EU PROFICIENCY TEST
Residues of Pentachlorophenol (PCP) in guar gum samples (EUPT-PCP), 2008

Final Report

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EUROPEAN COMMISSION PROFICIENCY TEST ON PENTACHLOROPHENOL IN GUAR GUM SAMPLES, (EUPT-PCP, 2008)

INTRODUCTION

Guar gum is an edible thickening agent extracted from guar beans. Food grade guar gum powder is authorized as a food additive and used as a thickening, emulsifying, binding and gelling agent in a very wide range of processed foods. Industrial grade guar gum powder is used in various non-food sectors. India accounts for approximately 80 % of the world's total production of guar beans.

In July 2007, a case of contamination by dioxins and pentachlorophenol (PCP) in guar gum originating from India was found. The contamination levels of dioxins and PCP in certain batches of guar gum were very high (about 1000 times the level that might be considered as normal background contamination). In the interest of a uniform approach within the EU, the Commission services derived the following reference points of action for unacceptably high levels of dioxins and pentachlorophenol in guar gum:

> **Pentachlorophenol:** Any level of pentachlorophenol in guar gum exceeding 0.01 mg/kg, taking into account measurement uncertainty, is to be considered as unacceptable.
>
> **Dioxins:** Levels of dioxins (PCDD/F) in guar gum should be lower than 0.75 pg WHO-PCDD/F-TEQ /g product (or 0.75 ng WHO-PCDD/F-TEQ /kg product). Levels higher than 0.75 pg WHO-PCDD/F-TEQ /g product are to be considered as unacceptable.

A comparison of the analytical results for these contaminants generated by different laboratories analyzing the same samples, raised questions regarding the reliability of the applied methods. Therefore it was decided that a comparative exercise involving the determination of dioxins (PCDD/F), PCBs (dioxin-like PCBs and indicator PCBs) and pentachlorophenol (PCP) in guar gum samples should be organised. This PT was co-organised by the CRL for Dioxins in Food and Feed and the CRL for pesticide residue analysis using single residue methods (CRL-SRM).

Two samples of guar gum were sent for analysis covering very roughly the range of PCP-levels encountered in real samples. It is intended to make these two samples available for use as proficiency-test-checked reference materials.

This study was open for participation of:

- **NRLs and official laboratories (OFLs) for dioxins and PCBs** in food and feed
- **NRLs and official laboratories (OFLs) for pesticides** performing analyses of PCP by multi or single residue methods in food or feed that were prompted to determine only this contaminant.

- **Private laboratories** analyzing dioxins and dioxin-like PCBs, only, or dioxins, PCBs and PCP (This means that the PT was only open for private labs regularly analysing samples for at least dioxins and PCBs).

For official pesticide laboratories this PT was to be considered as an additional test complementing the annual EUPT on Single Residue Methods and aiming to help laboratories to check their performance.

1. TEST MATERIALS

1.1 Preparation of the test material

Three different 75 kg batches of guar gum originating from India and contained in unopened 25 kg bags, were provided to the CRL for dioxins and PCBs by the Swiss official food control authorities for scientific use. Two of the batches were selected for the PT as they were considered to represent both low and highly contaminated samples.

- **Sample A** (No 0801-A-xxx) reflected the lower end of the range of contamination.
- **Sample B** (No 0801-B-xxx) had clearly elevated levels of PCP and dioxins.

The material was used as such, without any spiking. Each of the batches was mixed for 10 min using a compulsory mixer. The test materials were then bottled in PE-containers for shipment. All sub-samples of the test materials were individually numbered and stored at room temperature prior to their distribution.

No 'blank' material was provided.

1.2 Analytical Methods

Before this proficiency test the CRL-SRM has published a method for the determination of PCP residues in guar gum samples on the CRL-portal (www.crl-pesticides.eu) that the participating laboratories could use. This method was a modified version of the well-known QuEChERS[1] method involving addition of acetonitrile prior to the addition of water, extraction via shaking, and liquid-liquid partitioning following the addition of a citrate-buffer-containing salt mixture. Determinative analysis was accomplished by LC-MS/MS. This particular method was used for the homogeneity and stability tests.

Laboratories participating at the PT were free to use any method of their choice but were asked to submit details about their methods in the result submission sheet.

1.3 Homogeneity test

Ten bottles of each sample (A and B) were randomly chosen and analyses were performed on duplicate portions taken from each bottle. Extractions and LC-MS/MS analyses were run in random order. The quantification was performed using a 6-point calibration curve constructed from matrix-matched standards.

The statistical evaluation was performed according to the International Harmonized Protocol published by IUPAC, ISO and AOAC[2]. The individual residue data from the homogeneity tests,

[1] EN-15662; Foods of plant origin - Determination of pesticide residues using GC-MS and/or LC-MS(/MS) following acetonitrile extraction/partitioning and cleanup by dispersive SPE - QuEChERS-method

[2] Thompson M., Ellison S. L. R. and Wood R., The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories. Pure & Appl Chem 78, 145-196 (2006.)

as well as the results of the statistical analyses, are given in Table 1. The acceptance criteria for the test material to be sufficiently homogenous for the proficiency test was that $S_s/\sigma > 0.3$, with S_s being the between sampling standard deviation and σ = RSD (25 %) x the mean concentration of each sample.

Both samples passed the homogeneity test and the test material was considered to be sufficiently homogenous and suitable for the use in the EUPT-PCP.

Table 1: Homogeneity data for both samples (A and B) and statistical evaluation

	Sample A (using 1 g)		**Sample B (using 1 g)**	
Sample	**Portion 1 mg/kg**	**Portion 2 mg/kg**	**Portion 1 mg/kg**	**Portion 2 mg/kg**
1	0.161	0.158	16.1	16.3
2	0.153	0.155	14.9	15.7
3	0.162	0.165	15.4	14.5
4	0.163	0.159	14.9	15.3
5	0.155	0.156	15.4	15.4
6	0.152	0.151	16.2	15.9
7	0.159	0.146	15.3	15.2
8	0.156	0.153	15.5	16.3
9	0.154	0.160	15.2	14.9
10	0.156	0.153	15.3	16.3
Mean in mg/kg	**0.156**		**15.490**	
S_s/σ	**0.12**		**0.11**	
Pass/Fail	**Pass**		**Pass**	

1.4 Stability test

The stability test involved analyses on two occasions as follows:

Day 1: shortly before shipment of test materials, February 4th 2008

Day 2: after the deadline for result submission, May 22nd 2008

Two different storage conditions were compared, room temperature and -18°C. In both cases the analyses were performed on 5 randomly chosen samples employing duplicate measurements.

The individual results for both samples are given in Table 2.

The stability test showed that that PCP-levels remained sufficiently stable in both samples over the entire period of the test regardless of storage in the freezer or at ambient temperature.

Table 2: Stability test data for both samples (A and B) and statistical evaluation

	Sample A	Sample B
Day 1 (mean in mg/kg)	0.170	14.2
-18℃		
Day 2 (mean in mg/kg)	0.162	14.4
% Deviation	**- 5 %**	**+ 1 %**
Room Temperature		
Day 2 (mean in mg/kg)	0.162	14.2
% Deviation	**- 5 %**	**+/- 0 %**
Pass/Fail	**Pass**	**Pass**

1.5 Organisational details

1.5.1 Access of documents and confidentiality

Participants were able to register for this EUPT by downloading a registration form the CRL-web-portal and sending it to the CRL for Dioxins and PCBs in Food and Feed. There they were assigned a laboratory code and received further documents via email.

1.5.2 Submission of results

A data-reporting sheet based on Excel was developed and sent to the participants. The participants were asked to fill-in their results and method information, and then send the file back to the Organizers via email by the stipulated deadline (May 16th 2008).

1.5.3 Distribution of the test material

Shipment of the test material to the participants was conducted by the CRL for Dioxins and PCBs in Food and Feed on February 15th 2008. Each participant received two individually numbered bottles (A and B), each containing 250 g of test material with two different concentrations of PCP. A covering letter with instructions to the participants, including a warning of possible cross-contamination in the laboratory resulting from the elevated levels in sample B, was also included. Further instructions and reports were provided by e-mail and via the CRL-website.

2. STATISTICAL METHODS

2.1 False positives and false negatives

2.1.1 False positives

Due to the nature of this proficiency test no false positive results could be reported.

2.1.2 False negatives

Results reported as 'ND' (not detected) by the laboratories would have been considered as false negatives if exceeding the MRRL and the laboratory reporting limit (RL).

2.2 Estimation of the assigned values

In accordance to the International Harmonized Protocol published by IUPAC, ISO and AOAC, the assigned (consensus) value was estimated as the median of the participants' results. Despite having significantly different distributions of the values reported by laboratories using the PCP-method published by the CRL and those values reported by laboratories using other methods (see Figure 1 and Figure 2), the Scientific Committee and the Organizer agreed, to use the median of the entire population of results as the assigned value.

2.3 Fixed target standard deviation

The Organizer and the Scientific Committee decided to apply the fixed fit-for-purpose relative standard deviation (FFP RSD) of 25 % based on previous experience from EU proficiency tests on pesticide residues in food. The target standard deviation (σ) was calculated by multiplying this FFP RSD by the assigned value. In addition, the robust Qn standard deviation was calculated as a measure for the broadness of the result distribution.

2.4 Z-scores

As main criteria for assessing the results, z-score values were applied using the following approach:

1. Calculation of consensus median
2. Conversion of participants' results into z-scores

$$z = (x - x_a) / \sigma_p$$

x_a: assigned values
x: participants result
σ_p: target standard deviation (FFP-RSD of 25%)

Any z-score values of /z/ > 5 is reported as '+5'. For a FFP RSD value of 25% this resulted in a theoretical z-score-range from -4 to +5.

z-score classification was as follows:

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

3. RESULTS

As can be seen in Table 3, 49 laboratories from 21 different countries (worldwide) registered to participate in this PT, but only 41 laboratories from 16 different countries actually reported PCP-results. As regards the EU-Member States, 44 laboratories from 16 countries (including 9 NRLs for Single Residue Methods) registered for this PT, but only 40 laboratories from 15 countries submitted results. A list of all participating laboratories can be found in Table 9 in the Annex.

Table 3: Participating laboratories by country

Country	Labs registered		Labs sending results		Notes
	All Labs	NRL-SRM	All Labs	NRL-SRM	
AT	1	0	1	0	
BE	2	1	2	1	
CZ	2	0	1	0	
DE	17	1	16	1	
ES	1	0	1	0	
FI	1	0	1	0	
FR	4	0	4	0	
GR	2	1	2	1	
HU	1	0	1	0	
IT	6	1	6	1	
LT	1	1	1	1	
NL	2	1	1	0	
PT	1	0	0	0	
SI	1	1	1	1	
SK	1	1	1	1	
UK	1	1	1	1	
EU SUM	**44**	**9**	**40**	**8**	**From 15 EU-Countries**
AU	1	0	1	0	
CA	1	0	0	0	
IND	1	0	0	0	
TW	1	0	0	0	
US	1	0	0	0	
OVERALL SUM	**49**		**41**		**From 16 Countries**

3.1 Overview

An overview of the results can be seen in Table 4 and a detailed compilation of the results is shown in Table 5. The histograms showing the distribution of the results submitted by the laboratories are presented in Figure 3 and Figure 4 and the histograms showing the corresponding z-scores are presented in Figure 1 and Figure 2, in the Annex.

A compilation of the method details submitted by the labs is listed in Table 10 and Table 11 in the Annex.

3.1.1 False negatives

As was clear from the beginning both samples contained PCP, so no laboratory reported a 'ND'.

3.2 Data Distribution and Assigned Values

The histograms showing the distribution of the laboratory results for both samples can be found in Figure 1 and Figure 2. Looking at the entire population of the results the distribution is very broad with Qn (robust RSD) values being at 46.4 % for sample A and 56.9 % for sample B (see Table 4).

When looking at laboratories using the method published by the CRL, the distribution of the reported PCP-levels is much narrower (Qn values around 25 %) and closer to Gaussian compared to the distribution of the results of the rest of the laboratories with Qn values > 70 %. Nevertheless, the Scientific Committee and the Organizer agreed to still use the entire population of results to calculate the assigned value.

Table 4: Overview of results and comparison of CRL-method with other methods

	All labs			Labs using CRL-method			Labs using other methods		
	No of results	Median mg/kg	Qn %	No of results	Median mg/kg	Qn %	No of results	Median mg/kg	Qn %
Sample A	41	**0.158**	46.4	19	0.165	24.2	22	0.128	73.1
Sample B	40	**13.801**	56.9	18	14.683	27.4	22	7.857	113.8

Table 5: Compilation of results

	NRL-SRM	Sample1			Sample2			
Median mg/kg		0.158			13.801			
Qn %		46.4			56.9			
No. of Results		41			40			
Labcode		**Result mg/kg**	**z-score FFP RSD**	**Ranking**	**Result mg/kg**	**z-score FFP RSD**	**Ranking**	**Notes**
Lab 001		0.224	1.7	27	16.170	0.7	14	
Lab 002		0.187	0.7	18	13.920	0.0	3	
Lab 003	yes	0.181	0.6	15	11.985	-0.5	13	
Lab 004		0.152	-0.2	6	14.996	0.3	10	
Lab 006		0.209	1.3	22	19.481	1.6	21	
Lab 007		0.210	1.3	23	14.762	0.3	9	
Lab 008		0.181	0.6	16	13.802	0.0	1	
Lab 009		0.011	-3.7	36	1.193	-3.7	36	
Lab 012	yes	0.158	0.0	1	16.721	0.8	17	
Lab 013		0.205	1.2	21	21.771	2.3	27	
Lab 014		0.150	-0.2	9	26.900	3.8	37	
Lab 016		0.056	-2.6	31	6.729	-2.0	24	
Lab 019								No results submitted
Lab 020		0.103	-1.4	25	1.430	-3.6	35	

	NRL-SRM	Sample1			Sample2			Notes
Median mg/kg		0.158			13.801			
Qn %		46.4			56.9			
No. of Results		41			40			
Labcode		Result mg/kg	z-score FFP RSD	Ranking	Result mg/kg	z-score FFP RSD	Ranking	
Lab 021	yes	0.050	-2.7	32	5.128	-2.5	29	
Lab 023		0.211	1.3	24	22.160	2.4	28	
Lab 024		0.070	-2.2	29	2.700	-3.2	30	
Lab 026		0.094	-1.6	26	10.184	-1.0	19	
Lab 027								No results submitted
Lab 028		0.630	5.0	39	86.209	5.0	40	
Lab 029								No results submitted
Lab 034	yes	0.021	-3.5	35	1.689	-3.5	33	The lab reported that a dilution factor of 10 was erroneously not used in te calculation of both results. This was reported after the deadline and publication of the preliminary report and could therefore not be accepted.
Lab 035								No results submitted
Lab 036		0.132	-0.7	17	12.900	-0.3	8	
Lab 037		0.358	5.0	38	6.041	-2.2	26	
Lab 038		0.160	0.1	3	16.200	0.7	15	

	NRL-SRM	Sample1			Sample2			Notes
Median mg/kg		0.158			13.801			
Qn %		46.4			56.9			
No. of Results		41			40			
Labcode		Result mg/kg	z-score FFP RSD	Ranking	Result mg/kg	z-score FFP RSD	Ranking	
Lab 039								No results submitted
Lab 040		0.126	-0.8	19	14.604	0.2	7	
Lab 041								No results submitted
Lab 043		0.140	-0.5	14	13.800	0.0	2	
Lab 048		0.010	-3.7	37	1.560	-3.5	34	
Lab 049		0.123	-0.9	20	8.894	-1.4	20	
Lab 051		0.069	-2.3	30	6.820	-2.0	23	
Lab 052		1.390	5.0	41	34.532	5.0	39	
Lab 053	yes							No results submitted
Lab 054	yes	0.155	-0.1	5	2.100	-3.4	31	
Lab 055		0.149	-0.2	10	11.193	-0.8	16	
Lab 057		0.160	0.1	4	10.414	-1.0	18	
Lab 059		0.092	-1.7	28	14.400	0.2	5	
Lab 060		0.032	-3.2	34	1.790	-3.5	32	
Lab 062		0.270	2.8	33	14.600	0.2	6	

	NRL-SRM	Sample1			Sample2			Notes
Median mg/kg		0.158			13.801			
Qn %		46.4			56.9			
No. of Results		41			40			
Labcode		Result mg/kg	z-score FFP RSD	Ranking	Result mg/kg	z-score FFP RSD	Ranking	
Lab 063		0.170	0.3	12	15.300	0.4	11	
Lab 064		0.171	0.3	13	15.300	0.4	12	
Lab 065		0.158	0.0	2	7.599	-1.8	22	
Lab 066	yes	0.148	-0.3	11	21.300	2.2	25	
Lab 067		0.165	0.2	7				Only results for sample1 accepted
Lab 069	yes	0.726	5.0	40	32.955	5.0	38	
Lab 073								No results submitted
Lab 074	yes	0.165	0.2	8	13.543	-0.1	4	

3.3 Assessment of laboratory performance

Z-scores have been calculated by using the FFP RSD of 25 %.

Table 5 above shows a compilation of the individual results, including z-scores, median values and Qn values. Furthermore, the ranking position of each laboratory based on the absolute z-scores achieved is displayed for each sample.

Table 6 shows the distribution of the z-scores as regards their classification. Looking at all laboratories together, the number of unacceptable z-scores (|z| > 3) is very high at 20% for sample A and 28 % for sample B.

Table 6: Distribution of z-score based on their classification

	All Labs			Labs using CRL-method		
	Acceptable |z| < 2	Questionable 2 < |z| < 3	Unacceptable |z| > 3	Acceptable |z| < 2	Questionable 2 < |z| < 3	Unacceptable |z| > 3
Sample A	28 (68 %)	5 (12 %)	8 (20 %)	17 (90 %)	1 (5 %)	1 (5 %)
Sample B	24 (60 %)	5 (13 %)	11 (28 %)	15 (83 %)	2 (11 %)	1 (6 %)

3.4 Analytical methods

Detailed information regarding the methods used by the participants can be found in the Annex in Table 10 and Table 11. As shown in Table 4 roughly 50 % of the submitted results were generated using the CRL-method. The other types of methods used were too diverse to allow any further sub-grouping. When comparing the z-scores obtained using the CRL-method with those obtained by all laboratories it is obvious that the percentage of acceptable z-scores (2 < z < +2) was clearly higher for both samples.

Effect of water-addition: Another interesting aspect concerned the addition of water during analysis. The laboratories were asked to indicate if they had added water in their reporting sheet. Unfortunately, the question placed in the questionnaire in this respect (“Did you add water prior to extraction”) was not precise enough with laboratories adding water after, or at the same time as the extraction solvent, being unsure what to answer. In order to clarify this issue, the laboratories were re-contacted, but unfortunately not all labs responded. Table 7 shows a comparison of the results achieved by laboratories using water to assist extraction against those that did not. Laboratories using the CRL-method were all considered as using water even if they did not explicitly mention it in the questionnaire. Seven laboratories using other methods could not be considered in this method comparison, as they did not answer this question. Although the number of laboratories (8 with 16 results) not adding water is too small to draw definitive conclusions, there does seem to be a trend for result underestimation, which implies that water-addition improves extraction efficiency.

Table 7: Method comparison: Effect of water addition

	Addition of water		No addition of water		All laboratories	
	Sample A	**Sample B**	**Sample A**	**Sample B**	**Sample A**	**Sample B**
No. of labs	23	22	8	8	41	40
Median mg/kg	0.160	14.602	0.097	7.812	0.158	13.801
Qn %	**27.8**	**32.2**	100.1	127.0	46.4	56.9
Acceptable results % (z-score)	**87**	**74**	**50**	**38**	**68**	**60**

Impact of isotopically labelled standards: Roughly 50 % of all laboratories have used an isotopically labelled PCP as internal standard (ISTD). Table 8 shows a comparison of the labs using isotopically labelled PCP against those that did not.

Table 8: Method comparison: Isotopically labelled standard

	Using Isotopically labeled PCP as ISTD		Not using Isotopically labeled PCP as ISTD		All laboratories	
	Sample A	**Sample B**	**Sample A**	**Sample B**	**Sample A**	**Sample B**
No. of labs	20	20	21	20	41	40
Median mg/kg	0.150	11.589	0.165	14.602	0.158	13.801
Qn %	38.6	84.0	60.5	32.2	46.4	56.9
Acceptable results % (z-score)	75	50	62	60	68	60

No clear trend can be observed here. This was to be expected, as it is clear that the use of an isotopically labelled ISTD can compensate for partitioning losses and/or measurement errors, depending at what stage of the procedure it is added, but it cannot compensate for poor extraction efficiency of incurred residues. The influence of the extraction method employed is obviously of much higher importance than the use of isotopically labelled PCP. Roughly one third of the laboratories employing the CRL-method also employed an isotopically labelled PCP as ISTD.

3.5 Conclusions

The results of the proficiency test for PCP in guar gum show a very broad distribution with robust RSD values clearly exceeding the levels typically achieved for pesticide residues in food (Qn=46 % for the low PCP-level, and Qn=57% for the high level). Using the fit-for-purpose RSD of 25%, the percentage of laboratories reporting unacceptable results ($|z| > 3$) were also elevated compared to what is typically observed in pesticide residue PTs (20 % for the low level and 28 % for the high level). This discrepancy is among others surely related to the differences in the extraction methods employed and the lower extraction efficiency of incurred PCP that seems to occur in absence of water.

Well in advance of the PT the CRL developed a simple modified QuEChERS method for the analysis of PCP in guar gum samples. This method was published on the CRL-web-portal. A very high percentage of 90 % (low level) and 83 % (high level) of laboratories using this method, reported acceptable results ($|z| < 2$) with the overall distribution of results being significantly narrower (Qn= 24 % low level, and 27 % high level) compared to the distribution of results from laboratories using other methods (Qn= 73 % low level, and 114 % high level).

4. ACKNOWLEDGEMENTS

The organisers wishes to thank the members of the Scientific Committee for their valuable advice.

5. ANNEX

DISTRIBUTION OF RESULTS

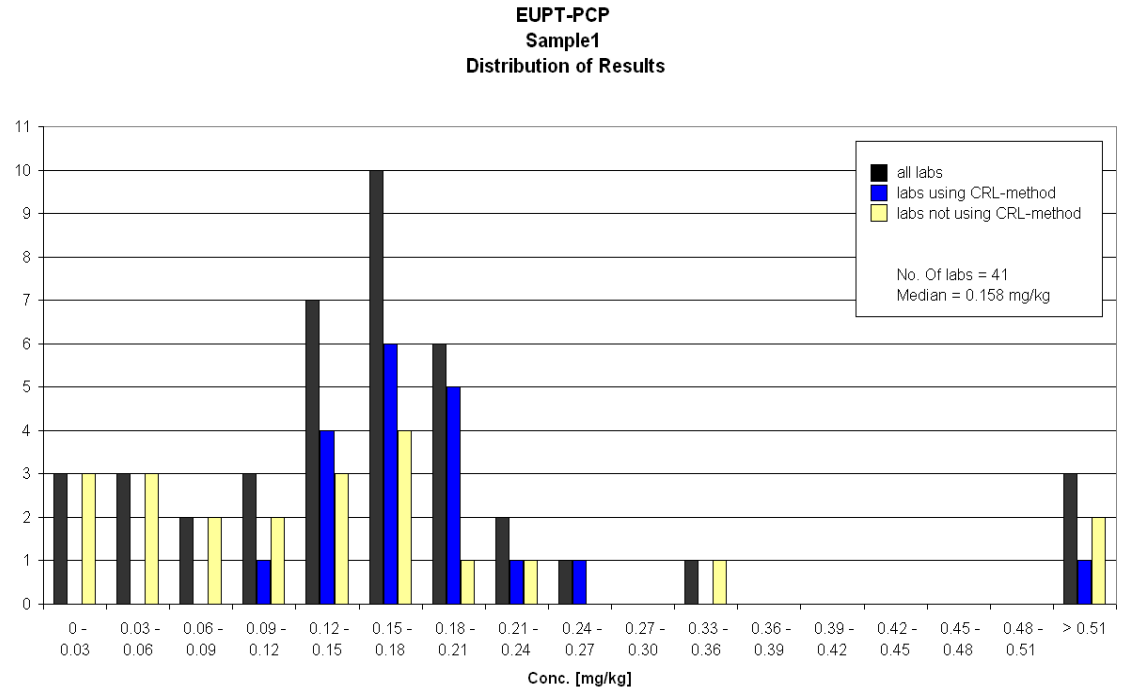

Figure 1: Distribution of results, Sample A

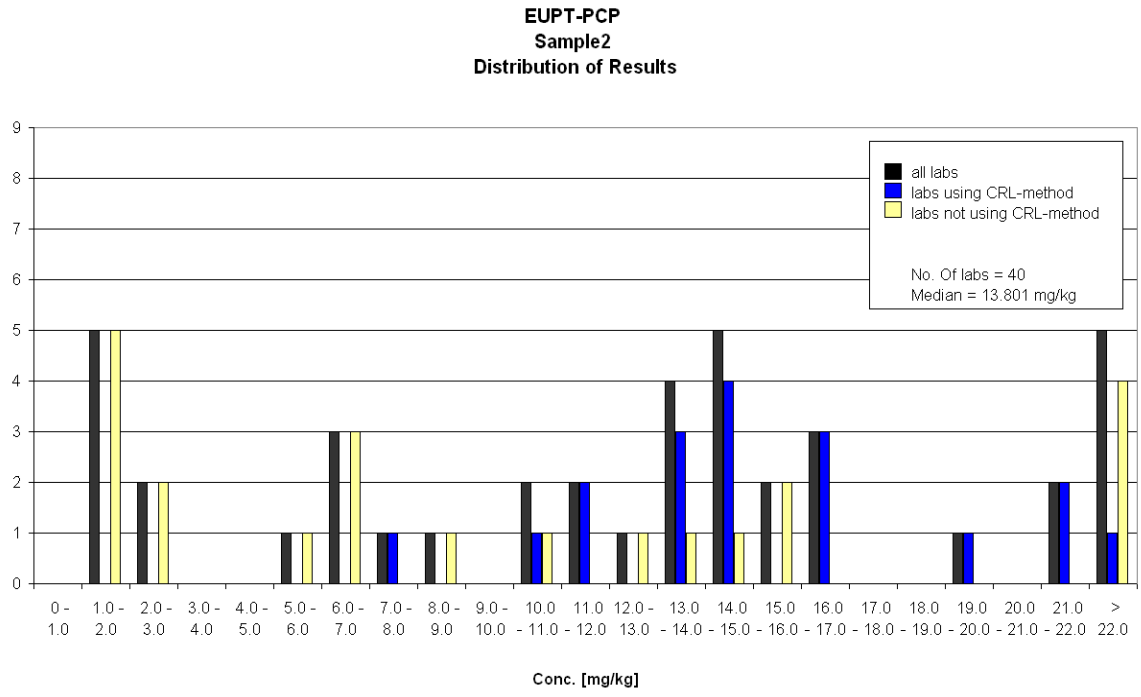

Figure 2: Distribution of results, Sample B

Z-SCORES (FIGURES)

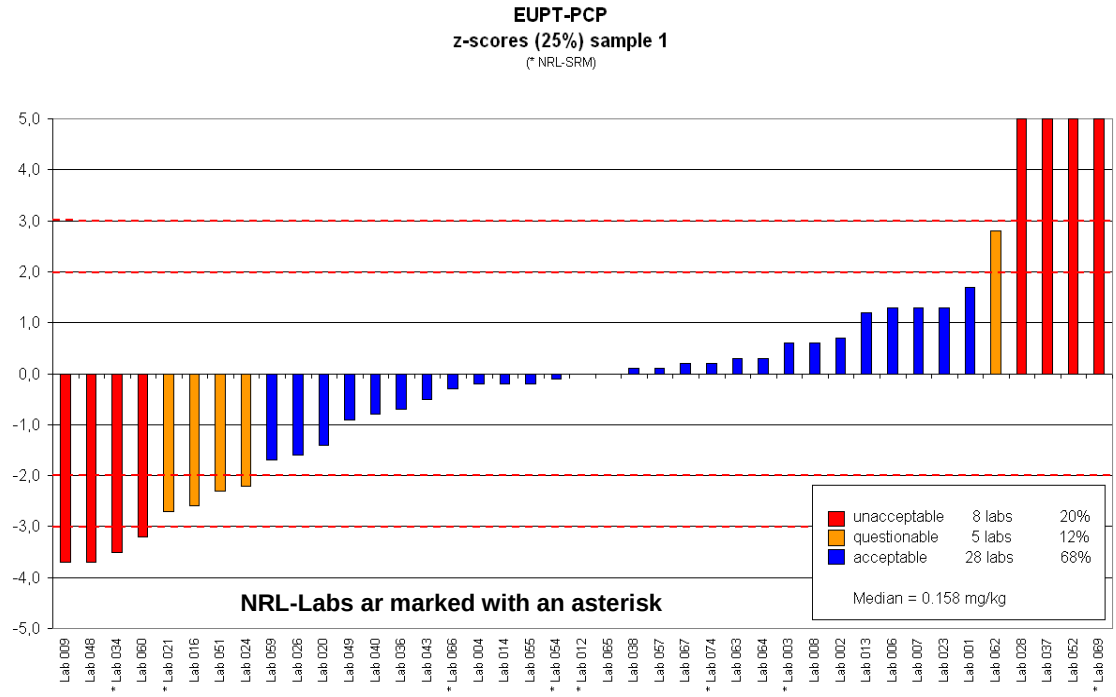

Figure 3: Sample A, z-scores

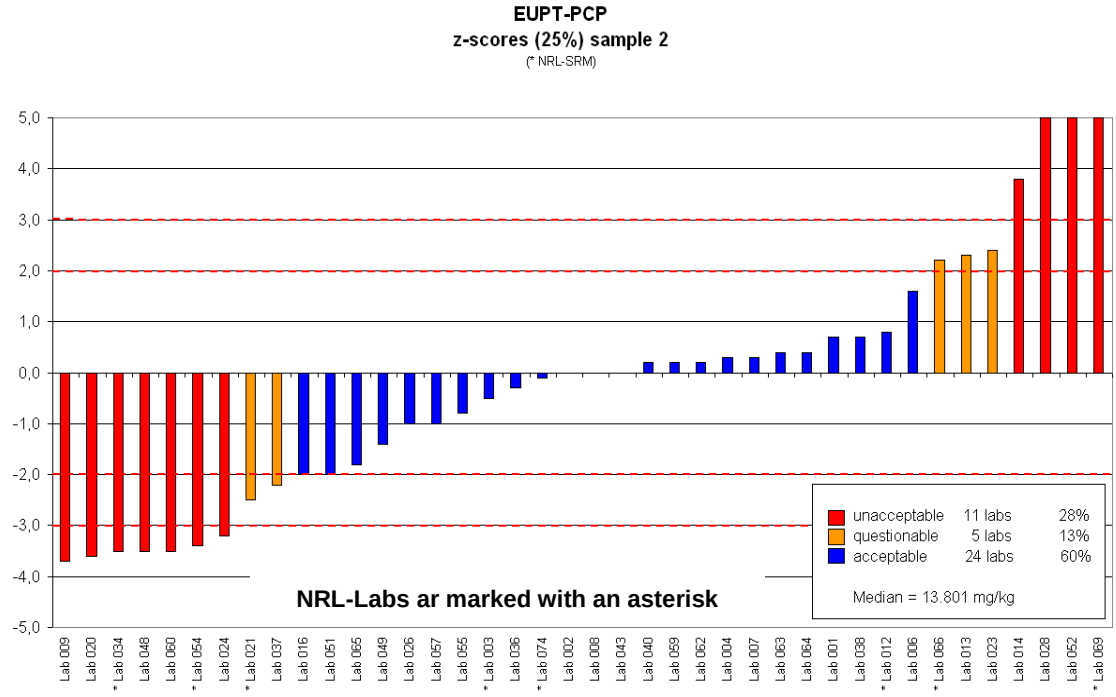

Figure 4: Sample B, z-scores

Table 9: List of participating laboratories

Laboratory Name	Country	City	NRL	Delivered results?
Umweltbundesamt GmbH	AT	Vienna		Yes
Dioxin Analysis Unit	AU	Sydney		**No**
Scientific Institute of Public Health	BE	Brussels	NRL-SRM	Yes
SGS Belgium	BE	Antwerp		Yes
Pacific Rim Laboratories Inc.	CA	Surrey		**No**
Institute of Chemical Technology	CZ	Prague		**No**
Institute of Public Health Ostrava,	CZ	Dobra		Yes
Bayerisches Landesamt für Gesundheit u. LM-sicherheit	DE	Erlangen		Yes
BBGes-ILAT	DE	Berlin		Yes
Bundesamt f. Verbrauchersch.u. LM-sich. (BVL)	DE	Berlin	NRL-SRM	Yes
CVUA Münster	DE	Münster		Yes
Food GmbH Jena	DE	Jena		Yes
GfA mbH	DE	Hamburg		Yes
Institut für Hygiene und Umwelt	DE	Hamburg		Yes
Landeslabor Schleswig-Holstein	DE	Neumünster		Yes
LAVES	DE	Oldenburg		Yes
LSGV-Lebensmittelchemie	DE	Saarbrücken		Yes
LUA-Lebensmittelchemie	DE	Speyer		**No**
LUFA-ITL GmbH	DE	Kiel		Yes
mas | münster analytical solutions gmbh	DE	Münster		Yes
Ökometric GmbH	DE	Bayreuth		Yes
Thüringer Landesanstalt für Landwirtschaft	DE	Jena		Yes
WESSLING Laboratorien GmbH	DE	Berlin		Yes
WESSLING Laboratorien GmbH	DE	Altenberge		Yes
Institut Quimic de Sarria - Env. Lab.	ES	Barcelona		Yes
National Public Health Institute	FI	Kuopio		Yes
CARSO	FR	Lyon		Yes
MicroPolluants Technologie	FR	Thionville		Yes
Ministère de l'Economie et des Finances	FR	Rennes		Yes

Laboratory Name	Country	City	NRL	Delivered results?
SCL Ministère de l'Economie et du Budget	FR	Pessac		Yes
General Chemical State Laboratory (GCSL)	GR	Athens	NRL-SRM	Yes
NCSR "Demokritos"	GR	Athens		Yes
Central Agricultural Office	HU	Budapest		Yes
Vimta Labs Ltd., Life Science Facility	IND	Hyderabad		Yes
Consorzio Interuniversitario Nazionale la Chimica	IT	Venezia		Yes
ISS-Pesticide Section	IT	Rome	NRL-SRM	Yes
Istituto Zooprof. Sperimen. d. Lombardia	IT	Bologna		Yes
Istituto Zooprof. Sperimen. d. Piemonte, Liguria e v. D'aosta	IT	Torino		Yes
R&C LAB S.r.l.	IT	Vicenza		Yes
Toxicological Chemistry Unit	IT	Rome		Yes
National Veterinary Laboratory	LT	Vilnius	NRL-SRM	Yes
RIKILT	NL	Wageningen	NRL-other	Yes
VWA - Food and Consumer Prod. Safety Authority	NL	Amsterdam	NRL-SRM	**No**
INETI	PT	Lisboa		**No**
Institute of Public Health Maribor	SI	Maribor	NRL-SRM	Yes
State Vet. and Food Institute	SK	Bratislava	NRL-SRM	Yes
Super Micro Mass Research and Techn. Center, CSU	TW	Koahsiung		**No**
Central Science Laboratory	UK	York	NRL-SRM	Yes
Analytical Perspectives	US	Wilmington		**No**

Table 10: Methods - part 1

Labcode	Reference Method	Reporting Level (mg/kg)	Sample Weight (g)	Extr.Solvent	Water Addition	pH adjustment	Liquid-Liquid Partitioning (LLP) step	Solvent for LLP	pH adjustment for partitioning	If no LLP, how was analyte isolated?	Cleanup	Derivatization step?	Derivatization approach	SolvEXchng	Instrumentation
Lab 001	QuEChERS as in CRL-website	0,001	1	Acetonitrile	no	no	yes, upon addition of salts only		no		none	no	0	no	LC-MS/MS
Lab 002	QuEChERS as in CRL-website	0,001	1	Acetonitrile	yes	no	yes, upon addition of salts only		no	no isolation, direct injection	none	no	0	no	LC-MS/MS
Lab 003	QuEChERS as in CRL-website	0,010	1	Acetonitrile	no	no	no			no isolation, direct injection	none	no	0	no	LC-MS/MS
Lab 004	QuEChERS as in CRL-website	0,010	1	not apply	yes	no	yes, upon addition of salts only	Acetonitrile	no	-	none	no	-	no	LC-MS/MS
Lab 006	QuEChERS as in CRL-website	0,005	1	Acetonitrile	yes	yes, pH 5	yes, upon addition of salts only				none	no	0	no	LC-MS/MS
Lab 007	QuEChERS as in CRL-website	0,000	1	Acetonitrile	yes	no	no		no	no isolation, direct injection	none	no	0	no	LC-MS/MS
Lab 008	internal method (HRGC-HRMS)	0,000	20	Acetone - Hexane	no	no						yes	0		HRGC/HRMS
Lab 009		0,000	30-0.5	Acetonitrile	yes	yes, pH 2	yes, upon addition of a solvent and salts	Hexane	no		none	yes	acetic anhidride	yes	GC-ECD
Lab 012	QuEChERS as in CRL-website	0,010	1	Acetonitrile	no	no	no		no	no isolation, direct injection	none	no	0	no	LC-MS/MS
Lab 013	QuEChERS as in CRL-website	0,005	1	Acetonitrile	yes	no	yes, upon addition of a solvent and salts	Acetonitrile	no		none	no	0	no	LC-MS/MS
Lab 014		0,001	1	Acetone	yes	yes, pH 2	yes, upon addition of a solvent only	Hexane	no		reextraction LL	yes	Essigsäureanhydrid	no	GC-MS/NCI
Lab 016	Modified from Muir et. al. J Agric Food Chem 28 (4) 1980, 711-714	0,001	0.1-0.3	isopropanol:hexane (2:8) Note: isopropanol was added to samples prior to extraction	no	yes, pH 1	yes, upon derivatization. Acetylated PCP was separated from isopropanol-hexane to hexane only, see below "Derivatization"				none	yes	Acetic acid anhydride derivatization of isopropanol-hexane (2:8) extract using 0.1M kalium carbonate buffer. After derivatization hexane was separated for GC-MS analysis. K2CO3 buffer separated isopropanol from extraction solvent.	no	GC-MS
Lab 019															
Lab 020	Modified QuEChERS	0,000	1	Acetonitrile	no	yes, pH 1	no			no isolation, direct injection			0		LC-MS/MS
Lab 021	Home-made method (solvent extraction with buffered methanol)	0,010	1	Methanol	no	yes, pH 5	no			no isolation, direct injection	none	no	0	no	LC-MS/MS
Lab 023	mod. DIN ISO 14154 (HCL pretreatment, ultrasonic extraction (hexane:aceton 1:1), filtration / Na2SO4) derivatization	0,003	0.5 (A) 0.13 (B)	hexane:aceton 1:1	no		no			no isolation, direct injection	none	yes	MSTFA	no	GC-MS
Lab 024		0,000	0		no	yes, pH 3	no					yes	Acetyl-ation	no	GC-MS/MS

Labcode	Reference Method	Reporting Level (mg/kg)	Sample Weight (g)	ExtrSolvent	Water Addition	pH adjustment	Liquid-Liquid Partitioning (LLP) step	Solvent for LLP	pH adjustment for partitioning	If no LLP, how was analyte isolated?	Cleanup	Derivatization step?	Derivatization approach	SolvExchng	Instrumentation
Lab 026	QuEChERS as in CRL-website	0,010	1	Acetonitrile	yes	no	yes, upon derivatisation				none	yes	Acetylation with Acetanhydrid	yes	GC-MS
Lab 027		0,000													
Lab 028	modified QuE-ChERS (EN 15662)	0,010	2	Methanol	no	no	no		no	no isolation, direct injection	none	no	0	no	LC-MS/MS
Lab 029															
Lab 034		0,010	1	Acetonitrile	no	yes, pH 2	no		no	no isolation, direct injection	none	no	0	no	GC-ECD
Lab 035															
Lab 036	Isotopenverdün-nungsanlyse	0,010	10	n-Hexane/Acetone (80/20)	no	yes, pH 5	no		no	no isolation, direct injection	none	yes	TMSH	yes	GC-MS
Lab 037	Solid-Liquid extraction LC-MSMS Analysis	0,010	10	Dichloromethane	no	no	no			no isolation, direct injection	none	no	0	yes	LC-MS/MS
Lab 038	QuEChERS as in CRL-website	0,000	200 mg	Acetonitrile	no	yes, pH 3	yes, upon addition of salts only		no	no isolation, direct injection	none	no	0	no	LC-MS
Lab 039															
Lab 040	QuEChERS (EN 15662; citrate buffered)	0,010	2	Acetonitrile	yes	no	yes, upon addition of a solvent and salts		yes, pH 5		none	no	0	no	LC-MS/MS
Lab 041															
Lab 043	QuEChERS as in CRL-website	0,002	1	Acetonitrile	no	no	yes, upon addition of a solvent and salts	Acetonitrile	no		none	no	0	no	LC-MS/MS
Lab 048		0,005	5		yes	no	yes, upon addition of a solvent and salts	Dichloromethane	no		SPE	no	0	no	LC-MS/MS
Lab 049	In house	0,002	35	Toluene/ethanol 1/1 V/V	no	no	no		no	Soxhlet extraction with tolue-ne/ethanol 1/1 V/V	GPC	no	0	yes	GC-MS
Lab 051	S-19	0,010	2		yes	yes, pH 1	yes, upon addition of a solvent only	Aceto-ne/Petroleum Ether	no		GPC / Silica Gel Column	yes	Acetic Anhydride	yes	GC-ECD
Lab 052	Internal Method	0,500	0,001	Acetonitrile	no	yes, pH 9	no		no	no isolation, direct injection	none	yes	Br-ethyl	no	GC-MS/MS
Lab 053															
Lab 054	Laboratory internal method	0,010	1	HEXANE AND DICHLOROMETHA-NE	yes	yes, pH 1	yes, upon addition of a solvent only	Dichloromethane	no		none	yes	MTBSTFA	no	GC-MS
Lab 055	QuEChERS as in CRL-website 'PCP version'	0,010	1	Acetonitrile	no	no	yes, upon addition of a solvent and salts	water	no		none	no	0	no	LC-MS/MS
Lab 057	in house	0,030	1	TBME	no	yes, pH 2	yes, upon addition of a solvent and salts (acid slush)	Hexane	yes, pH 1		none	no	0		GC-MS/MS
Lab 059	inhouse-method	0,001	0.2 and 5	Acetonitrile	no	yes, pH 1	no		no	no isolation, direct injection	none	no	0	yes	LC-MS/MS

Labcode	Reference Method	Reporting Level (mg/kg)	Sample Weight (g)	Extr.Solvent	Water Addition	pH adjustment	Liquid-Liquid Partitioning (LLP) step	Solvent for LLP	pH adjustment for partitioning	If no LLP, how was analyte isolated?	Cleanup	Derivatization step?	Derivatization approach	SolvExchng	Instrumentation
Lab 060	OEN EN 12673	0,010	5	Acetone/n-Hexane (1/1)	no	no			yes, pH 10	addition of 2% aqueous sodium-carbonate, evapo-ration of the organic phase	extraction of the aqueous sodiumcar-bonate with n-hexane	yes	Acetanhydride/Petroleumbenzine	yes	GC-MS
Lab 062	QuEChERS as in CRL-website	0,100	1	Acetonitrile	no	no	no		no	SPE following dilution with water	SPE	no	0	yes	LC-MS/MS
Lab 063	QuEChERS (EN 15662; citrate buffered), only extraction procedure!	0,001	1	Acetonitrile	yes	yes, pH 5	solvent exchange acetonitril to toluene; liq.-liq. partitioning tolue-ne/NaOH; H2SO4; extraction with toluene; silica-column (tolue-ne);liq.-liq. partitioning toluene/KOH; derivatisa-tion				Mini-silica column	yes	acetic anhydride	yes	GC-MS
Lab 064	German § 35 LMBG, B 82.02-8 ; Acetylierung von PCP nach DIN 12673	0,010	5	Isohexane	yes	yes, pH 1	no			watersteam destillation	none	yes	Acetic anhydride	no	GC-MS
Lab 065	QuEChERS as in CRL-website	0,003	2	Acetonitrile	yes	no	yes, upon addition of salts only		no		none	no	0	no	LC-MS/MS
Lab 066	QuEChERS as in CRL-website but using C13 PCP rather than nicarbazin	0,010	1	Acetonitrile	no	no	no			no isolation, direct injection	none	no	0	no	LC-MS/MS
Lab 067	QuEChERS as in CRL-website	0,001	1	Acetonitrile	yes	no	yes, upon addition of salts only	Acetonitrile	no		none	no	0	no	LC-MS/MS
Lab 069	QuEChERS as in CRL-website	0,201	1	Acetonitrile	yes	no	yes, upon addition of salts only		no		none	no	0	no	LC-MS/MS
Lab 073															
Lab 074	QuEChERS as in CRL-website	0,004	1	Acetonitrile with 0.4% acetic acid	no	no	yes, upon addition of a solvent and salts	Water	no		none	no	0	no	LC-MS/MS

Table 11: Methods - part 2

Labcode	Reference method	Reporting Level (mg/kg)	Quantitation Approach	Recovery Correction?	Recovery (low level, %)	Recovery (high level, %)	Isotopically labelled standard used?	ISTD type	Instrumentation
Lab 001	QuEChERS as in CRL-website	0,001	external calibration using standard in pure solvent	no			no	nicarbazine	LC-MS/MS
Lab 002	QuEChERS as in CRL-website	0,001	external calibration using standard added to blank matrix solution (matrix-matched)	no			no	Nicarbazin	LC-MS/MS
Lab 003	QuEChERS as in CRL-website	0,010	external calibration using standard added to blank matrix solution (matrix-matched)	yes, automatically via isotopically labelled standard			yes	Pentachlorphenol 13C6	LC-MS/MS
Lab 004	QuEChERS as in CRL-website	0,010	external calibration using standard in pure solvent	yes, using a recovery rate	95	95	no		LC-MS/MS
Lab 006	QuEChERS as in CRL-website	0,005	using standard additions procedure (Art. 47, SANCO/2007/3131)	yes, automatically via standard addition procedure (Art. 47, SANCO/2007/3131)			yes	Pirimicarb D6	LC-MS/MS
Lab 007	QuEChERS as in CRL-website	0,000	external calibration using standard in pure solvent	no			no		LC-MS/MS
Lab 008	internal method (HRGC-HRMS)	0,000		yes, automatically via isotopically labelled standard	95	90	yes	PCP13C6	HRGC/HRMS
Lab 009		0,000	external calibration using standard in pure solvent	no			no	2-Bromophenol	GC-ECD
Lab 012	QuEChERS as in CRL-website	0,010	external calibration using standard in pure solvent	no			no	Nicarbazin	LC-MS/MS
Lab 013	QuEChERS as in CRL-website	0,005	performing standard addition to aliquots of sample extracts (Art. 48, SANCO/2007/3131)	yes, via standard addition to aliquots of sample extracts (Art. 48, SANCO/2007/3131)			no	Nicarbazin	LC-MS/MS
Lab 014		0,001	external calibration using standard in pure solvent	yes, automatically via isotopically labelled standard			yes	PCP-13C6	GC-MS/NCI
Lab 016	Modified from Muir et. al. J Agric Food Chem 28 (4) 1980, 711-714	0,001	external calibration using standard in pure solvent	yes, automatically via isotopically labelled standard			yes	13C labelled pentachlo-rophenol	GC-MS
Lab 019									
Lab 020	Modified QuEChERS	0,000	external calibration using standard in pure solvent	yes, automatically via isotopically labelled standard			yes	13C6 PCP	LC-MS/MS
Lab 021	Home-made method (solvent extraction with buffered methanol)	0,010	external calibration using standard in pure solvent	yes, automatically via isotopically labelled standard			yes	C13-PCP	LC-MS/MS
Lab 023	mod. DIN ISO 14154 (HCL pretreatment, ultrasonic extraction (hexane:aceton 1:1), filtration / Na2SO4) derivatization	0,003		yes, automatically via isotopically labelled standard			yes	13C PCP	GC-MS
Lab 024		0,000		no			yes	13C6 - PCP	GC-MS/MS
Lab 026	QuEChERS as in CRL-website	0,010	external calibration using standard in pure solvent	no	87	98	no	2-Bromphenol; 2,4,6-Tribromphenol; Pen-tabromphenol	GC-MS
Lab 027		0,000							
Lab 028	modified QuEChERS (EN 15662)	0,010	external calibration using standard in pure solvent	yes, via standard addition to aliquots of sample extracts (Art. 48, SANCO/2007/3131)	91	91	no		LC-MS/MS
Lab 029									
Lab 034		0,010	using standard additions procedure (Art. 47, SANCO/2007/3131)	no			no		GC-ECD
Lab 035									
Lab 036	Isotopenverdünnungsanlyse	0,010	external calibration using standard in pure solvent	no			no	2,4,6-Tribromphenol	GC-MS
Lab 037	Solid-Liquid extraction LC-MSMS Analysis	0,010	external calibration using standard in pure solvent	no			no		LC-MS/MS
Lab 038	QuEChERS as in CRL-website	0,000	external calibration using standard in pure solvent	no			no		LC-MS
Lab 039									
Lab 040	QuEChERS (EN 15662; citrate buffered)	0,010	performing standard addition to aliquots of sample extracts (Art. 48, SANCO/2007/3131)	no			no	Bis-nitrophenyl urea (nicarbazin)	LC-MS/MS
Lab 041									
Lab 043	QuEChERS as in CRL-website	0,002	external calibration using standard in pure solvent	yes, automatically via isotopically labelled standard	94	94	yes	13C-PCP	LC-MS/MS
Lab 048		0,005	external calibration using standard in pure solvent	no			no		LC-MS/MS
Lab 049	In house	0,002	external calibration using standard in pure solvent	yes, automatically via isotopically			yes	13C-HCB	GC-MS

Labcode	Reference method	Reporting Level (mg/kg)	Quantitation Approach	Recovery Correction?	Recovery (low level, %)	Recovery (high level, %)	Isotopically labelled standard used?	ISTD type	Instrumentation
				labelled standard					
Lab 051	S-19	0,010	external calibration using standard added to blank matrix solution (matrix-matched)	no			no	2,4,6-Tribromophenol	GC-ECD
Lab 052	Internal Method	0,500	external calibration using standard added to blank matrix solution (matrix-matched)	yes, using a recovery rate	82	82	yes	PCP-ethyl-ether-D5	GC-MS/MS
Lab 053									
Lab 054	Laboratory internal method	0,010	external calibration using standard added to blank matrix solution (matrix-matched)	yes, automatically via isotopically labelled standard			yes	13C6 PCP	GC-MS
Lab 055	QuEChERS as in CRL-website 'PCP version'	0,010	external calibration using standard in pure solvent	yes, automatically via isotopically labelled standard		80	yes	13C6-PCP	LC-MS/MS
Lab 057	in house	0,030	external calibration using standard added to blank matrix solution (matrix-matched)	yes, automatically via isotopically labelled standard			yes	Labelled PCP	GC-MS/MS
Lab 059	inhouse-method	0,001	using standard additions procedure (Art. 47, SANCO/2007/3131)	yes, automatically via isotopically labelled standard			yes	13-C6-PCP	LC-MS/MS
Lab 060	OEN EN 12673	0,010	external calibration using standard in pure solvent	yes, automatically via isotopically labelled standard			yes	Naphthaline-d8	GC-MS
Lab 062	QuEChERS as in CRL-website	0,100	external calibration using standard added to blank matrix solution (matrix-matched)	no			no		LC-MS/MS
Lab 063	QuEChERS (EN 15662; citrate buffered), only extraction procedure!	0,001		yes, automatically via isotopically labelled standard			yes	13C6-PCP	GC-MS
Lab 064	German § 35 LMBG, B 82.02-8 ; Acetylierung von PCP nach DIN 12673	0,010	external calibration using standard added to blank matrix solution (matrix-matched)	yes, using a recovery rate	130	110	no	3,4,5,6-Tetrachloro-2-methoxyphenol	GC-MS
Lab 065	QuEChERS as in CRL-website	0,003	external calibration using standard in pure solvent	yes, automatically via isotopically labelled standard			yes	PCP-13C6	LC-MS/MS
Lab 066	QuEChERS as in CRL-website but using C13 PCP rather than nicarbazin	0,010	using standard additions procedure (Art. 47, SANCO/2007/3131)	yes, automatically via standard addition procedure (Art. 47, SANCO/2007/3131)			yes	C13-PCP	LC-MS/MS
Lab 067	QuEChERS as in CRL-website	0,001	external calibration using standard in pure solvent	no			no	4-(2,4-dichlorophenoxy)butyric acid	LC-MS/MS
Lab 069	QuEChERS as in CRL-website	0,201	external calibration using standard in pure solvent	no			no		LC-MS/MS
Lab 073									
Lab 074	QuEChERS as in CRL-website	0,004	external calibration using standard added to blank matrix solution (matrix-matched)	no			no	nicarbazine	LC-MS/MS

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