		Yes	< 1 y	0.0866	-2.02	0.01	5	10 mL	No	acidified ACN 5 g sample +10 g H_20 +10 mL(CH_3CN + 0.1 % HAc)	1) 0.1 % HAC in ACN during extraction; 2) citrate buffer during separation		No	
31		Yes	1 – 2 y	0.09	-1.94	0.020	5	10 ml	No	ACN	No	None	No	
62	x	No	> 2 y	0.11	-1.49	0.05	5	Yes	No	EtAc	No	None	No	
7		Yes	> 2 y	0.116	-1.35	0.02	5	Yes	No	ACN	No	None	No	
53		No	None	0.134	-0.94	0.02	2	10 ml	No	ACN	100µl 1 % HCOOH at the end	dSPE (PSA/ $MgSO_4$)	No	
21		No	None	0.137	-0.87	0.01	1	No	No	MeOH	acidic conditions	None	No	
6	x	Yes	1 – 2 y	0.14	-0.80	0.02	5	Yes	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$)	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Pirimicarb-D6	No	70 %	SB-EUPT	3	QuEChERS (original version) J. AOAC 86 (2003)
	LC-MS/MS (QQQ)	No	Std add. to sample portions	TPP	Yes-2				EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	TPP	No	125 % (0.02 mg/kg)	SB-Other	1	AOAC Official Method 2007.01 (QuEChERS - Acetate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	TPP	No	100 % (spiked blank)	SB-EUPT	1	QuEChERS (original version) J. AOAC 86 (2003)
	LC-MS/MS (QQQ)	No	MM-ML	Linuron-D6	No	24 % (0.05 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	additional standard addition to extract aliquots	MM-ML	No	No	105 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	Oxfenda-zole	Yes-2		SB-EUPT	1	other, MeOH extraction
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to Extract	No	No	49,6 % (0.04 mg/kg)	SB-EUPT	4	EN 151662 (QuEChERS - Citrate Buffer) modified, Acetonitrilie used with 0.1 % HAc
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	62 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-SL	No	No	83,7 %	SB-EUPT	2	other, EN 12393
	LC-MS	LC-MS	MM-ML	No	No	86,2 %	SB-EUPT	2	QuEChERS (modified version for orgaNotins -EURL-mth), EU-RL SRM, Analysis of OrgaNotin Compounds via QuEChERS and LC-MS/MS
	LC-MS/MS (QQQ)	No	Std add. to extract aliquots	No	No	None			EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	TPP	No	57 %	SB-EUPT	1	other, in house method based upon EURL-SRM method
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	Yes-1	51 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fenbutatin Oxide

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
85		No	> 2 y	0.145	-0.69	0.01	1	10 ml	No	EtAc	sodium hydrogen carbonate	None	No	
109	x	No	1 – 2 y	0.15	-0.57	0.03	5	5 ml	No	ACN	Citrate Buffer		No	
50	x	Yes	1 – 2 y	0.153	-0.50	0.02	5	10 ml	No	ACN	No	Freeze-out	No	
19	x	No	< 1 y	0.162	-0.30	0.05	5	10 ml prior to extraction	No	EtAc	3 g $NaHCO_3$	Centrifugation, Filtration	No	
96	x	Yes	1 – 2 y	0.169	-0.14	0.05	1	Yes	No	EtAc	No		No	
23	x	Yes	< 1 y	0.17	-0.11	0.01	5	10 ml	No	ACN	No	dSPE (PSA/ $MgSO_4$), Centrifugation, Filtration	No	
14	x	Yes	> 2 y	0.175	0.00	0.006	5	10 ml before extraction	No	ACN	No	only desiccation with $mgSO_4$	No	
127		No	None	0.181	0.14	0.02	5	5 ml	No	ACN	No		No	
37	x	Yes	< 1 y	0.19	0.34	0.02	5	Yes	No	ACN	No	dSPE (PSA/ $MgSO_4$)	No	
34		Yes	> 2 y	0.193	0.41	0.01	5	No	No	ACN, Citrate Buffer	Citrate Buffer	Centrifugation, Freeze-out	No	
13		No	> 2 y	0.199	0.55	0.01	5	10 ml	No	ACN	Citrate Buffer	dSPE (PSA/ $MgSO_4$)	No	
4	x	Yes	> 2 y	0.201	0.59	0.02	5	Yes	No	ACN	No	None	No	
18		Yes	1 – 2 y	0.21	0.80	0.01	5	Yes	No	EtAc	No	None	No	
80		Yes	> 2 y	0.214	0.89	0.04	5	10 g water	No	Acetone, CH, EtAc	No	GPC, Gel-Permeation Chr/phy	No	
99		Yes	> 2 y	0.216	0.94	0.01	5	10 g	No	ACN, Water, 10 mL	No		No	
118	x	No	< 1 y	0.226	1.17	0.02	5	No	No	ACN	No		No	
29		No	None	0.23	1.26	0.02	5	Yes	No	EtAc	HAc 1 %	Filtration	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2nd MSMS transition	MM-ML	Carbendazim-D4	No	56 % (0.02 mg/kg)	SB-EUPT	2	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, EtOAc extraction, solvent exchange into MeOH
	LC-MS	LC-Ion Trap, MS/MS	MM-ML	No	No	110 % (0.1 mg/kg)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-Ion Trap	LC-Ion Trap, relevant ions	MM-ML	No	Yes-1	25 % (0.16 mg/kg)	SB-EUPT	3	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	No	Yes-2	69,8 % (0.05 mg/kg)	QC	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, 5 g sample,10 ml water+10 ml EtAC
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	92,5 %	SB-EUPT	3	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-SL	No	Yes-2	25 % (0.4 mg/kg)	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	TPP	No	80 % (0.05 mg/kg)	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer), QuEChERS without PSA
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	TPP	No	80 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	82 %	QC	>5	QuEChERS (original version) J. AOAC 86 (2003)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	Yes-1	82,6 % (0.098, 0.196, 0.294 mg/kg)	SB-EUPT	3	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	Yes, other (unspecifies)	Yes-1	43 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	No	No	95 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	85 %	SB-EUPT	5	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	75,2 % (0.06 mg/kg)	SB-EUPT	1	S-19 (§ 64 LFGB L00.00-34), E2, GPC
	LC-MS/MS (QQQ)	No	MM-ML	Cyromazine-D4	Yes-2	95 %	SB-EUPT	4	QuEChERS (original version) J. AOAC 86 (2003)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	Yes-1	26 %	SB-EUPT	2	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	MM-SL	Pirimicarb-D6	No	76 %	SB-EUPT	1	SweEt type (e.g. T. Pihlström et al. Anal. Bioanal. Chem (2007) 389, 1773-1789, EtAc with 1 % HAc, National Food Administration, Sweden

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fenbutatin Oxide

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
3		Yes	1 – 2 y	0.254	1.81	0.01	5	20 ml	No	MeOH	No	Filtration, Centrifugation	No	
25		Yes	> 2 y	0.261	1.97	0.01	1	Yes	No	ACN, Water	No	LLP	No	
78		No	None	0.28	2.40	0.28	5	8 ml	No	ACN	No	dSPE (PSA/ $MgSO_4$)	No	
28		Yes	> 2 y	0.289	2.61	0.02	1	Yes	No	Acetone, Water, H_2SO_4, EtAc,	H_2SO_4	LLP, with EtAc/C_6H_{12}	Yes, Methylation with tert. butylmethylether/ methylmagnesiumchloride	
20	x	Yes	1 – 2 y	0.306	2.99	0.02	2	10 ml before extraction	No	Other acidified ACN	Citrate Buffer	Freeze-out (2 hours at -18 °C) Centrifugation	No	
12		Yes	< 1 y	0.311	3.11	0.02	2	Yes	No	ACN	0.2 ml HAc	Centrifugation	No	
113	x	Yes	> 2 y	0.32	3.31	0.02	5	5 mL	No	ACN	Acetate Buffer QuEChERS		No	
30	x	No	< 1 y	0.323	3.38	0.01	5	10 ml water	No	ACN	No	None	No	
123		Yes	< 1 y	0.35	4.00	0.01	3	10 ml	No	ACN	Acetate Buffer QuEChERS		No	
1		No	1 – 2 y	0.389	4.89	0.02	3	7.5 mL 1 % HCOOH in water	No	ACN	with 1 % HCOOH	None	No	
103	x	Yes	< 1 y	0.416	5.51	0.02	2	Yes	No	ACN	Citrate Buffer		No	
89		Yes	> 2 y	0.507	7.59	0.1	1	No	No	ACN	No	Centrifugation, solvent exchange	No	
2		No	None	0.55	8.57	0.01	1	2 ml (extraction solution A)	No	EtAc, 1 M HCl, 15 % NaCl	1 M HCl	LLP	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	No	Yes-1	10.7 % (Normally we use QuECh-ERS and there are No recovery problems, this is a very stranage sample)	SB-EUPT	2	QuEChERS (original version) J. AOAC 86 (2003)
	LC-MS/MS (QQQ)	No	Std add. to sample portions	Isoprotu-ron	Yes-2	44 %	SB-EUPT		EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-SL	No	No	None			EN 151662 (QuEChERS - Citrate Buffer)
	GC-MSD	GC-MSD, via second m/z	MM-SL	No	No	109 %	SB-EUPT	1	other, extraction, derivatisation, meth-ylation, GC-MSD detection
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	TPP	Yes-2	68,2 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-Ion Trap	LC-Ion Trap	Std add. to extract aliquots	Pirimicarb-D6	Yes-1	45 %	SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), Ion ratio	MM-ML	No	Yes-1	16 % (0.05 mg/kg)	SB-EUPT	1	AOAC Official Method 2007.01 (QuECh-ERS - Acetate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	TPP	Yes-1	33,3 % (0.1 and 0.5 mg/kg)	SB-EUPT	>5	EN 151662 (QuEChERS - Citrate Buffer), w/o dSPE
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	No	Yes-2	100 %	QC	>5	AOAC Official Method 2007.01 (QuECh-ERS - Acetate Buffer)
	LC-MS/MS (QQQ)	No	MM-ML	TPP	Yes-1	83 % (0.2 mg/kg)	SB-EUPT	2	QuEChERS (original version) J. AOAC 86 (2003), acidified water addition
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	No	Yes-2		SB-EUPT	1	EN 151662 (QuEChERS - Citrate Buffer)
	LC-MS/MS (QQQ)	No	Std add. to sample portions	No	Yes-2	Standard addition with A-Spikes, strong Signalin-hibition approx. factor 2 cp. with extern Standard)	SB-EUPT	4	other, ACN extraction
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	Std add. to sample portions	No	Yes-2	46 % (0.75 mg/kg based on solvent standard)	SB-EUPT	1	other, in-house

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Glyphosate

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation
84		Yes	1 – 2 y	0.202	-3.02	0.05	5	prior to extraction	No	Water, MeOH, DCM, DM for purification	Borate-buffer	LLP, DM	Yes, with FMOC-Cl/ Borate-buffer
31		Yes	< 1 y	0.236	-2.86	0.010	5	Yes	No	Water	No	None	Yes, with FMOC
30	x	No	> 2 y	0.347	-2.32	0.05	5	8.5 ml	No	MeOH, Water	1 % HCOOH in MeOH	None	No
90		No	None	0.4122	-2.01	0.05	5	in extr. solvent	No	Other water w. 0.5 % HCOOH	0.5 % HCOOH	Centrifugation, SPE-column, C18 ec	No
60		No	> 2 y	0.42	-1.97	0.02	5	10 ml	No	MeOH, Water, 10 ml MeOH (1 % HCOOH)	1 % HCOOH in MeOH	Centrifugation	No
96	x	No	None	0.456	-1.79	0.1	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH		No
7		Yes	> 2 y	0.457	-1.79	0.05	5	Yes	No	Water, MeOH, DCM, HCOOH	1 % HCOOH in MeOH	None	No
21		Yes	< 1 y	0.515	-1.51	0.05	5	Yes	No	Water, MeOH	No	None	Yes, with FMOC
79	x	Yes	> 2 y	0.576	-1.21	0.01	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	None	No
11		Yes	< 1 y	0.596	-1.12	0.1	1	100 mL	No	100 ml water / 100 ml MeOH	first acidic, at derivatization alkaline	SPE-column (specify under details), C18	Yes, with FMOC-Cl
10	x	Yes	> 2 y	0.602	-1.09	0.05	5	10 ml	No	MeOH, Water,	1 % HCOOH in MeOH	None	No
123		Yes	< 1 y	0.62	-1.00	0.05	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH		No
3		Yes	None	0.69	-0.66	0.01	5	in extr. solvent	No	aqueous HCl , DCM	Yes, acidic pH (due to aq. HCl for extraction)	Chelex 100 resin, Ionexchange resin	Yes, post column with OPA
93		Yes	1 – 2 y	0.694	-0.64	0.1	5	10 ml	No	MeOH, Water	pH 12 before derivation	None	Yes, Isobutylchloroformate
66		Yes	1 – 2 y	0.708	-0.58	0.05	2	contained in buffer solution	No	Water, MeOH, EtAc, Extraction w. water-MeOH-borat-buffer, EA for partitioning after derivation	during extraction w. borate buffer; after SPE-elution to pH 9 with NH_3	SPE-column (specify under details), Oasis MAX, 30 µm, elution with ACN/HCl	Yes, with FMOC

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	No	MM-ML	IL-Glyphosate	Yes-3	90 %	QC	>5	other, derivatised with FMOC-Cl
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	82 %	SB-EUPT	1	other, with FMOC derivatisation
	LC-MS/MS (QQQ)	No	MM-ML	IL-Glyphosate	Yes-3	56 % (0.5 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	other method	MM-ML	IL-Glyphosate	Yes-3	94,2 % (IS added before measurement)	SB-Other	1	other, 5 g sample+20 mL water / 0.5 % HCOOH, hand shake 1 min, soak 10 min, hand shake 1 min, mech. shake 30 min, centrifuge, pass 10 ml through 500 mg C18 ec, calib. on blank-wheat, IL-comp. to final extr. but No corr., LC-MS/MS
	LC-MS/MS (QQQ)	No	MM-ML	No	No	112 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	Std add. to extract aliquots	IL-Glyphosate	Yes-4	89 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS	LC-MS	MM-ML	No	No	88,6 %	SB-EUPT	2	Dilute with MeOH/Water/HCOOH, cleanup w. DCM, LC-MS, PA 048, EPRW 2010, Use of Ion Chromatography-Electrospray Mass Spectrometry for the Determination of
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	IL-Glyphosate	Yes-3	80 %	SB-EUPT	1	other, in house method
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	PS-ML	IL-Glyphosate	Yes-3	110 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	Std add. to sample portions	No	Yes-2				other, extraction, derivatization, SPE cleaning, concentration, analysis
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	IL-Glyphosate	Yes-3	86 % (spiked blank)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	IL-Glyphosate	Yes-4	100 % (using Labeled IS)	QC	>5	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-Fluorescence Det.	LC-Fluorescence Det.	PS-SL	No	No	48 %	SB-EUPT	2	DFG methode S 405, Extraction with diluted HCL, clean-up w. chelex and anion-exchanger, determination w. HPLC-FLD
	LC-MS/MS (QQQ)	No	MM-ML	IL-Glyphosate	Yes-3	87 %	SB-EUPT	2,00	other, QuPPe-type extraction followed by derivatizsation
	LC-MS/MS (QQQ)	additional standard addition to sample portions	PS-ML	IL-Glyphosate	Yes-4	103 %	QC	>5	other, extr. with buffer, derivation with FMOC-Cl, extr. with EtAc, SPE, elution with ACN/HCl

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated); Yes-5: Yes, using procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Glyphosate

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
28		Yes	> 2 y	0.723	-0.50	0.05	1	in extr. solvent	No	aqueous HCl , DCM	acidic pH (due to aq. HCl for extraction)	Chelex 100 resin, Ionex-change resin	Yes, post column with OPA	
22		Yes	> 2 y	0.746	-0.39	0.01	25	No	No	Water	No	SPE-column, Filtration, Oasis column	No	
24	x	Yes	< 1 y	0.768	-0.29	0.04	5	No	No	Water acidified w. HCOOH	2 % HCOOH	None	No	
99		Yes	> 2 y	0.813	-0.07	0.01	1	10 mL	No	Water 10 mL	No		Yes, with FMOC-Cl 37°C 30 min	
57		Yes	> 2 y	0.827	0.00	0.05	2	in extr. Solvent; aliquot diluted with water	No	Water w.0.1 M HCl, DCM, A:100 ml 0.1m HCl, B: 35 ml DCM	pH 1.5 - 2.5 with HCl	Chelex 100 resin, Ionex-change resin, AG1-X8,	Yes, post column with OPA	
4	x	Yes	> 2 y	0.837	0.05	0.025	1	Yes	No	Water, MeOH, DCM, DM for purification	Borate buffer pH9	LLP	Yes, with FMOC-Cl	
12		Yes	> 2 y	0.842	0.07	0.05	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	None	No	
43		No	< 1 y	0.88	0.26	0.25	2	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	None	No	
47	x	Yes	> 2 y	0.9	0.35	0.05	5	Yes	No	Water, MeOH, conc HCl	Yes, acidified with HCl	Centrifuga-tion, LLP, 2) partition with DCM, centri-fuge & filter	No	
2		Yes	> 2 y	0.905	0.38	0.05	3	10 mL in extrac-tion solvent	No	MeOH, Water	1 % HCOOH in MeOH	None	No	
101	x	Yes	None	0.94	0.55	0.05	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH		No	
34		Yes	1 – 2 y	0.956	0.62	0.05	1	for fill-ing up volu-metric flask	No	Water, DCM, partitioning with 20 ml HCl, 10 ml DCM	extraction acidic then neutralized with NaOH to pH 6-8	Centrifuga-tion, ion-exchange	Yes, with FMOC	
128		Yes	1 – 2 y	0.962	0.65	0.05	5	Yes	No	Water	No		Yes, with FMOC deri-vatisation	
36		Yes	< 1 y	0.964	0.66	0.05	5	15 mL	No	Water, MeOH, DCM, DM for purification	No	LLP, DMe	Yes, with FMOC	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-Fluorescence Det.	LC-Fluorescence Det.	PS-SL	No	No	113 %	SB-EUPT	1	DFG methode S 405, Extraction w. aqueous HCL, clean-up w. chelex and anion-exchanger, determination w. HPLC-FLD
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	PS-ML	IL-Glyphosate	Yes-3	100 %	SB-EUPT	1	other, Mth by Danish Plant directorate
	LC-MS/MS (QQQ)	No	MM-ML	IL-Glyphosate	No	99,8 % (0.1 mg/kg)	SB-EUPT	1	other, Journal of chromatography A, 1218 (2011) 3675, 2 % HCOOH in water (20 mls), Obelisc N column.
	LC-MS/MS (QQQ)	No	MM-ML	IL-Glyphosate	Yes-4	95 %	SB-EUPT	4	other, SLE water, DSPE, with FMOC-Cl, LC-MS-MS
	LC-Fluorescence Det.	Different Method, post-column derivatisation	PS-ML	No	No	89 % (0.5 mg/kg)	SB-EUPT	2	DFG methode S 405, extraction, clean-up, LC-FLD, post-column derivatisation
	LC-MS/MS (QQQ)	No	MM-ML	IL-Glyphosate	Yes-3	100 %	SB-EUPT		other, Precolumn with FMOC-Cl
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to extract aliquots	IL-Glyphosate	Yes-4	112 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-Orbitrap	No	MM-ML	IL-Glyphosate	Yes-3				QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	IL-Glyphosate	No	102 % (0.1 mg/kg)	SB-Other	1	other, in house
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ), 2 transitions	Std add. to sample portions	IL-Glyphosate	Yes-4	91 % (0.25 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	Std add. to sample portions	IL-Glyphosate	Yes-4	80 % (spiked at 0.5 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides), QuPPe EURL-SRM method for polar pesticides v.6
	LC-Fluorescence Det.	LC-Fluorescence Det.	MM-SL	No	Yes-5	None*	SB-EUPT	None	other, acid extraction,neutralized,ion-exchange,LC-Fluorescense-Detection after derivatisation with FMOC
	LC-MS/MS (QQQ)	No	MM-ML	No	Yes-2		SB-EUPT		other, Extraction into water, with FMOC derivatization and analysis of with FMOC-derivate by LC/MS/MS
	LC-MS/MS (QQQ)	No	MM-ML	No	No	96 % (1.0 mg/kg)	SB-EUPT	1	other, derivatisation with FMOC

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated); Yes-5: Yes, using procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

*1 matrix-matched level was treated like recovery value and form the "calibration curve", so this level is a virtually recovery. Every other level would only be aNother level for calibration, but No real recovery value. In spite of that the value for the pesticide is "automatically" recovery corrected.)

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Glyphosate

Lab-Code SRM7-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	Derivatisation	
103	x	Yes	> 2 y	0.978	0.73	0.05	3	Yes	No	Water	No		Yes, with FMOC-Cl	
29		No	< 1 y	0.988	0.78	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Filtration	No	
14	x	Yes	> 2 y	1.01	0.89	0.05	5	10 ml before extraction	No	MeOH, water	1 % HCOOH in MeOH	None	No	
1		Yes	1 – 2 y	1.02	0.93	0.04	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	Filtration	No	
32	x	No	1 – 2 y	1.02	0.93	0.02	1	10 mL	No	Water, MeOH, DCM,	No	LLP	Yes, with FMOC-Cl	
17		Yes	1 – 2 y	1.03	0.98	0.02	5	10 ml	No	MeOH, Water	1 % HCOOH in MeOH	None	No	
121	x	Yes	> 2 y	1.07	1.18	0.02	3	used for extraction	No	Water 50 ml	No		No	
18		Yes	< 1 y	1.11	1.37	0.04	5	Yes	No	Water, EtAc, EtAc for purification	No	LLP EtAc	Yes, with FMOC	
25		Yes	> 2 y	1.14	1.51	0.01	1	Yes	No	Water, DCM	No	LLP	Yes, with FMOC-Cl	
20	x	Yes	1 – 2 y	1.37	2.63	0.05	2	10 ml prior to extraction	No	MeOH, Water, acidified MeOH	1 % HCOOH in MeOH	Centrifugation, Filtration	No	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtAc: ethyl acetate; HAc: acidic accid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	IL-Glyphosate	Yes-1		SB-EUPT	1	other, In-house method
	LC-MS/MS (QQQ)	No	PS-ML	IL-Glyphosate	Yes-3	117 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	No	PS-ML	IL-Glyphosate	Yes-3	99 % (1 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides), M. Anastassiades:Method for Analysis of Residues of Highly Polar Pesticides in Foods of Plant Origin
	LC-MS/MS (QQQ)	No	MM-ML	IL-Glyphosate	Yes-3	112 % (0.4 mg/kg)	SB-EUPT	3	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	IL-Glyphosate	Yes-4	1 & 2 mg/kg	SB-EUPT	2	other, S. Goscinny, Food Anal Methods 2012
	LC-MS/MS (QQQ)	No	MM-ML	IL-Glyphosate	Yes-3	104 % (1.6 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)
	LC-MS/MS (QQQ)	GC-MS/MS (QQQ)	PS-ML	IL-Glyphosate	Yes-3	114 %	SB-EUPT	1	other, FP054.1
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	93 %	SB-EUPT	5	other, water extraction, with FMOC, purification by EtAc before injection
	LC-MS/MS (QQQ)	No	Std add. to sample portions	IL-Glyphosate	Yes-4	106 %	SB-EUPT		other, derivatisation with FMOC
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	Std add. to sample portions	IL-Glyphosate	Yes-4	119.4 %	SB-EUPT	1	QuPPe-Method (EURL-SRM method for polar pesticides)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated); Yes-5: Yes, using procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 8 Possible reasons for poor performance (ordered by z-scores)

A: Technical problems with measurement instrumentation
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of analytical standard
F: Error in the evaluation/interpretation of measurement data
G: Use of inappropriate procedure
H: Reporting level to close to assigned value
I: No or inappropriate correction for recovery
J: Inappropriate storage of sample
K: Transcription error
L: Cross contamination

2.4-D (free acid) Assigned value: 0.278 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
118	-3.42	yes	1) problems with sensitivity of the LC-MS/MS for this compound; 2) the operator did not add water prior to extraction"	A, B
130	-2.20		Possibilities: The lab result was inferior to the conventional true value, so, 1) our standard was more concentrated, 2) the sample was a concentration inferior to the "true" value, 3) degradation of 2,4-D or 4) normal distribution not adequate. Real possibilities: 1): Human error. On volumetric steps during preparation of standard solution (it is always possible). 2): Normal model used by organization is not ok. Using Grubbs test it is possible identify two outliers. Without these results the distribution became Normal with a RSD of 28 %. With this RSD the result of -2,19 became -1.93 (satisfactory). **NOTES OF THE ORGANIZERS:** 1) As the Qn-RSD differs only slightly from the FFP-RSD (of 25 %) the latter is applied in accordance with the General EUPT Protocol. 2) Applying the Grubbs' test (as recommended in DIN ISO 5721-2:2002-12) one statistical outlier and one straggler were identified within the population of the 2,4-D results. The straggler was not regarded as an outlier.	–
116	2.07	yes	Extracts containing high level residues (0.254 ppm) and the concentration of matrix extract not adjusted for subsequent quantification.	C
9	4.07	(yes)	no experience with the commodity "lentils" and in general only very little experience with pesticides requiring single methods.	D

Bromide ion Assigned value: 41.4 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
56	-3.71 (FN)	yes	Our standard solution had the wrong concentration due to an error of the analyst. After recalculation our result should be 36.7 mg/kg.	E
21	3.47	yes	The interpretation of the chromatogram was wrongly performed by the operator. There was a blank-interference due to the matrix, which was wrongly calculated as a bromide value.	F

Appendix 8 (cont.) Possible reasons for poor performance

Chlorothalonil Assigned value: 0.104 mg/kg; possible assigned value: 0.122 mg/kg

**z-scores were calculated based on the z-scores calculated using the assigned value given in the preliminary report, which was based on the median*

LabCode	z-score*	Source of error localized?	Reason / Remarks	
111	-3.68	(yes)	I think that the problem was in that, that I don´t have experiences with such analysis, we routinly don´t measure pesticides in such matrices, therefore we don´t had a suitable reference material for such commodity.	D
23	-3.62 (FN)	yes	By a mistake the wrong peak has been taken for chlorothalonil. And the citate buffered QuEChERS (EN15662) was applied, giving very low recovery for chlorothalonil. We have now tested the Modified QuEChERS method for chlorothalonil (pH ~1) and got much better and acceptable recoveries for chlorothalonil both for spiked lentil samples and the PT-sample.	G, F
107	-3.62	yes	We have used the QuEChERS method and analyzed by GC/MS/MS.Our quantification limit for chlorthalonil is 0.1 mg/kg. This pesticide is not accredited, in most of the products recoveries are very low. **NOTES OF THE ORGANIZERS:** 1) The fact that the lab's LOQ is very close to the assigned value may have contributed to the false negative result. 2) Using QuEChERS acidification during the extraction/partitioning step is absolutely necessary for this matrix /compound combination to minimize degradation during sample preparation and measurement.	G, H
110	-3.62	yes	We didn't detect chlorothalonil at 0.104 mg/kg inspite of our reporting limit of 0.1 mg/kg. The sensitivity of our GC might have been less than expected when mesured, however I believe it was rather due to lower recovery due to the special matrix for this PT (swelling of proteins/starch making QuEChERS extraction questionable). It is impossible to meet MRRLs of 0.01 mg/kg with our GC-MS. We were however lucky to get the budget for an MS/MS this year, so we hopefully can lower our reporting limits. **NOTES OF THE ORGANIZERS:** See notes 1) and 2) under lab 107	G, H
3	-3.37	yes	1. Chlorthalonil standard. The standard is correct. 2. Raw data, The data was typed correct. 3. Recovery of the samples. The recovery of the sample was 74 %. Normally for fruit and vegetables we weigh in 15 grams and add standard addition of the sample at a level of 0.10 mg/kg. Only for this analysis we have weighed in 5 g instead of 15 g which is normal for fruit and vegetables. This sample is wetted with 10 ml water, stand for 2 hours, and extracted. When you only weigh in 5 g of sample the theoretical value of the sample isn't 0.1 mg/kg but 0.3 mg/kg. The recovery value which was found was 0.074 mg/kg. When you calculate the recovery of the sample the recovery isn't (0.074/0.1)*100= 74 %, but (0.074/0.3)*100=24.7 %. We have to correct the measured value for recovery 0.0164/0.247=0.0665 New z-score is about -1.6. The sample is extracted and analyzed again. The new value is 0.062 mg/kg. This is equal to the first analysis. Reason for the bad z-score is mistake in the recovery. **NOTES OF THE ORGANIZERS:** Chlorothalonil is highly susceptible to degradation. Letting the sample soak with water for 2h surely contributed to the losses. Experiments by the Organizer have confirmed this. Soaking with acidified water minimized degradation.	B, I
123	-3.04	(yes)	the spiked blanc lentils with chloorthalonil have recovery is within the range 70 – 120 %. The possible reason is degradation of chlorthalonill in the sample after storage by 4 °C for some days.	J
84	-2.85	no	–	–

Appendix 8 (cont.) Possible reasons for poor performance (ordered by z-scores)

A: Technical problems with measurement instrumentation
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F: Error in the evaluation/interpretation of measurement data
G: Use of inappropriate procedure
H: Reporting level to close to assigned value
I: No or inappropriate correction for recovery
J: Inappropriate storage of sample
K: Transcription error
L: Cross contamination

Chlorothalonil Assigned value: 0.104 mg/kg; possible assigned value: 0.122 mg/kg
**z-scores were calculated based on the z-scores calculated using the assigned value given in the preliminary report, which was based on the median*

LabCode	z-score*	Source of error localized?	Reason / Remarks	
62	-2.08	yes	Our laboratory does not have an experience in the analysis of lentils and other dry pulses. The method that was used in EUPT-SRM7 (EN 12393 with ethyl acetate extraction) is not suitable for analyzing chlorothalonil despite acceptable results of recovery experiments. Further investigations showed that ethyl acetate was not good enough to extract all residue of chlorothalonil from lentils sample.	D, G
90	-2.07	(yes)	1) no experience with lentils 2) using organic wheat als blank for matrix mached calibration (different matrix-effect) as lentils 3) non recovery corrected (75 %) **NOTES OF THE ORGANIZERS:** See notes 1) and 2) under lab 107	C, D, I
6	2.62	(yes)	we analysed it with the recommended method (QuEChERS adding sulphuric acid). However we also analysed it with the simple QuEChERS, without adding sulphuric acid and we had found 0.122 mg/kg which would produce z = 0.73! We are therefore interested to see how other lab analysed it. **NOTES OF THE ORGANIZERS:** As the preliminary "assigned value" for chlorothalonil is derived from the entire population of results (including those that were produced by labs that have not acidified during the extraction/partitioning step and those that have applied cleanup with PSA it is likely that the real assigned value is higher. This has surely contributed to the strongly positive z-score	–
20	3.00	no	The result was observed using matrix calibration. This means the calibration samples were spiked with chlorothalonil before the extraction of the analytes. When the samples were quantified using matrix-matched calibration, a concentration value of 0.099 mg/kg resulted, which is close to the assigned value. In this case, however, recovery samples produced by spiking the blank material provided by the EURL for this PT and evaluated in the same batch as the PT test material showed a recovery of only 51 %. A recovery correction using this figure would lead to a concentration of 0.194 mg/kg of chlorothalonil. The use of ethylacetate instead of acetonitrile as extraction solvent delivers very similar results.	–
109	3.46	no	Using extrapolation of our low recovery results to calibration curve in method applicable for fresh vegetables (Mini - Luke Method).	I
46	3.50	no	The method used is the EURL-SRM (modified QuEChERS-Method) in GC-MS/MS, and no reason for the high z-score could be found. **NOTES OF THE ORGANIZERS:** See note under lab 6	–
89	6.12	no	We checked our calculations, standard solutions (were freshly prepared) etc. and were not able to find any inconsistencies	–

Appendix 8 (cont.) Possible reasons for poor performance

Cyromazine Assigned value: 0.351 mg/kg; possible assigned value: 0.380 mg/kg, 0.395 mg/kg

**z-scores were calculated based on the z-scores calculated using the assigned value given in the preliminary report, which was based on the median*

LabCode	z-score*	Source of error localized?	Reason / Remarks	
31	-3.77 (FN)	(yes)	QuEChERS method applied for the sample preparation was not a suitable one. Better results were obtained using SweET method.	G
29	-3.60	no	We have checked our standard solution and calculations but can´t find anything wrong. We have no experience of the substance in the past and it is not included in our method.	D
79	-3.11	(yes)	Results were not corrected for recovery (65 %).	I
28	-2.77	no	validation data of different matrices show recovery under 70 %, different recoveries but all stable appr. 30 %, no corrective action **NOTES OF THE ORGANIZERS:** The lab reported a recovery of 26 % and did not correct for recovery. Using a procedure that corrects for recovery, e.g. standard additions to sample portions or the use of isotope labeled cyromazine as ISTD would have resulted in an acceptable z-score	I
17	-2.53	(yes)	For both compounds low recovery figures were obtained with the QuEChERS-Method with acidification (pH = 5). If we had reported the recovery-corrected concentrations as quantitative results (for Cyromazin 0.339 mg/kg and for Fenbutatin Oxide 0.188 mg/kg), we would have had acceptable z-scores.	I
6	-2.35	no	We supposed the QuEChERS method applied for the sample preparation was not a suitable method.	G
89	-2.21	no	We checked our calculations, standard solutions (were freshly prepared) etc. and were not able to find any inconsistencies	–
9	2.23	(yes)	no experience with the commodity "lentils" and ingeneral only very little experience with pesticides requiring single methods.	D
13	2.33	(yes)	we encounter difficulties with cyromazine extraction, doping efficiency achieved in the matrix of the sample was 21 %, performance was taken into account in the calculation. Such a performance involved in the calculation leads to high variability in the final result, a recovery of 22 % would have allowed us to have a satisfactory result.	I
11	2.38	no	Actually we do not know exactly the reason for bad performance. We looked more detailed the results of analysis. We made quantization on 2 different way: -with standard addition in the sample and '-from calibration curve in blank matrix. We got the same result from standard addition where recovery was included and from calibration curve with correction for recovery. Specially in case of analysis of cyromazin we observe in longer period of time that we have lower values for recovery between 50-70 % in different matrixes- so it was the reason for correction. When we got the results we saw that values without correction for recovery measurements would be correct. Determinated recovery from 4 measurements on different calibration levels was 60 % - for which we assume that is quite OK regarding measurements in longer period of time. After getting the results we repeat analysis. Determinated values for cyromazin was 0.44 mg/kg and determinated recovery from 4 parallels were 92 %. Resume of all - we should be carful with correction of recovery, we should do more parallels to get values of recovery-in situation of real sample is that more feasible because in this case we have more available sample.	I

Appendix 8 (cont.) **Possible reasons for poor performance** (ordered by z-scores)

A: Technical problems with measurement instrumentation
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of analytical standard
F: Error in the evaluation/interpretation of measurement data
G: Use of inappropriate procedure
H: Reporting level to close to assigned value
I: No or inappropriate correction for recovery
J: Inappropriate storage of sample
K: Transcription error
L: Cross contamination

Dithiocarbamates (sum) expr. as CS_2 Assigned value: 0.615 mg/kg				
LabCode	z-score	Source of error localized?	Reason / Remarks	
10	-3.68 (FN)	yes	The tip of gas inlet tube was blocked by lentils powder, therefore the carrier gas nitrogen couldn't take CS2 to absorption tubes with colour reagent. The amount of lentils powder was insufficient for another experiment.	B
118	-3.68 (FN)	yes	problems with the reducing agent (SnCl2) - no CS2 was formed during derivatazation	B
108	-3.68 (FN)	yes	Error in Calculation of LoQ	H
31	-2.00	(yes)	Method according to Keppel is not very good for low levels	G
96	2.03	(yes)	"The analysis of the sample has been repeated in three different days, at least 2 replicates in each day. Recoveries have been carried out also with the samples, 3 replicates each time. The recoveries were lower than 70 % and not consistent from day to day allthough the repeatability within the day was less than 20 %. The reason for that was that the samples could not been extracted in the same way as the water bath used was not a shaking water bath and the sample could not been mixed well with the hydrolysis reagent (sample stucked to the cap). For the calculation of the final result the result was corrected using the lower recovery achieved instead of the average recovery which would have given result with z score < 2."	B, G
104	2.45	(yes)	"We performed the analyses by gas chromatography with headspace. Analyses were performed several times with a recovery experiment (blank lentil sample spiked). The results were the following: 0.79 mg/kg and 1.0 mg/kg (this result was sent for the test). The quantification was performed with a matrix-matched calibration; the control sample provided presented no interference at retention time of carbone disulfide. So we didn't think our result would be too high. Another analysis was performed after receipt of preliminary report; the result was 0.83 mg/kg (with matrix-match calibration). So with these different results, we confirm a mean result higher than the reference value. However, we calculated also the dithiocarbamates level in the lentil sample with standard solutions in solvent instead of matrix. The level found was 0.59 mg/kg (instead of 0.83 mg/kg), value near the reference value. It seems to have a matrix effect. Dou you have any information about calibration of the other laboratories?"	–
14	3.10	yes	We found that unsatisfactory result for dithiocarbamates came from incorrect concentration of CS2 in our calibration standard. Due to the limited time reasons fresh standard solution was not prepared and „old" one was used.	E
116	3.55	yes	Error in quantification! Using the correct method 0.747 ppm was obteined.	F

Appendix 8 (cont.) Possible reasons for poor performance

Dithiocarbamates (sum) expr. as CS_2 Assigned value: 0.615 mg/kg				
LabCode	z-score	Source of error localized?	Reason / Remarks	
27	4.00	no	"No reason found sofar (no error in calcualtion or analysis. Recovery rate for the PT was 78 %. For the sample preparation iso-octane was added firstly and followed by hydorlyzing reagent to avoid loosing of CS2 released.)"	–
37	4.90	yes	The reason for poor performance for dithiocarbamates was CS2 solution with expired date. The purchasing of new CS2 solution was delayed and in the EUPT we shall use old standard solution.	E

Ethephon Assigned value: 0.210 mg/kg				
LabCode	z-score	Source of error localized?	Reason / Remarks	
32	-3.18	yes	After several tests, we can confirm that the extraction step is problematic for lentils. So an agitation mode of extraction works for fruits but lentils require an ultra-turrax extraction. With doing that, the concentration found (43 ppb by agitation) rises to 153 ppb (Ultra-turrax).	G
13	8.00	yes	we made a calculation mistake, on the spreadsheet technician reported a concentration erroneous. Our really result for ethephon in the sample was 0.29 mg/kg.	K

Fenbutatin oxide Assigned value: 0.175mg/kg; possible assigned value: 0.214 mg/kg **z-scores were calculated based on the z-scores calculated using the assigned value given in the preliminary report, which was based on the median*				
LabCode	z-score*	Source of error localized?	Reason / Remarks	
88	-3.20		HPLC used with norm-conditions, usually recovery is near 70 %, in dry Lentils recovery is ca. 20 %. **NOTES OF THE ORGANIZERS:** : Acidification is necessary to quantitatively extract fenbutatin oxide from lentils.	G
84	-3.13		problems during extraction; due to soaking of the test material during extraktion it was not possible to get enough from acetonitril phase for further analysis in some cases; poor reproducibility of results. **NOTES OF THE ORGANIZERS:** : See note for lab 88.	G
10	-3.04	yes	The experiment with organotin compounds had be carried out in acidic condition. The HPLC column was not the most appropriate for this experiment.	G
17	-2.97	(yes)	For both compounds low recovery figures were obtained with the QuEChERS-Method with acidification (pH = 5). If we had reported the recovery-corrected concentrations as quantitative results (for Cyromazin 0.339 mg/kg and for Fenbutatin Oxide 0.188 mg/kg), we would have had acceptable z-scores	G, I
66	-2.41	yes	Now we have found the source of this error. Due to a defective septum of the vial of stock solution there was a loss of solvent, so that the concentration of the solution was too high. We used this solution to prepare the calibration solutions and so our result became too low. With a new stock solution we obtained in a further examination of the sample the result 0.124 mg fenbutatinoxid/kg. Some time before the proficiency test we had checked the quality of our stock solutions, but then the septum must have been misplaced. It's a pity! Next time we will do it better.	E
32	-2.13	(yes)	New molecule added in the scope. Clearly recovery problem in the dry lentils	D

Appendix 8 (cont.) **Possible reasons for poor performance** (ordered by z-scores)

A: Technical problems with measurement instrumentation
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of analytical standard
F: Error in the evaluation/interpretation of measurement data
G: Use of inappropriate procedure
H: Reporting level to close to assigned value
I: No or inappropriate correction for recovery
J: Inappropriate storage of sample
K: Transcription error
L: Cross contamination

Fenbutatin oxide Assigned value: 0.175mg/kg; possible assigned value: 0.214 mg/kg

**z-scores were calculated based on the z-scores calculated using the assigned value given in the preliminary report, which was based on the median*

LabCode	z-score*	Source of error localized?	Reason / Remarks	
130	-2.02		Possibilities: The lab result was inferior to the conventional true value, so, 1) our standard was more concentrated, 2) the sample was a concentration inferior than the "true" value, 3) degradation of pesticide or 4) normal distribution not adequate. Real possibilities: H1: Human error. On volumetric steps during preparation of standard solution (it is allays possible). H2: Normal model used by organization is not adequate Grubbs test doesn't identify outliers Shapiro-Wilk test shows that distribution is not normal (P = 0.016; W = 0.936). RSD of distribution is too high (66 %). We think that organization shouldn't use the RSD of 25 % for this pesticide. H3: The result would be corrected by the recovery as our recovery was less than 50 %. If we have used a recovery factor, the final result would be 0.087:0.496 = 0.175 and z-score would be (0.175-0.181)/(0.25*0.181) = -0.13 (satisfactory). [In our opinion results corrected by recovery and without recovery should be treated separately] **NOTES OF THE ORGANIZERS:** As indicated by the participant the FFP-RSD of 25 % is not applicable in this case due to the very broad distribution of results (Qn-RSD = 58.2 %) and the associated uncertainty of the assigned value. The preliminary assigned value any z-scores in the preliminary report or this final report are for information only. Please note that when correction of results for recovery is considered the possible assigned value increases from 0.175 to 0.214.	I
28	2.61	no	result calculated against derivatization reagent with seperate test method (organotin method), result of multimethod QuEChERS was 0.110 mg/kg with 30 % recovery, so results are valid; result in the near of spiking level, no corrective action	–
20	2.99	no	Using matrix-matched calibration 0.161 mg/kg (close to the assigned value of 0.175 mg/kg) were determined with recoveries < 70 %. With recovery correction 0.236 mg/kg were determined. In addition the samples were quantified using standard addition leading to a value of 0.306 mg/kg. Further investigations yielded identical results. Therefore the result obtained by standard addition was reported.	–
12	3.11	no	We had high matrix effects and low recovery; therefore we used the recovery in the calculation. In this case (lentils) it seems to be better not using the recovery in the calculation. And we did not have experience with Fenbutatin Oxide in lentils.	D

Appendix 8 (cont.) Possible reasons for poor performance

Fenbutatin oxide Assigned value: 0.175mg/kg; possible assigned value: 0.214 mg/kg

**z-scores were calculated based on the z-scores calculated using the assigned value given in the preliminary report, which was based on the median*

LabCode	z-score*	Source of error localized?	Reason / Remarks	
30	3.38	no	This was the first time to analyse fenbutatin oxide. For experiences, we checked the method tree times on both levels 0.1 and 0.5 mg/kg and the recoveries were between 30.8 % and 38,8 %. The sample was processed in 3 parallel and the average was 0.107 mg/kg (RSD: 4 %). Due to very low recoveries, we used correction which coused too high result.	D, I
123	4.00	yes	Error in the calculation due to: 1) the analysed product is outside the scope of fresh fruit and vegetables, 2) for determination of the concentration the standard addition method to the blanc is applied where an incorrect concentration of the standard of fenbutatin oxide is used. The correct determined concentration is 0.35/2= 0.175 mg/kg	D, E
1	4.89	yes	due to contamination of laboratory water/appliance used in our analytical method, the result for fenbutatin oxide was significantly overestimated (0.389 mg/kg). After elimination of this problem, we re-analyzed the sample and we obtain new result: 0.212 mg/kg	L
89	7.59	no	We checked our calculations, standard solutions (were freshly prepared) etc. and were not able to find any inconsistencies	–
2	8.57	no	After receiving the deviating Z-score, the following actions were done: 1) Going through the raw data/calculations: not errors found 2) In July, new standards were freshly prepared. A repeat recovery test was done using blank lentils. In addition, a sample of grape leaves was included in the set. Both samples were extracted using QuEChERS and our own method which involves addition of 2 ml 1M HCl+15 % NaCl in water to 1 g of sample, and, after 15 min, extraction into 5 ml ethyl acetate (the raw EtAc extract is injected into the LC-MS/MS) The recoveries for both samples, using both methods, were determined at a spike level of 0.1 mg/kg. Matrix-matched calibration. The results were as follows: QuEChERS lentil 33 %, grape leaves 88 %; in-house method: lentils 45 %, grape leaves 76 %. Recoveries in lentils is poor, better in grape leaves. Our in-house method seemed to give somewhat higher recovery for lentils. 3) The EUPT residue-containing lentil sample was re-analysed by standard addition. To portions of the sample 0, 0.5 and 0.75 mg/kg FBTO were added. The 3 samples were analysed and the concentration was calculated (this results in an automated correction for recovery as well as matrix effect). Again this was done using QuEChERS and our in-house method. The extracts were analysed as such and after a 10-fold dilution. The results were as folllows: QuCEhERS (diluted) = 0.481 (0.553); in-house method 0.587 (0.582) mg/kg. These results, obtained using a fresh standard solution, compared good with our initially submitted result of 0.550 mg/kg. Conclusion: Repeated analysis of the lentil sample gave a similar result as previously reported. No obvious error was found. Reason for our deviating high concentration remains unsolved.	G

Glyphosate Assigned value: 0.278 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
84	-3.02	no	–	–
31	-2.86	no	Use of method with FMOC derivatisation with variable recoveries : use of marqued standards in the futur should improve recoveries	G
30	-2.32	(yes)	"Glyphosate was analysed by QuPPe method using isotop-labelled glyphosate internal standard. According to our experience the anion-selective HPLC column (suggested by QuPPe) has very low capacity. We think, the column results difference peaks with stretched peak shape during perform matrix-matched calibration compering to calibrations in pure solvents which results 'normal' shapes. The sensitivity and retention time depends notably on different matrices causing low recoveries and high deviations. Due to stretched shape (long tailing), determination of correct baseline is doubtful. (problem with lentils as matrix)"	
90	-2.01	(yes)	1) no experience with lentils 2) using organic wheat als blank for matrix mached calibration (different matrix-effect) as lentils 3) non recovery corrected (94.2 %) 4) no confirmation performed	D
20	2.63	no	Using matrix-matched calibration 0.942 mg/kg were determined with recoveries > 150 %. Recovery correction leads to 0.620 mg/kg. Additionally the samples were quantified using standard addition leading to a value of 1.37 mg/kg which was reported.	–

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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-SANCO[1] by the four European Union Reference Laboratories (EURLs) for pesticide residues in food and feed. These EUPTs are directed at all National Reference Laboratories (NRLs) and Official Laboratories (OfLs) within the EU Member States. Laboratories outside of this EURL/NRL/OfL-Network[2] may be permitted to participate on a case-by-case basis after consultation with DG-SANCO.

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

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

NRLs are appointed by Member State based on the provisions of Regulation 882/2004/EC, whereas OfLs are laboratories that are actively involved in official controls following Article 26 of Regulation 396/2004/EC (e.g. by conducting pesticide residue analyses within the framework of national and/or EU-controlled programmes).

[1] DG-SANCO = European Commission, Health and Consumer Protection 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

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According to Article 28 (3) of Regulation 396/2005/EC[4], all laboratories analysing samples for the official control of pesticide residues shall participate in the European Union Proficiency Test(s) organised by the European Union. The aim of these EUPTs is to obtain information regarding the quality, accuracy and comparability of the pesticide residue data in food and feed sent to the European Union within the framework of the national control programmes and the co-ordinated multiannual community control programme[5]. Participating laboratories will be provided with an assessment of their analytical performance and the reliability of their data – compared to the other participating laboratories.

EUPT-Panel

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

An **Organising Team** is appointed from the EURL(s) in charge. This team is responsible for all administrative and technical matters concerning the organisation of the PT, e.g. PT-announcement; Test Item production; undertaking the homogeneity and stability tests; packing and shipment of Test Item, as well as the handling and first assessment of participants' results.

Approved by DG SANCO, expert scientists with long-term experience in pesticide residue analysis will be chosen as members of a joint **EUPT-Scientific Committee** (SC). This Committee is made up of the following two subgroups:

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

b) An **Advisory Group** (AG)

The SC's role is to help the organisers make decisions regarding the EUPT design: the selection of pesticides to be included in the Target Pesticide List (see below); the establishment of the Minimum Required Reporting Levels (MRRLs); the evaluation and statistical treatment of the results and the drafting of the protocol and final report. The

[4] 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.

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

QCG has the additional function of supervising the quality of the EUPT and to assist the EURL in confidential aspects such as the choice of the pesticides to be present in the Test Item and the concentration levels at which they should be present in the Test Item.

The EUPT-Organising Team and the EUPT-Scientific Committee (the AG and the QCG) together form the **EUPT-Panel**.

The present EUPT General Protocol was drafted by the EUPT-Panel and was approved by DG-SANCO.

EUPT Participants

All NRLs operating in the same area as the organising EURL are legally obliged to participate in EUPTs - as well as all OfLs whose scope overlaps with that of the EUPT. The four EURLs will be annually issuing and distributing via the EURL website, a joint list of all OfLs that shall participate in all EUPTs to be conducted within a given year. The "list of obliged labs" is to be considered as tentative as it will be only based on information submitted by OfLs concerning their commodity scope and status. The legal obligation of NRLs and OfLs to participate in EUPTs arises from:

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

If necessary the "list of obliged labs" will be updated within the same year to take account of any changes in the lab profiles.

NRLs are responsible for checking whether all relevant OfLs within their network are included in the list of obliged laboratories and whether the contact information is correct.

The NRLs should further make arrangements to urge all relevant OfLs within their network to participate in all EUPT relevant to them.

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

Any OfL not intending to participate in a given EUPT will have to explain to the EURL its reasons for non-participation without prejudice of any legal action taken against it for not

participating. This also applies to initially participating laboratories that do not deliver results.

Official labs from EFTA countries and EU-candidate countries are also welcome to participate in the EUPTs. In special cases, the Organisers, upon consultation with DG-SANCO, will also allow laboratories outside of the EURL/NRL/OfL-Network to participate in EUPTs.

Confidentiality

The proprietor of all EUPT data is DG-SANCO and thus has access to all information.

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

As laid down in Regulation 882/2004, NRLs are responsible for evaluating and improving their own OfL network. For this reason, the EURLs will provide the OfL laboratory codes to their NRLs together with the final report. This will allow NRLs to correlate the laboratories within their network and their performance. Furthermore, the EURLs reserve the right to share EUPT results and codes among themselves: for example, for the purpose of evaluating overall lab performance as requested by DG-SANCO.

Communication

The official language used in all EUPTs is English.

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

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Announcement / Invitation Letter

The announcement of the individual EUPT will be issued at least 3 months before the Test Item is distributed to the laboratories. The announcement will be published on the EURL portal and additionally distributed via e-mail to the NRL/OfL mailing list available to the EURLs. The announcement will contain an invitation letter, details on how to register and where to find additionally-related documents, as well as some preliminary information on the specific protocol such as the tentative calendar, the name of the commodity expected to be used, and the tentative Target Pesticide List.

Target Pesticide List

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

In some cases, that will be clearly marked, results calculated according to the pesticide residue definition may be requested with those residue definitions differing from the legal ones in certain cases.

Specific Protocol

For each EUPT a Specific Protocol will be published at least 2 weeks before the Test Item is distributed to the laboratories. This protocol will contain all the information previously included in the Invitation Letter but in its final version, in addition to information on payment for delivery service and/or participation. It will furthermore include instructions on how to handle the Test Item upon receipt, on how to submit results, and any other relevant information.

General procedures for reporting results

Laboratories are responsible for reporting their results to the Organiser within the stipulated deadlines. Any pesticide that was targeted by a participating laboratory should be reported as “analysed”. Each laboratory must report only one result for each of the analytes detected in the Test Items, using the analytical procedure(s) that they

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would routinely use for each compound for monitoring purposes. The residue levels of the pesticides detected should be expressed in mg/kg and in some cases for products of animal origin in µg/kg fat.

One Test Item is intentionally treated with pesticides and one is not. Both Test Items have to be analysed by the laboratories and any pesticide detected in them shall be reported.

Correction of results for recovery

According to the Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed, (Document SANCO), 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 with good precision), therefore, if residue data are adjusted for recovery, then this must be indicated on the specific field of the ‘reporting result form’. Laboratories are required to report whether their results were adjusted for recovery and, if this was the case, the recovery (as percentage) used should be also reported. No recovery data are required where correction for recovery results automatically from using the ‘standard addition(s)’ approach, or isotopically-labelled internal standards (in both cases with spiking of the Test Item at the beginning of the extraction procedures). In these cases, the laboratories should report the calculation technique used for the results instead of the recovery data.

Methodology information

All laboratories are requested to provide information on the analytical method(s) they have used. 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.

Results evaluation

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

– ***False Positives***

These are results reported above the MRRLs that suggest the presence of pesticides that were listed in the Target Pesticide List, but which 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 pesticide. However, in certain instances, case-by-case decisions by the EUPT-Panel may be necessary.

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

– ***False Negatives***

These are results for pesticides reported by the laboratories as "analysed" but without reporting numerical values although they were used by the Organiser to treat the Test Item and were detected by the Organiser and the majority of the participants that had targeted these specific pesticides, at or above the MRRL. Results reported as <RL (RL= Reporting Limit of the laboratory) will be considered as not detected and will be judged as false negatives. However, 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 not be assigned as this is not statistically justifiable.

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

The "true" concentration (assigned value) will be typically estimated using the median of all the results. In special justifiable cases, the EUPT-Panel may decide to use only part of the population of results to establish the median (e.g. only results with z-scores ≤ 5.0, or by excluding results generated by a method that demonstrably generates significantly biased results, e.g. due to incomplete extraction).

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

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

$$\delta = b_i * \mu_i \qquad \text{with } b_i = 0.25 \text{ (25\% FFP-RSD)}$$

The percentage FFP-RSD is set at 25% based on experience from previous EUPTs[6]. The EUPT-Panel reserves the right to also employ other approaches on a case-by-case basis considering analytical difficulties and experience gained from previous proficiency tests.

– ***z-scores***

This parameter is calculated using the following formula:

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

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

Any z-scores of > 5 will be reported as >5 and where combined z-scores are calculated a value of "5" will be used.

z-Scores will be interpreted in the following way:

$\lvert z \rvert \leq 2$	Acceptable
$2 < \lvert z \rvert \leq 3$	Questionable
$\lvert z \rvert > 3$	Unacceptable

[6] 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.

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

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

z-Scores will not be calculated for any false positive result.

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

The EUPT-Panel will decide whether to classify the laboratories into two groups - A or B. Laboratories that detect a sufficiently high percentage of the pesticides present in the Test Item (e.g. at least 90%) and reported no false positives will have demonstrated 'sufficient scope' and will therefore be classified into Category A. The 90% criterion will be applied following Table 1.

Table 1. No. of pesticides needed to be detected to have sufficient scope.

No. of Pesticides Present in the Sample (N)	90%	No. of Pesticides needed to be detected 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	
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	N - 2
16	14.4	14	
17	15.3	15	
18	16.2	16	
19	17.1	17	
20	18.0	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	

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For evaluation of the overall performance of laboratories within Category A, the Average of the Squared z-Score (AZ^2)[7,8] will be used.

Laboratories within Category B will be ranked according to the total number of pesticides present in the sample. The number of acceptable z-scores achieved will be presented too. The EURL-Panel retains the right to calculate combined z-scores (see below) also for Category B labs, e.g. for informative purposes, provided that a minimum number of results (z-scores) is available.

– ***Combined z-scores***

For evaluation of the overall performance, the Average of the Squared z-Score (AZ^2) will be used. The AZ^2 is calculated as follows:

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

This formula multiplies each z-score by itself and not by an arbitrary number. Based on the AZ^2 achieved, the laboratories are classified as follows:

Formula	Good	Satisfactory	Unsatisfactory
AZ^2	≤ 2	$2 < AZ^2 \leq 3$	$AZ^2 > 3$

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. In the case of EUPT-SRMs, where only few results per lab are available,

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

[8] 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.

the Average of the Absolute z-scores (AAZ) will be calculated for informative purposes, but only for labs within Category A and as long as 5 or more z-scores are available.

Publication of results

The EURLs will publish a preliminary report, containing tentative medians and z-score values for all pesticides present in the test sample, within 2 months from the deadline for result submission.

The Final 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 to discuss the results of all EUPTs organised annually by the EURLs in the running year, the final report may be published up to 8 months after the deadline for results submission.

Certificates of participation

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

Feedback

After the distribution of the final report of an EUPT, participating laboratories will be given the opportunity to give their feedback to the Organiser and make suggestions for future improvements.

Follow-up activities

Laboratories are expected to undertake follow-up activities to trace back to the source of any erroneous or (strongly) deviating results - including all false positives and false negatives, along with results with |z|>2.

Upon request, the laboratory's corresponding NRL, or EURL, are to be informed of the outcome of these traceability activities.

According to instructions by DG-SANCO, 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" will be followed for NRLs.

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.

Laboratory Rights

After the Final Report has been sent, the laboratories will have the right to communicate the nonconformity of their result evaluation in written form. Any detected errors in the preliminary report should also be reported to the Organiser. The Organiser, assisted by the Scientific Committee, will decide upon any re-evaluation and will give a corresponding explanation.

APPENDIX 9: GENERAL PROTOCO (3rd Ed.)

European Union Reference Laboratory for Residues of Pesticides
Pesticides Requiring Single Residue Methods

SPECIFIC PROTOCOL

for the 7th EU Proficiency Test on Pesticides requiring Single Residue Methods EUPT – SRM7 (2012)

(last updated: 08.05.2012)

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-SRM7 is organised by the EU Reference Laboratory for pesticides requiring Single Residue Methods (EURL– SRM) and deals with the analysis of SRM-pesticides in dry lentils. This EUPT 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-SRM7. The commodity "dry lentils" is to be considered as representative for commodities with "high starch and/or protein content and low water and fat content" (see **SANCO document 12495/2011**). A **Tentative List of obliged labs for EUPTs in 2012** has been published in the EURL-website. Obliged labs not intending to participate in this EUPT were requested to state the reasons for non-participation.

Test Items (Test Materials)

This EUPT deals with the analysis of pesticide residues in **dry lentils**.

Participants will receive two bottles containing:

1) ca. 400 g **Spiked-Test Item**, containing spiked pesticides from the **Target Pesticide List**
2) ca. 400 g **Blank-Test Item**, 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 spiked Test Item for sufficient homogeneity as well as for stability under conditions representing sample shipment and storage during the duration of the test. The blank Test Item will be also checked to prove that the target analytes are not contained at any relevant levels. All these tests will be conducted by the EURL-SRM that is ISO 17025 accredited.

Analytical parameters

The Test Item contains several pesticides from the **Target Pesticide List**.
Laboratories should carefully read the Target Pesticides List, where important information about reporting of results, as well as the **Minimum Required Reporting Levels (MRRLs)** is given.
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.
It should not be assumed that only pesticides registered for use on lentils are present in the Test Item.

For practical reasons, the residue definitions listed in the Target Pesticides List, in some cases, do not fully match with the legal ones.

Shipment of Test Items

The Test Materials are planned to be shipped on 23 April, 2012.
Test Material will be shipped frozen and packed in thermo-boxes together with a freeze gel pack. The organisers will aim to ensure that all participating laboratories will receive their shipments on the same day.

Prior to shipment a reminder will be sent to the participating laboratories by e-mail.

Laboratories must make their own arrangements for the receipt of the package. They should inform the Organiser 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.

Instructions on handling of Test Items

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

The Test Material should be mixed thoroughly in its entirety before a portion is taken for analysis.

All participants should use their own routine standard operating procedures for extraction, clean-up and analytical measurement as well as their own reference standards for identification and quantification purposes. Considering the available amount of Test Item, laboratories employing methods requiring large analytical portions are advised to scale them down. As the test material is already milled and sufficiently homogeneous, method sensitivity is the only major factor to consider when deciding about the size of the analytical portion.

The homogeneity tests will be conducted using 2-5 g of Test Item depending on the analyte. As variability increases with decreasing analytical portion size, sufficient homogeneity can only be guaranteed for sample portions that are equal or larger than those employed for the homogeneity test.

Results submission website

Sample receipt acknowledgement, analytical results and method information are to be submitted via the **EUPT-SRM7 Result Submission Website** (**http://thor.dfvf.dk/eupt-SRM7**) that will be **accessible from 24 April 2012 onwards for sub-page 0 and 27 April 2012 onwards for sub-pages 1-3**.

This website also contains a link to specific instructions on how to enter the required data in the various submission forms (sub-pages).

To access the data submission forms participants must use their unique login data (username and password) given in the confirmation e-mails sent to the laboratories upon registration.

The deadline for result submission is 29 May 2012 at 15.00 CET

- Sample Receipt and Acceptance (Sub-Page 0)

Once the laboratory has received the Test Items it must report to the organiser, via the **EUPT-SRM7 Result Submission Website** (sub-page 0) the date of receipt, the condition of the Test Item, and its acceptance. The deadline for acceptance is the 26 April 2012. If a laboratory does not respond by this deadline the Organisers will assume that the Test Items have been received and accepted. If any participants have not received the Test Items by the 27 April at noon, they must inform the Organiser immediately by e-mail (**EUPT-SRM@cvuas.bwl.de**), so that a new shipment can be managed.

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

To report their results, laboratories must access the **EUPT-SRM7 Result Submission Website**.

All results must be reported on the above website by the 29.May 2012 at 15:00 (3 p.m.) CET, at the latest. The website will not be accessible after this deadline and all results submitted afterwards will be not included in the statistical treatment or in the final report.

Before entering the results, please study the **Target Pesticide List**. The residue definitions are not given on the Result Submission Website carefully.

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 normal lab 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" 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 Pesticides List determined in the blank (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.

- **"Is your result recovery-corrected?":** Please specify, via dropdown-menu, whether the reported result was recovery-corrected and the of recovery-correction approach used.

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

Additional information on how each recovery figure was derived will be asked in separate fields.

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

In **sub-page 3 within of** the "**EUPT-SRM7 Result Submission Website** all laboratories must provide information on the analytical method(s) employed to analyze the pesticides for which results where reported.

The laboratories are urged to thoroughly fill-in this important information in order to minimize the administrative burden of collecting this information a posteriori.

- Reporting missing information after result submission deadline (Sub-page 4)

In case of false negative results the affected laboratories will be asked to provide details on the methodology used after the deadline for result submission. This can be done by accessing sub-page 4 within the **EUPT-SRM7 Result Submission Website**.
The dates sub-page 4 will be accessible will be announced in due time. Where sub-page 4 is empty when accessed, no further information is needed from you the lab.
If no sufficient information on the methodology used is provided, the Organiser reserves the right not to accept the analytical results reported by the participant.

Follow-up actions

According to instructions by the Commission, 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 for NRLs.

Documents

All documents relating to EUPT–SRM7 can be found in the **EURL-Document Repository (CIRCA/FIS-VL).**
Links to the documents can be found in the **EUPT-SRM7 Website.**
For further information please contact the organizers **EUPT-SRM@cvuas.bwl.de**

Participation fees and payment details

To cover the costs of production, handling and shipment of the Test Materials the following participation fees will be charged to each participating laboratories,:

- OfLs (including NRLs) from EU countries, EU-candidate countries and EFTA countries: 175 €
- Labs based in third countries: 250 €

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

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

To facilitate tracking of money transfer mind to include your special payee identification text (= invoice number) as shown in the invoice. **Payments without this identification text may not be considered as paid!**

Bank Details:

Bank account holder:	**CVUA Stuttgart**
Bank Name :	**Baden Wuerttembergische Bank**
IBAN:	**DE 72 6005 0101 7469 5341 03**
BIC/SWIFT:	**SOLADEST**
Payee identification text:	**See invoice** (VERY IMPORTANT!)

Calendar

(see also http://www.crl-pesticides.eu/library/docs/srm/EUPT_SRM7_Calendar.pdf)

Activity	Who ?	Dates
Opening of the **EUPT-SRM7 Website** with links to all relevant documents and to the **EUPT-General Protocol**	EURL-SRM	Jan 2012
Distribution of "**EUPT-SRM7-Calendar**"	EURL-SRM	Jan 2012
Distribution of "**Target Pesticides List**",	EURL-SRM	Jan 2012
Distribution of "**Announcement/Invitation-Letter**"	EURL-SRM	Jan 2012
Accessibility of "**EUPT-Registration Website**" To **sign up for EUPT-SRM7** and to **explain the reasons for non-participation**	**- Obliged OfLs from EU-MSs** (regardless if not participating) - **OfLs from EFTA countries** & **EU-candidate countries**	**8 Feb – 27 Feb 2012**
Distribution of "**EUPT-SRM7-Specific Protocol**"	EURL-SRM	Mar 2012
Preparation of EUPT-SRM7-Test Material	EURL-SRM	Oct 2011 - Mar 2012 (preliminary tests)
		Mar 2012 (Spiking / Homogenization)
Homogeneity tests	EURL-SRM	Mar-Apr 2012
Stability tests	EURL-SRM	Apr-May 2012
Distribution of EUPT-SRM7 Test Material (Reminder to the labs about upcoming shipment)	EURL-SRM	**23 Apr 2012**
Deadline for Receipt and Acceptance of Test Material: Online Submission of Form 0 (sub-page 0)	**Participating Labs**	**within 48 hr of receipt**
Activation of "**Result Submission Website!**	EURL-SRM	**27 Apr 2012**
Deadline for Result Submission **Pesticide scope, Results, Method Information** Submission of Form 1 – 3 (sub-pages 1 – 3)	**Participating Labs**	**29 May 2012 (at 15:00 CET)**
EUPT Evaluation Meeting	EUPT-Scientific Committee, DG-SANCO	Jul 2012
Preliminary Report (only compilation of results)	EURL-SRM	Jul 2012
Final Report	EURL-SRM	Nov 2012

Contact information

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Dr. Sonja Masselter	AGES, Austria
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Quality Control Group

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Stewart Reynolds	FERA, York, United Kingdom

TARGET PESTICIDE LIST

for the EUPT – SRM7 2012

(last updated: 20.04.2012)

Pesticides/Residue Definitions	In MACP 2012	MRRL (mg/kg)
2.4-D (free acid)	Yes	0.02
Avermectin B1a	Yes	0.02
Bromide ion	Yes	3
Chlormequat (cation)	Yes	0.02
Chlorothalonil	Yes	0.01
Cyromazine	Yes	0.02
Dichlorprop (2,4-DP) including Dichlorprop-P (free acids)		0.02
Dithiocarbamates (incl. maneb, mancozeb, metiram, propineb, thiram and ziram) expr. as CS2	Yes	0.05
Ethephon	Yes	0.02
Fenbutatin Oxide	Yes	0.02
Fluazifop including Fluazifop-P (free acids)	Yes	0.02
Glyphosate	Yes	0.05
Haloxyfop including Haloxyfop-R (free acids)	Yes	0.02
MCPA (free acid)		0.02
Mepiquat (cation)	Yes	0.02
Propamocarb	Yes	0.02

MACP= EU Multiannual Community Control Program

Notes:

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

The EUPT-SRM7 Team

EU Reference Laboratory for pesticides requiring Single Residue Methods (EURL-SRM)
c/o CVUA Stuttgart, Schaflandstr. 3/2, DE-70736 Fellbach

APPENDIX 11: TARGET PESTICIDE LIST

Picture on the book cover: www.clipdealer.com (95661_photo_jpg_m.jpg)

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