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LABORATORY NUMBER: Available to participants from FAPAS SecureWeb

FAPAS® Proficiency Test 0944

Pesticide Residues in Wheat Flour

August – October 2006

Report

Prepared on behalf of FAPAS® by

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0009 PT

SUMMARY

1. The test material for FAPAS® Proficiency Test 0944 was dispatched in August 2006. Each participant received a wheat flour test material to be analysed for pesticide residues. One hundred and forty nine test materials were ordered by participants from 39 countries. One hundred and thirty eight participants, i.e. 93%, returned results for some combination of the three analytes present in the test material within the time-scale demanded by the Scheme.

2. The assigned value ($\hat{X}$) for each analyte (unadjusted for recovery) was calculated from the most appropriate measure of central tendency of participants' results [1, 2, 3].

3. The target standard deviations (σ_p) were calculated using the appropriate form of the Horwitz equation [4] and in conjunction with the assigned values ($\hat{X}$) were used to derive z-scores for participants' results. z-Scores are considered satisfactory if $|z| \leq 2$.

4. Results for this test are summarised as follows:

analyte	assigned value $\hat{X}$, µg/kg	number of satisfactory scores $\|z\| \leq 2$	total number of scores	satisfactory %
chlorpyrifos	163.5	94	119	79
bifenthrin	85.6	79	96	82
permethrin	151.5	76	110	69

5. Surplus test materials from the batch used in this test are available for sale, see APPENDIX III.

6. Whereas this Report has been produced in good faith and in accordance with best industry practice, neither the Central Science Laboratory nor the Secretary of State for Environment, Food and Rural Affairs accepts any liability whatsoever as to the application or use of the information contained therein.

CONTENTS

1. INTRODUCTION

1.1. Proficiency Testing

The demand for independent proof of competence from regulatory bodies and customers means that proficiency testing is relevant to all laboratories testing food and feed for quality and safety in every country. Hence, it is a requirement of accreditation to ISO 17025 [5] that the laboratory takes part in a proficiency testing scheme, if a suitable scheme exists. Further, for laboratories entrusted with the official control of food and feeds, Article 12 of EU Regulation (EC) 882/2004 [6] requires such laboratories to be assessed and accredited in accordance with ISO 17025, i.e. proficiency testing is a legal requirement for these laboratories. Thus, together with the use of validated methods, proficiency testing is an essential element of laboratory quality assurance.

The analysis of an external quality check sample as part of a laboratory's routine procedures provides objective standards for individual laboratories to perform against and permits them to compare their analytical results with those from other laboratories. Such standards and comparisons can go beyond the actual chemical analysis. For example, the ability to report results in specified units and within a given time scale are important aspects of quality. Hence, participants in FAPAS® who submit results after the closing date of a proficiency test are only included in the statistical evaluation if there are extenuating circumstances.

It is important to understand the statistical limitations of this external means of quality assessment when gauging the competence of a laboratory. The results of a typical chemical analysis will be normally distributed. That is to say, the majority of results will be centred on a mean value but, inevitably, some results will lie at the extremes of the distribution. The statistics of a normal distribution mean that about 95% of data points will lie between a z-score of –2 and +2. Performance in a FAPAS® proficiency test, therefore, is considered 'satisfactory' if a participant's z-score lies within this range. It follows that if a participant's z-score lies outside $|z| > 2$ there is about a 1 in 20 chance that their result is in fact an acceptable result from the extreme of the distribution. If a participant's z-score lies outside $|z| > 3$ the chance that their result is actually acceptable is only about 1 in 300.

2. TEST MATERIAL

2.1. Preparation

The test material was prepared by a laboratory contracted to do so by FAPAS®.

A portion of organic white wheat flour material was screened for the presence of residues given in the FAPAS® list. No residues were found at or above 25 µg/kg.

A standard solution was prepared to give the following approximate final pesticide concentrations in the wheat flour:

chlorpyrifos	220 µg/kg
bifenthrin	100 µg/kg
permethrin	180 µg/kg

The standard solution was added dropwise to a 500 g portion of wheat flour and mixed (Kenwood Chef Mixer, approximately 1 hour). This portion was left in a fume cupboard (approximately 12 hours) to vent any remaining solvent.

The spiked wheat flour was then added in stages to 11.5 kg of blank wheat flour and the resulting bulk mixed (Winkworth Tumble Mixer, approximately 12 hours). The mixed wheat flour was then stored in a fridge for approximately 3 weeks before remixing (Winkworth Tumble Mixer, approximately 12 hours). Individual sub-samples (at least 50 g) were weighed into plastic bags. Each bag was individually numbered and stored at -4°C prior to distribution.

2.2. Homogeneity

Ten randomly selected test materials were analysed in duplicate for chlorpyrifos, bifenthrin and permethrin. The results, together with their statistical evaluation [7], are given in APPENDIX I. These data show sufficient homogeneity and are NOT included in the subsequent calculation of the assigned values.

2.3. Distribution

The dispatch date was 25 August 2006. Each participant received an individually numbered wheat flour test material packed in a padded envelope together with a covering letter, instructions for electronic submission and the result form (for participants without access to the internet).

3. RESULTS

Participants were required to report their data in µg/kg as received for those analytes that they detected, uncorrected for recovery, together with the percentage recovery and limit of quantification (LoQ). Results were submitted by 138 participants before the closing date for this test, 6 October 2006.

Each participant was given a laboratory number, assigned in order of receipt of results. The results reported for chlorpyrifos, bifenthrin and permethrin are given in Table 1.

If a participant failed to identify the presence of chlorpyrifos, bifenthrin and permethrin, and their limit of quantification (LoQ) was below the level needed for a satisfactory z-score, then as required by the FAPAS® Protocol, the reported result was assigned a zero value.

Any participants identifying pesticides other than chlorpyrifos, bifenthrin and permethrin at levels greater than 25 µg/kg are listed in Table 2 together with the pesticides reported and the levels determined.

The analytical methods used by each participant are summarised in APPENDIX II. In this section, participants with z-scores outside the satisfactory range (i.e. $|z| > 2$) are no longer shown in bold. However, in Table 1, z-scores outside the satisfactory range are shown in bold.

4. STATISTICAL EVALUATION OF RESULTS

The object of the statistical procedure employed is to obtain a simple and transparent result, which the participant and other interested parties can readily appreciate. Further details, including worked examples, are given in the FAPAS® Protocol [1]. The procedure follows that recommended in the IUPAC/ISO/AOAC International Harmonised Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories [8].

4.1. Calculation of the Assigned Value, $\hat{X}$

The assigned value, $\hat{X}$, i.e. the best estimate of the true concentration of each analyte, was set as the consensus of the results submitted by participants. The procedure used to derive this consensus involved:

- Removing non valid data, i.e.:
  - i) participants reporting "not detected" and subsequently assigned a result of 0 µg/kg,
  - ii) results from participants not quoting a percentage recovery,
  - iii) results from participants whose recovery is outside the range 70 – 110% [9],
  - iv) results below the stated LoQ,
  - v) results with no LoQ stated,
  - vi) results assumed to be reporting errors (i.e. exceeding 10x greater or smaller than the mean value).
- Minimising the influence of outliers by the use of a robust statistical procedure to derive the mean [3].
- Considering the normality (Kolmogorov-Smirnov test), or otherwise, of the distribution of the selected results.
- Assessing the uncertainty (u) of the robust mean.

$$u = \frac{\hat{\sigma}}{\sqrt{n}}$$

where $\hat{\sigma}$ = the standard deviation of the robust mean
(NB this is NOT the target standard deviation for the proficiency test, σ_p)
and n = the number of data points used to calculate the robust mean.

For all analytes this procedure was straightforward and the robust means were taken as the assigned values.

The robust means used as the consensus to set the assigned values ($\hat{X}$), together with n, u and $\hat{\sigma}$ are shown in Table 3.

4.2. Target Standard Deviation for the Round, σ_p

The value of σ_p determines the limits of satisfactory performance in a FAPAS® proficiency test. It is set at a value that reflects best practice for the analyses in question. The standard deviation of reproducibility found in collaborative trials is generally considered an appropriate indicator of the best agreement that can be obtained between laboratories. However, not all analyses have been characterised in this manner. In such cases, the

predictive models of the appropriate form of the Horwitz equation [4] are valuable indicators of best practice.

For all analytes, σ_p was derived from the appropriate form of the Horwitz equation [4]. This equation predicts a standard deviation from a given concentration, c, and requires c to be expressed as a dimensionless mass ratio, e.g. 1 ppm ≡ 10^{-6} or % ≡ 10^{-2}. It follows therefore that to express the dimensionless standard deviation predicted by the equation in the original concentration units it must be divided by the relevant mass ratio:

i) for analyte concentrations <120 ppb

$$\sigma_p = \frac{0.22c}{mr}$$

ii) for analyte concentrations ≥120 ppb and ≤13.8%

$$\sigma_p = \frac{0.02c^{0.8495}}{mr}$$

iii) for analyte concentrations >13.8%

$$\sigma_p = \frac{0.01c^{0.5}}{mr}$$

where, in all three cases, c = concentration, i.e. the assigned value, $\hat{X}$, expressed as a dimensionless mass ratio, e.g. 1 ppm ≡ 10^{-6} or % ≡ 10^{-2}

and mr = dimensionless mass ratio, e.g. 1 ppm ≡ 10^{-6} or % ≡ 10^{-2}.

The values of σ_p used to calculate z-scores from the reported results in this test are given in Table 3.

4.3. Individual z-Scores

Participants' z-scores were calculated as:

$$z = \frac{(x - \hat{X})}{\sigma_p}$$

where x = the participant's reported result

$\hat{X}$ = the assigned value

and σ_p = the target standard deviation.

Participants' z-scores, unadjusted for recovery, for each pesticide are given in Table 1 and shown as histograms in Figures 1 – 3.

The number and percentage of z-scores in the satisfactory range, |z| ≤2, for each pesticide are given in Table 4.

It is possible for the z-scores published in this report to differ slightly from the z-score that can be calculated using the formula given above. These differences arise from the necessary rounding of the actual assigned value(s) and target standard deviation(s) prior to their publication in Table 3.

Table 5 shows the number and percentage of participants correctly identifying chlorpyrifos, bifenthrin and permethrin and obtaining satisfactory z-scores for all analytes. This

information is not a measure of satisfactory performance in the test. Satisfactory performance is indicated in Table 1, and summarised in Table 4.

5. REFERENCES

1 Food Analysis Performance Assessment Scheme (FAPAS®), 2002, *Protocol for the Organisation and Analysis of Data*, 6th Edition.

2 Lowthian, P.J. and Thompson, M., 2002, Bump-hunting for the proficiency tester – searching for multimodality, *Analyst*, **127**, 1359-1364.

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4 Thompson, M., 2000, Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing, *Analyst*, **125**, 385-386.

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6 Regulation (EC) 882/2004 of the European Parliament and of the Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules, *Official Journal* **L 165**, 30/04/2004, 0001-0141.

7 Fearn, T. and Thompson, M., 2001, A new test for sufficient homogeneity, *Analyst*, **126**, 1414-1417.

8 Thompson, M. and Wood, R., 2006, The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, *Pure Appl. Chem*., **78(1)**, pp. 145–196.

9 Quality Control Procedures for Pesticide Residue Analysis. Guidelines for Residues Monitoring in the European Union, 4th edn, Document No SANCO/10232/2006.

Table 1: Results and z-Scores, Wheat Flour Test Material

laboratory number	analyte											
	chlorpyrifos assigned value 163.5 µg/kg				bifenthrin assigned value 85.6 µg/kg				permethrin assigned value 151.5 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
001	167	76	5	0.1	81	66	20	-0.2	148	95	10	-0.1
002	161.0	84.5	2.0	-0.1	79.0	107.6	8.0	-0.3	143.0	80.2	14.0	-0.3
003	55.4	78	20	**-3.1**	77.6	100	10	-0.4	119	128	20	-1.0
004	330	95	10	**4.8**	210	114	10	**6.6**	420	119	10	**8.3**
005	180	83	5	0.5	80	78	5	-0.3	160	82	5	0.3
006	0.13	110		**-4.8**	0.07	110	0.05	**-4.5**	0.11	140	0.05	**-4.7**
007	190			0.8	80			-0.3	0			**-4.7**
008	75	105	10	**-2.6**	#				#			
009	#				#				#			
010	138	86	5	-0.7	#				130	90	10	-0.7
011	150			-0.4	110			1.3	220			**2.1**
012	#				#				#			
013	#				#				#			
014	#				#				#			
015	#				#				#			
016	224.92	96	5	1.8	#				158.00	89	5	0.2
017	#				#				#			
018	#				#				#			
019	#				#				#			
020	#				#				#			
021	#				#				#			
022	#				#				#			
023	#				#				#			
024	#				#				#			
025	221		10	1.7	117		10	1.7	236		10	**2.6**
026	157	84	30	-0.2	#				145	84	50	-0.2
027	#				#				#			
028	106	96	10	-1.7	72	97	10	-0.7	80	97	10	**-2.2**
029	173	97	0.010	0.3	68.7	86	0.00080	-0.9	133	91	0.00050	-0.6

# = pesticide not analysed for
LoQ = limit of quantification

z-scores where |z| <2 are highlighted in **bold**

Table 1 (Continued): Results and z-Scores, Wheat Flour Test Material

laboratory number		analyte											
		chlorpyrifos assigned value 163.5 µg/kg				bifenthrin assigned value 85.6 µg/kg				permethrin assigned value 151.5 µg/kg			
		result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
030		#				#				#			
031		155.5	91.2	6	-0.2	69.6	73.0	8	-0.8	137.6	84.0	15	-0.4
032	†	164		10	0.0	81.5		5	-0.2	0		5	**-4.7**
033		151	89.5	10	-0.4	#				#			
034		149.1	86.2	50	-0.4	#				154.1	81.5	50	0.1
035		145.23	88.00	10.00	-0.5	#				140.12	84.00	40.00	-0.4
036		129	87.7	10.0	-1.0	#				#			
037		650	122.3	158	**14.2**	226	95.2	7	**7.5**	580	123.8	21	**13.3**
038		#				#				#			
039		165	98	0.001	0.0	107	90	10	1.1	179	98	50	0.9
040		398	130	10	**6.8**	230	129	5	**7.7**	386	124	10	**7.3**
041		#				#				#			
042		#				#				#			
043		#				#				#			
044		190	76	10	0.8	140	73	10	**2.9**	180	75	10	0.9
045		194		10	0.9	116		10	1.6	156		10	0.1
046		168	78	20	0.1	120	116	69	1.8	251	120	69	**3.1**
047		151	95	10	-0.4	84	110	10	-0.1	163	106	10	0.4
048		163	94.2	20	0.0	86.6	96.5	20	0.1	192	104.3	20	1.3
049		210	102	10	1.4	140	97	10	**2.9**	170	92	10	0.6
050		130	92.3	20	-1.0	60	94.4	20	-1.4	120	90.2	20	-1.0
051		0	72	40	**-4.8**	0	113	34	**-4.5**	21.2	71	8	**-4.0**
052		194	94	50	0.9	77	94	30	-0.5	173	100	30	0.7
053		170		10	0.2	90		10	0.2	350		10	**6.2**
054		177.7		50	0.4	74.4		10	-0.6	122.9		10	-0.9
055		158.5	98.6	10	-0.1	79.3	76.1	20	-0.3	153.7	85.4	20	0.1
056		141	115	20	-0.7	145	116	15	**3.2**	126	77	10	-0.8
057		150	96	50	-0.4	#				211	113	200	1.8
058		262	80	10	**2.9**	#				234	104	10	**2.6**

= pesticide not analysed for
z-scores where |z| <2 are highlighted in **bold**

† = additional pesticides identified > 25 µg/kg
LoQ = limit of quantification

Table 1 (Continued): Results and z-Scores, Wheat Flour Test Material

laboratory number		chlorpyrifos assigned value 163.5 µg/kg				bifenthrin assigned value 85.6 µg/kg				permethrin assigned value 151.5 µg/kg			
		result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
059		156	70	10	-0.2	77	82	10	-0.5	150	88	10	0.0
060		145	72	15	-0.5	#				244	61	15	**2.9**
061		102.0	90	20	-1.8	56.1	88	20	-1.6	114.5	86	50	-1.1
062		156.32	101.71	10.0	-0.2	87.76	101.96	10.0	0.1	157.88	96.62	10.0	0.2
063		206	86	4	1.2	#				134	80	1	-0.5
064		160		10	-0.1	81		10	-0.2	150		10	0.0
065		153		10	-0.3	53		10	-1.7	106		10	-1.4
066		181	79	10	0.5	114	91	10	1.5	231	79	10	**2.5**
067		185	99.2	10	0.6	100	92.2	10	0.8	188	102.0	20	1.1
068		282.95	100	2.4	**3.5**	77.78	100	1.9	-0.4	742.98	100	17	**18.4**
069		188	100	13	0.7	106	110	7	1.1	186	117	12	1.1
070		139.2	70-110	10.0	-0.7	#				213.0	70-110	10.0	1.9
071		102	85	20	-1.8	#				#			
072		88	71	10	**-2.2**	52	68	10	-1.8	61	69	10	**-2.8**
073		157	82.5	10	-0.2	85	92	50	0.0	158	89	50	0.2
074		145		10	-0.5	83		10	-0.1	94		10	-1.8
075		176	95	5	0.4	94	105	5	0.4	175	115	10	0.7
076		145	85	5	-0.5	71	88	10	-0.8	156	92	10	0.1
077		140	101	10	-0.7	65	101	10	-1.1	137	101	60	-0.4
078		236.5	104.8	17	**2.1**	114.2	99.3	9	1.5	0	97.5 / 95.7	27 / 15	**-4.7**
079		157	80	10	-0.2	44.3	80	20	**-2.2**	75.9	75	50	**-2.3**
080		202	110	10	1.1	94	81	10	0.4	144	91	10	-0.2
081		110	97	20	-1.6	80	90	20	-0.3	140	93	20	-0.4
082		140	95	10	-0.7	70	76	10	-0.8	90	77	10	-1.9
083	†	156.3	76.3	10	-0.2	85.4	75.9	10	0.0	162.8	76.6	10	0.4
084		150	90	5	-0.4	100	90	5	0.8	200	90	5	1.5
085		218.60	99	6.00	1.6	80.80	104	10.00	-0.3	168.30	100	10.00	0.5
086		190	103.9	10	0.8	50	98.2	5	-1.9	130	100.6	20	-0.7
087		44.57*	99	50	**-3.5**	8.81*	90.5	10	**-4.1**	49.41*	85.32	50	**-3.2**

= pesticide not analysed for
z-scores where |z| <2 are highlighted in **bold**
* = result < LoQ

† = additional pesticides identified > 25 µg/kg
LoQ = limit of quantification

Table 1 (Continued): Results and z-Scores, Wheat Flour Test Material

laboratory number		chlorpyrifos assigned value 163.5 µg/kg				bifenthrin assigned value 85.6 µg/kg				permethrin assigned value 151.5 µg/kg			
		result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
088		205.14	89	5	1.2	#				95.98	92	5	-1.7
089	†	6842952	0.007	0.50	**199192.8**	#				#			
090		239	115	50	**2.2**	104	109	50	1.0	179	115	50	0.9
091		182	90		0.5	97			0.6	231			**2.5**
092		202	48.5		1.1	95	39.5		0.5	207	56.4		1.7
093		92.3	90	10	**-2.1**	81.1	90	10	-0.2	216	90	10	2.0
094		180	104	10	0.5	76	90	10	-0.5	#			
095		148	97	5	-0.5	75	87	5	-0.6	114	105	10	-1.2
096		118	110	10	-1.3	78.2	113	20	-0.4	94.5	82.2	30	-1.8
097		164	84.4	5	0.0	84	94.8	5	-0.1	188	116.5	5	1.1
098		158	87.5	5	-0.2	82	88.3	5	-0.2	186	107.8	5	1.1
099		160	96.4	5	-0.1	94	103.6	5	0.4	213	106.7	5	1.9
100		182.0	87.5	10.0	0.5	82.5	81.8	20.0	-0.2	134.0	104.0	20.0	-0.5
101		179	96	10	0.5	79	83	10	-0.3	166	96	10	0.5
102		0.19	85.8	0.01	**-4.8**	0.09	84.0	0.01	**-4.5**	0.22	104.4	0.01	**-4.7**
103		0		10	**-4.8**	0		10	**-4.5**	0		10	**-4.7**
104		199	98	30	1.0	70.5*	84	100	-0.8	125	105	50	-0.8
105		168	93	10	0.1	104	111	50	1.0	337	106	50	**5.8**
106		110.00	64.00	1.00	-1.6	#				87.00	61.00	3.00	-2.0
107		110	78	35	-1.6	#				#			
108	†	0			**-4.8**	66.78	86	10	-1.0	130.59	88	20	-0.6
109		185		5	0.6	97.3		5	0.6	180		5	0.9
110		180	101	10	0.5	80	91	10	-0.3	140	93	10	-0.4
111		156.9	81	8	-0.2	93.4	112	8	0.4	140.4	81	8	-0.3
112		154		10	-0.3	102		5	0.9	144		20	-0.2
113		183.0	90	<10	0.6	111.6	90	<10	1.4	577.0	90	<30	**13.2**
114		133.5	76	50	-0.9	#				#			
115	†	133.8	98	20	-0.9	#				636.5	58	20	**15.1**
116		199	82.1	10	1.0	94	99.7	2	0.4	209	89.9	10	1.8

= pesticide not analysed for
z-scores where |z| <2 are highlighted in **bold**
* = result < LoQ

† = additional pesticides identified > 25 µg/kg
LoQ = limit of quantification

Table 1 (Continued): Results and z-Scores, Wheat Flour Test Material

laboratory number		chlorpyrifos assigned value 163.5 µg/kg				bifenthrin assigned value 85.6 µg/kg				permethrin assigned value 151.5 µg/kg			
		result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
117		203.2	142	5	1.2	64.7	63	10	-1.1	146.2	71	20	-0.2
118		171	101	50	0.2	108	111	50	1.2	180	115	50	0.9
119		0.129	78	0.01	**-4.8**	0		0.02	**-4.5**	0.157	82	0.02	**-4.7**
120		184	99	10	0.6	74	72	10	-0.6	114	90	10	-1.2
121		279	106	10	**3.4**	168	70	20	**4.4**	321	104	20	**5.3**
122		172	108	10	0.2	76	87	10	-0.5	125	105	10	-0.8
123		218.36		8	1.6	76.68		10	-0.5	140.14		30	-0.4
124		200	100	10	1.1	110	100	10	1.3	100	100	10	-1.6
125		134.00	106	20	-0.9	62.50	85	20	-1.2	84.82	61	70	**-2.1**
126		147	90	5	-0.5	67	73	5	-1.0	141	70	10	-0.3
127		230	86	10	1.9	200	75	10	**6.1**	160	81	10	0.3
128		0.31	80	0.01	**-4.8**	0			**-4.5**	0.68	80	0.01	**-4.7**
129	†	170		5	0.2	90		20	0.2	125		20	-0.8
130		210	80	10	1.4	100	80	10	0.8	120	80	10	-1.0
131		0		10	**-4.8**	#				64	81	10	**-2.7**
132		136	89.90	10	-0.8	74	82.75	10	-0.6	#			
133		185	104	50	0.6	73	83	50	-0.7	129	92	50	-0.7
134		160.34	95.02	0.70	-0.1	#				215.43	97.25	32.75	2.0
135		40	95	10	**-3.6**	#				22	104	10	**-4.0**
136		164		10	0.0	58		10	-1.5	148		30	-0.1
137		77	101	14	**-2.5**	49*	79	50	-1.9	76	75	15	**-2.3**
138		670	85	5	**14.7**	300	85	10	**11.4**	474	85	10	**10.0**

= pesticide not analysed for
z-scores where |z| <2 are highlighted in **bold**
* = result < LoQ
† = additional pesticides identified > 25 µg/kg
LoQ = limit of quantification

Table 2: Additional Pesticides Identified in Wheat Flour Test Material

laboratory number	additional pesticides (>25 µg/kg)	result µg/kg	recovery %	LoQ µg/kg
032	lambda-cyhalothrin	106		5
083	lambda-cyhalothrin	52.9	115	20
089	chlorpyrifos-methyl	296100	3.784	0.10
089	diazinon	14316	81.046	0.10
089	dichlorvos	7392	0.109	0.10
089	fenitrothion	174340	65.301	0.10
089	malathion	14184	115.043	0.050
089	methacrifos	75108	95.93	0.50
089	phosphamidon	296100	96.167	0.10
089	deltamethrin	10641	0.109	0.10
108	chlorpyrifos-methyl	165.61	92	10
115	diazinon	80.0	102	20
129	phosmet	105		20

Table 3: Assigned Values and Target Standard Deviations

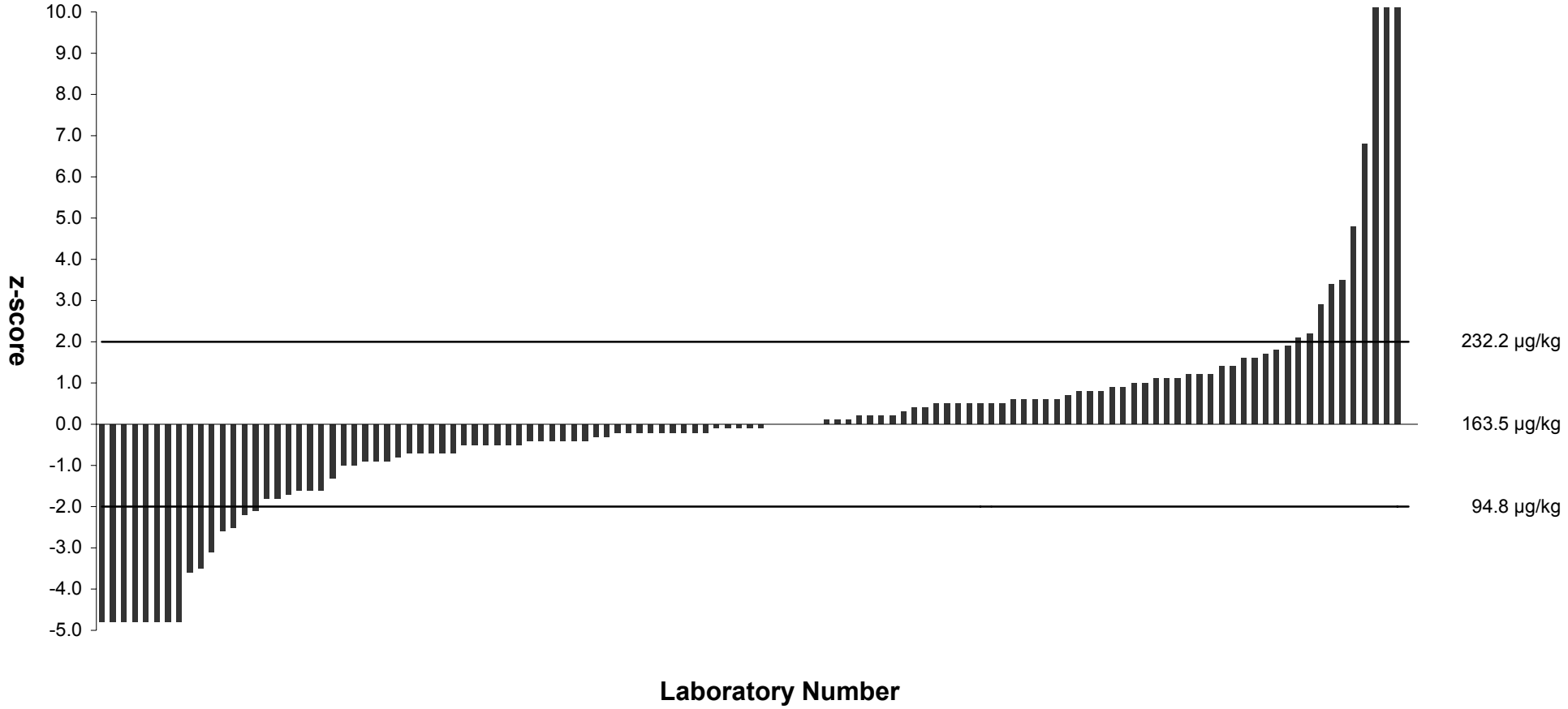
analyte	assigned value µg/kg				target standard deviation	
	data points *n*	robust mean $\hat{X}$	robust sd $\hat{\sigma}$	uncertainty *u*	derived from	σ_p
chlorpyrifos	86	163.5	38.7	4.17	Horwitz*	34.4
bifenthrin	59	85.6	19.8	2.58	Horwitz*	18.8
permethrin	70	151.5	47.1	5.63	Horwitz*	32.2

Table 4: Number and Percentage of Satisfactory z-Scores

analyte	number of satisfactory scores $\|z\| \leq 2$	total number of scores	satisfactory %
chlorpyrifos	94	119	79
bifenthrin	79	96	82
permethrin	76	110	69

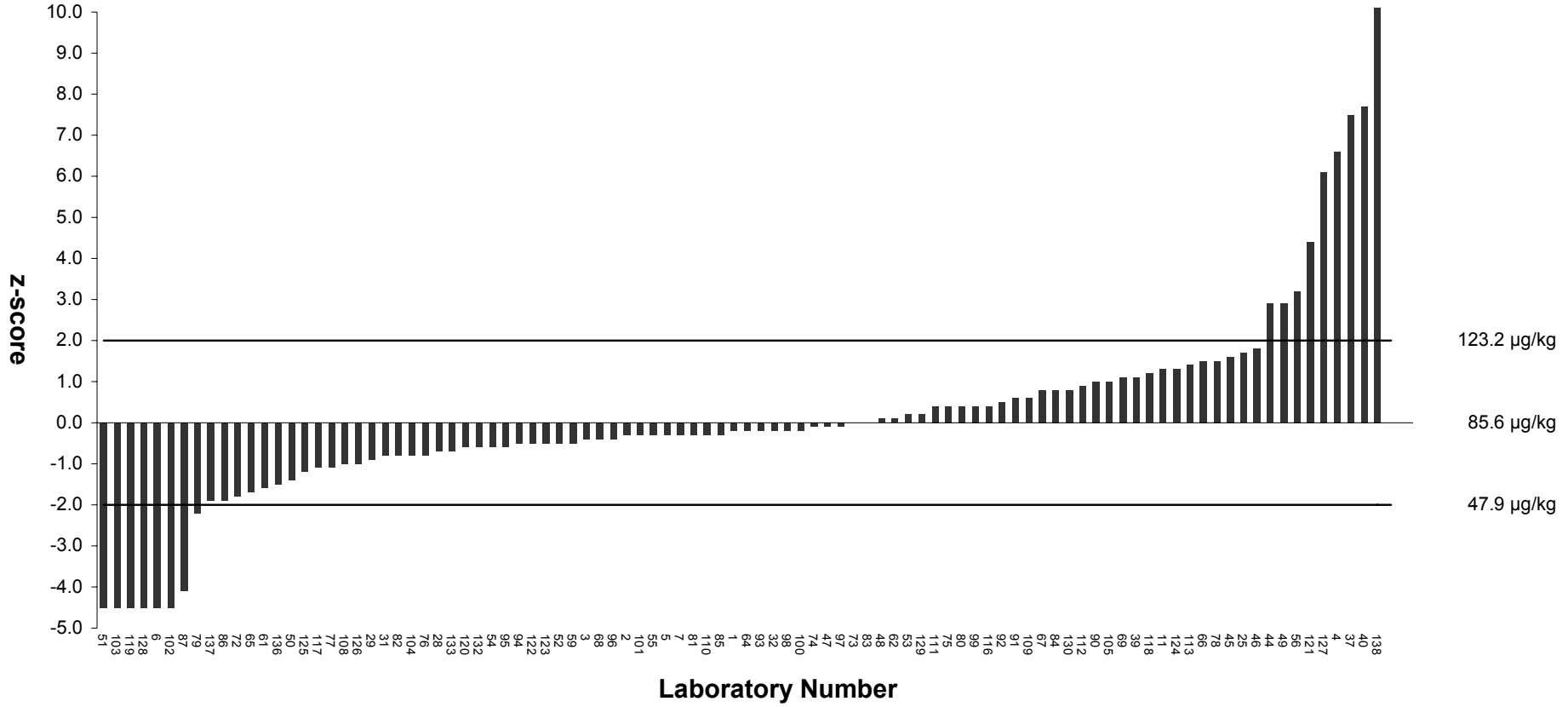
Table 5: Number and Percentage of Participants Correctly Identifying and Obtaining Satisfactory z-Scores for all Pesticides Present >25 µg/kg

criteria	number of satisfactory participants	total number participants	satisfactory %
correctly identified all pesticides present	84	138	61
satisfactory z-scores for all pesticides present	55	138	40



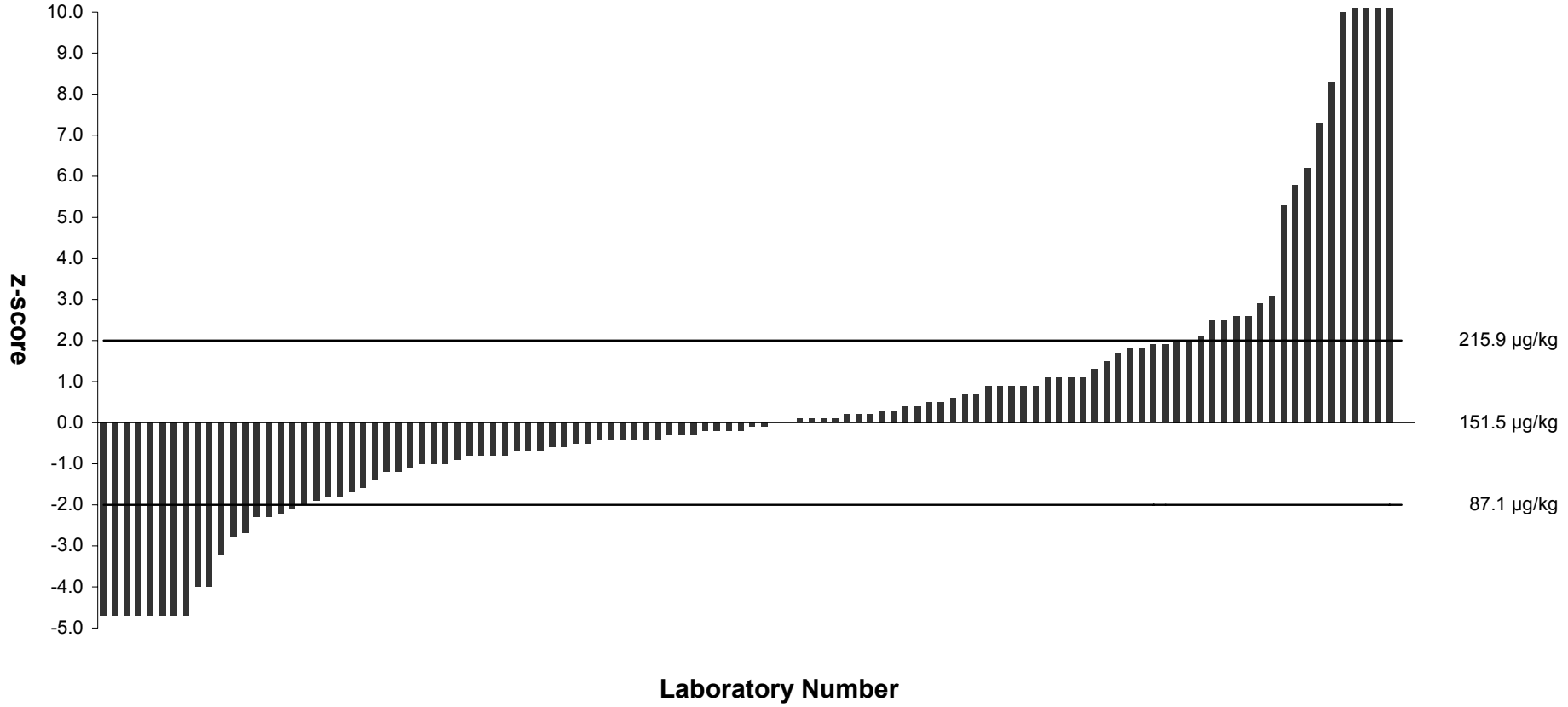
participants assigned a result of 0 µg/kg for chlorpyrifos obtain a z-score of -4.8

Figure 1: z-Scores for Chlorpyrifos (163.5 µg/kg) in Wheat Flour Test Material



participants assigned a result of 0 µg/kg for bifenthrin obtain a z-score of -4.5

Figure 2: z-Scores for Bifenthrin (85.6 µg/kg) in Wheat Flour Test Material



participants assigned a result of 0 µg/kg for permethrin obtain a z-score of -4.7

Figure 3: z-Scores for Permethrin (151.5 µg/kg) in Wheat Flour Test Material

APPENDIX I: Homogeneity Data for Wheat Flour Test Material

sample identity	analyte						
	chlorpyrifos µg/kg		bifenthrin µg/kg			permethrin µg/kg		
	replicate 1	replicate 2	replicate 1	replicate 2		replicate 1	replicate 2	
1	154.4	180.1	71.0	83.6	r	131.8	159.1	r
2	174.1	177.2	84.5	85.8		159.4	158.0	
3	175.5	193.9	81.6	87.9		151.4	163.2	
4	181.3	178.4	82.5	84.4		150.7	152.4	
5	190.8	170.6	83.0	79.6		148.0	145.8	
6	186.8	173.3	83.7	84.5		157.5	152.3	
7	178.4	172.9	83.6	79.9		141.4	153.5	
8	177.7	182.1	84.9	85.1		154.7	152.1	
9	175.5	173.7	83.7	81.5		149.2	150.8	
mean, *n*	177.6	18	83.5	16		152.5	16	
origin of target sd (σ_p)	Horwitz	original	Horwitz	<120ppb		Horwitz	original	
abs. target sd (σ_p) & as RSD%	36.85	20.75	18.37	22.00		32.38	21.23	
s_{an}	9.60		2.18			4.55		
s_{am}^2	0.00		0.00			8.50		
σ_{all}^2	122.20		30.38			94.36		
critical	339.45		66.98			215.58		
s_{am}^2<critical?	**ACCEPT**		**ACCEPT**			**ACCEPT**		

r =cochrans outlier

APPENDIX II: Analytical Methods Used by Participants

Notes:

1. Participants' methods are tabulated according to the information submitted electronically, but some responses may have been combined or edited for clarity.
2. Only methods relating to chlorpyrifos, bifenthrin and permethrin are tabulated.
3. Participants with performance(s) outside the satisfactory range, i.e. |z| >2, are no longer shown in **bold** in this section but their z-scores are now shown in **bold** in Table 1.

Chlorpyrifos

Is the Method used Accredited?	laboratory number
yes	001 002 003 004 005 008 010 025 026 028 031 033 034 035 037 039 044 046 047 048 049 050 052 055 056 057 062 063 064 066 067 068 069 070 073 075 076 077 078 082 083 084 090 091 093 094 095 096 097 098 099 100 101 102 104 105 106 110 112 116 117 120 122 123 124 125 126 128 129 130 132
no	006 011 016 029 036 054 058 060 071 072 074 079 080 081 085 086 087 089 092 109 114 115 118 119 121 133

Sample Weight (g)	laboratory number
≥1 - <2	063
≥2 - <5	003 004 006 010 028 029 031 033 034 035 040 046 060 062 070 106 123
≥5 - <10	036 047 048 056 061 067 068 081 082 089 090 102 109 113 120 121 127 128 130
≥10 - <25	001 008 011 016 026 037 039 049 050 052 054 055 057 059 064 065 066 069 071 073 074 075 077 079 080 083 084 086 087 088 091 092 093 094 095 097 098 099 100 101 105 107 110 112 114 115 116 118 119 122 124 129 132 133
≥25 - <50	005 025 058 076 078 096 104 125
≥50	002 044 072 085 117 126

Extraction Solvent	laboratory number
acetone	002 003 005 008 010 025 031 034 039 044 046 047 048 050 054 057 064 069 070 072 074 082 087 088 096 105 109 110 112 114 116 117 119 120 124 126 129 130 132
acetonitrile	001 004 006 016 029 033 036 037 040 049 065 066 067 071 078 079 080 081 083 084 085 086 092 094 095 097 098 099 102 107 121 126 127 133
cyclohexane	002 025 044 064 068 073 076 077 105 112 132
dichloromethane	005 046 047 050 054 062 096 115 117 119 123 132
diethyl ether	060
ethyl acetate	002 011 025 028 035 044 052 055 056 058 059 061 064 068 073 075 076 090 091 096 100 101 104 105 112 113 118 122 125 128
hexane	026 034 070 089 106
methanol	080 087
petroleum ether / spirit	046 050 063 132
water	008 010 046 079 086 112 114

Extraction pH Adjusted?	laboratory number
yes	028 049 089 095 105 116 121 124
no	001 002 003 004 005 006 008 010 011 016 025 026 029 031 033 034 035 036 037 039 040 044 046 047 048 050 052 054 055 056 057 058 059 060 061 062 063 064 065 066 067 068 069 070 071 072 073 074 075 076 077 078 079 080 081 082 083 084 085 086 087 088 090 091 092 093 094 096 097 098 099 100 101 102 104 106 107 109 110 112 113 114 115 117 118 119 120 122 123 125 126 127 128 129 130 132 133

Sample Clean-up Technique	laboratory number
Additional Cleanup with Charcoal & Alumina Acidic	087
alumina column	087
carbon based column	006 033 065 070 078 084 094

Sample Clean-up Technique (continued)	laboratory number
dispersive SPE with PSA	075
extraction	072 087 112
Extrelut	039 086 128
filter	058 063 113 119 122 132
florisil column	034 047 060 062 082 109 110 123 126
GPC / HPGPC	002 005 010 025 040 044 050 052 055 056 058 064 066 068 069 073 076 077 088 090 091 100 101 104 105 106 112 114 116 117 118 125
liquid / liquid extraction	016 031 055 057 069 074 082 084 087 096 097 098 099 110 112 114 115 120 124 129
NH_2 / aminopropyl column	001 049 085 094 097 098 099 127
PSA	066 067
QuEChERS	121
silica column	037 064 089 126
solid phase extraction (SPE)	003 004 008 011 028 048 059 061 071 080 081 084 085 086 092 095 097 098 099 102 133
none	026 035 036 046 054 079 083 107

SPE Column Type	laboratory number
alumina	029
C18	008 033 037 071 085 094 097 098 099 132 133
Envicarb / GCB	006 028 048 049 059 069 078
NH_2	001 003 039 092
silica	011 061 077 089 126
C18 / Envicarb / NH_2	016 081 086
C18 / Envicarb / PSA	004 095
C18 / NH_2	080
GCB / PSA	065
PSA	084 102

Were Certified Standards Used?	laboratory number
yes	001 002 003 004 005 008 010 011 016 025 026 028 029 031 033 034 035 036 037 039 040 044 046 047 048 049 050 054 055 056 057 058 059 060 061 062 063 064 065 066 067 068 069 070 071 072 073 074 075 076 077 078 079 080 084 085 086 087 089 091 093 094 095 096 097 098 099 100 101 102 104 105 106 107 109 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 132 133
no	006 052 081 082 083 088 090 092 110

MS Confirmation?	laboratory number
yes	001 002 003 004 005 006 008 016 025 028 033 037 040 044 046 047 048 049 050 052 054 055 056 058 059 060 061 062 065 066 067 068 069 072 073 074 075 077 078 080 081 083 084 085 086 088 089 090 093 095 097 098 099 100 101 102 104 105 109 110 113 114 115 116 117 118 120 121 122 124 125 126 127 128 130 132 133
no	010 011 026 029 031 034 035 036 039 057 063 064 070 071 076 079 082 087 091 092 094 096 106 107 112 119 123 129

Calibrations	laboratory number
matrix-matched	002 005 026 028 046 050 052 054 055 056 059 061 065 066 068 075 078 080 081 084 085 093 095 097 098 099 101 104 105 112 114 116 118 123 125 126 130
multi-level	001 002 008 016 025 028 029 031 033 034 035 036 044 046 047 048 049 050 054 055 056 060 061 063 068 069 070 072 074 077 079 080 082 084 085 086 090 091 092 097 098 099 102 105 106 109 110 113 115 116 118 121 122 123 125 127 128 129 132 133
single-level	004 005 006 011 037 039 057 058 062 064 067 071 076 081 083 088 090 093 100 107 112 114 117 130
solvent	003 010 025 044 057 058 064 067 069 071 073 076 082 091 096 100 117 120 122 127
standard addition	087 089 124

Is quoted percentage recovery measured in same analytical batch as test material?	laboratory number
yes	001 003 004 005 006 008 010 016 028 029 031 033 034 035 036 037 046 047 048 050 052 054 055 056 059 061 062 063 067 068 072 073 075 076 077 078 080 081 082 083 084 085 086 087 088 089 090 093 094 095 097 098 099 100 101 104 105 107 110 114 115 116 118 119 120 121 122 123 124 125 126 127 128 130 132 133
no	002 011 025 026 039 044 049 057 058 060 064 066 069 070 071 074 079 092 096 102 106 109 112 113 117 129

If measured in this batch, at what stage was the spike added?	laboratory number
prior to clean up	039 075 105 119
prior to extraction	001 003 004 005 006 008 010 016 028 029 031 033 034 035 036 037 046 047 048 050 052 054 055 056 059 061 062 063 067 068 069 071 072 073 076 077 078 080 081 082 083 084 085 086 087 088 089 090 093 094 097 098 099 100 101 102 104 107 110 113 114 115 116 118 120 122 123 124 125 126 127 128 133
prior to instrument measurement	121 130 132

Level Of Spike (µg/kg)	laboratory number
<25	003 006 008 029 044 054 059 061 068 087 089 102 128
≥25 - <50	059 063 078 088 100 105 118
≥50 - <100	061 075 076 084 085 093 097 098 099 101 107 113 114 120 121 122 127
≥100 - <150	001 004 005 008 010 028 031 035 037 046 047 050 056 067 069 071 073 076 080 082 083 086 095 110 115 117 119 126
≥150 - <200	016 034 036 039 055 066 116
≥200 - <250	048 081 090
≥250 - <300	124
≥300 - <400	057
≥400 - <500	052 062 077 104 125
≥500	033 094 130 133

Composition Of Blank Commodity Used For Spiking	laboratory number
barley	078
blank provided	001 004 005 006 010 028 029 031 035 046 047 048 049 055 057 059 061 062 063 068 069 075 081 084 087 088 093 094 095 098 099 100 104 105 113 114 115 117 118 122 123 128 132
cucumber	002
flour	067
maize flour	120
own blank	066 073
prepared matrix	121
pure solvent	089
rice flour	054 133
test material provided	003 033 034 039 050 077 090 097 119 124 127
wheat	016 076 085
wheat flour	008 044 052 056 071 080 082 101 110 116 125

GC Column Type	laboratory number
capillary	002 003 004 006 010 011 016 025 026 028 029 031 035 036 037 039 040 044 047 048 049 050 052 054 055 056 057 058 060 061 062 063 066 068 070 071 072 073 075 076 079 080 081 082 084 085 087 088 089 091 092 094 095 096 097 098 099 101 102 104 105 107 109 110 112 113 114 115 116 117 118 119 120 121 122 126 127 128 130 132 133
megabore	065 069 086 129
narrowbore <0.53 mm id	005 033 034 059 064 067 077 078 083 090 093 100 123 125
packed	001

GC Column Packing	laboratory number
100% methyl polysiloxane	058 068 089 126
14% cyanopropylphenyl 86%methyl polysiloxane	016 034 036 037 059 069 086 090 097 098 099 104 105 107 117 120 127
50% methyl 50% phenyl polysiloxane	035 039 052 055 057 060 102 106
65% methyl 35% phenyl polysiloxane	002 076 091 093
95% methyl 5% phenyl polysiloxane	001 002 003 004 005 006 010 011 025 028 029 033 040 044 047 048 049 050 054 056 057 061 062 063 064 065 066 067 070 072 073 075 076 077 079 080 081 083 084 085 087 088 092 093 094 095 096 100 101 105 109 112 113 114 115 116 117 118 120 122 123 124 125 128 129 130 133
trifluoropropyl methylpolysiloxane	082 110
OP Pesticide Specific	071
EPA Method 608 Specific	062
Varian VF	121

GC Injection Volume (µL)	laboratory number
<1	063 089
≥1 - <2	002 010 016 028 031 033 034 035 036 037 040 044 047 048 052 054 055 057 059 060 062 066 067 071 075 078 079 080 084 085 088 090 091 093 097 098 099 100 101 105 106 107 109 112 113 115 116 117 118 119 120 123 124 125 126 127 128 129 130 133
≥2 - <5	003 005 006 011 025 026 029 039 049 050 056 058 061 064 065 069 070 076 081 082 086 087 092 094 095 096 102 104 110 114 122
≥5 - <10	068 073 121
≥10	001 004 077 083 132

GC Injection Mode	laboratory number
CAS	067
on-column	010 055 073 089 117 121 129
PTV	001 004 058 068 076 083 124 127 128 130
pulse splitless	096
pulsed splitless	101
split	002 037 069 105 132
splitless	003 005 006 011 016 025 028 029 031 033 034 035 036 039 044 047 048 050 052 054 056 057 059 060 061 062 063 064 065 066 070 075 077 078 079 080 081 082 084 085 086 087 088 090 091 092 093 094 095 097 098 099 100 102 104 106 107 109 110 112 113 114 115 116 118 119 120 122 123 125 126 133

GC Detector	laboratory number
ECD	002 010 011 025 029 033 034 040 044 057 062 075 076 077 079 087 093 100 101 104 105 112 114 118 120 126
FID	087

GC Detector (continued)	laboratory number
FPD	010 011 016 025 026 034 035 036 037 039 054 062 064 069 073 076 082 084 085 086 090 091 093 097 098 099 102 106 110 112 118 120 125 133
HR-MS	044 113
ITD	056 058 066
MS	001 003 004 005 006 025 028 047 048 049 050 059 061 062 065 067 075 077 078 080 081 083 090 093 094 095 096 101 109 115 116 118 122 124 126 127 128 130 133
MS-MS	060 068 075 081 088 092 105 121 132
NPD	011 031 044 052 055 057 063 070 071 076 077 079 089 100 101 107 114 117 119 123 125 126 129

HPLC Column Packing	laboratory number
C18	008 046 074 121
endcapped	046
Waters Atlandis	105

HPLC Guard Column Used?	laboratory number
yes	008 046 074 105 121
no	006 016 029 034 063 087 089 128 130

Mobile Phase Programme	laboratory number
gradient	006 008 046 074 105 121 130

Mobile Phase Components	laboratory number
acetic acid	121
acetonitrile	074 121
ammonium formate	046
formic acid	074
methanol	008 046 105 121
water	008 046 105

HPLC Column Temperature (°C)	laboratory number
ambient	008
>ambient - <50	046 074 105 121

HPLC Injection Volume (µL)	laboratory number
≥5 - <10	046
≥10 - <25	008 105
≥50 - <100	121
≥100 - <150	074

Mobile Phase Flow Rate (mL/min)	laboratory number
<0.25	074 121
≥0.25 - <0.75	008 046 105

HPLC Detector Type	laboratory number
MS-MS	008 046 074 105 121

Bifenthrin

Is the Method used Accredited?	laboratory number
yes	001 002 003 004 005 025 028 031 037 039 044 046 047 048 049 050 052 055 056 062 064 066 067 068 069 073 074 075 076 077 078 082 083 084 090 091 093 094 095 096 097 098 099 100 101 102 104 105 108 110 112 116 117 120 122 123 124 125 126 129 130 132
no	006 011 029 054 072 079 080 081 085 086 087 092 109 118 121 133

Sample Weight (g)	laboratory number
≥2 - <5	003 004 006 028 029 040 046 062 123
≥5 - <10	031 047 048 056 061 067 068 081 082 090 102 109 113 120 121 127 130
≥10 - <25	001 011 037 039 049 050 052 054 055 059 064 065 066 069 073 074 075 077 079 080 083 084 086 087 091 092 093 094 095 097 098 099 100 101 105 108 110 112 116 118 122 124 129 132 133
≥25 - <50	005 025 076 078 096 104 125
≥50	002 044 072 085 126

Extraction Solvent	laboratory number
acetone	002 003 005 025 039 044 046 047 048 050 054 064 069 072 074 082 087 096 105 108 109 110 112 116 117 120 124 126 129 130 132
acetonitrile	001 004 006 029 037 040 049 065 066 067 078 079 080 081 083 084 085 086 092 094 095 097 098 099 102 121 126 127 133
cyclohexane	002 025 044 064 068 076 077 105 108 112 132
dichloromethane	005 046 047 050 054 062 096 117 123 132

Extraction Solvent (continued)	laboratory number
ethyl acetate	002 011 025 028 044 052 055 056 059 061 064 068 075 076 090 091 096 100 101 104 105 108 112 113 118 122 125
hexane	073
methanol	080 087
petroleum ether / spirit	031 046 050 132
water	046 079 086 112

Extraction pH Adjusted?	laboratory number
yes	028 049 095 105 116 121 124
no	001 002 003 004 005 006 011 025 029 031 037 039 040 044 046 047 048 050 052 054 055 056 059 061 062 064 065 066 067 068 069 072 073 074 075 076 077 078 079 080 081 082 083 084 085 086 087 090 091 092 093 094 096 097 098 099 100 101 102 104 108 109 110 112 113 117 118 120 122 123 125 126 127 129 130 132 133

Sample Clean-up Technique	laboratory number
Additional Cleanup with Charcoal & Alumina Acidic	087
alumina column	087
carbon based column	006 065 078 082 084 094
dispersive SPE with PSA	075
Extrelut	039 086
filter	113 122 132
florisil column	031 047 062 082 090 109 110 123 126
GPC/HPGPC	002 005 025 040 044 050 052 055 056 064 066 068 069 076 077 090 091 100 101 104 105 108 112 116 117 118 125

Sample Clean-up Technique	laboratory number
liquid / liquid extraction	055 069 074 082 084 087 096 097 098 099 110 112 120 124 129
NH_2 / aminopropyl column	001 049 085 094 097 098 099 127
PSA	066 067
QuEChERS	121
silica column	037 064 126
solid phase extraction (SPE)	003 004 011 028 048 054 059 061 073 080 081 084 085 092 095 097 098 099 102 133
none	046 079 083

SPE Column Type	laboratory number
alumina	029
C18	037 085 094 097 098 099 132 133
C18 / Envicarb / NH_2	081 086
C18 / GC-PSA	095
C18 / NH_2	080
C18 / Envicarb / PSA	004
Envicarb / GCB	006 028 048 049 059 069 078
GCB/PSA	065
NH_2	001 003 039 092
PSA	084 102
silica	011 054 061 073 077 126

Were Certified Standards Used?	laboratory number
yes	001 002 003 004 005 011 025 028 029 031 037 039 040 044 046 047 048 049 050 054 055 056 059 061 062 064 065 066 067 068 069 072 073 074 075 076 077 078 079 080 084 085 086 087 091 093 094 095 096 097 098 099 100 101 102 104 105 108 109 112 113 116 117 118 120 121 122 123 124 125 126 127 129 130 132 133
no	006 052 081 082 083 090 092 110

MS Confirmation?	laboratory number
yes	001 002 003 004 005 006 025 028 037 040 044 046 047 048 049 050 052 054 055 056 059 061 062 065 066 067 068 069 072 073 074 075 077 078 080 081 083 084 085 086 090 093 094 095 097 098 099 100 101 102 104 105 109 110 113 116 117 118 120 121 122 124 125 126 127 130 132 133
no	011 029 031 039 064 076 079 082 087 091 092 096 108 112 123 129

Calibrations	laboratory number
matrix-matched	002 005 028 046 050 052 055 056 059 061 065 066 068 075 078 080 081 084 085 093 095 097 098 099 101 104 105 116 118 123 125 126 130
multi-level	001 002 025 028 029 031 044 046 047 048 049 050 054 055 056 061 068 069 072 074 077 079 080 082 084 085 086 090 091 092 094 097 098 099 102 105 108 109 110 113 116 118 121 122 123 125 127 129 132 133
single-level	004 005 006 011 037 039 062 064 067 076 081 083 090 093 100 112 117 130
solvent	003 025 044 064 067 069 073 076 082 091 096 100 112 117 120 122 127
standard addition	087 124

Is quoted percentage recovery measured in same analytical batch as test material?	laboratory number
yes	001 003 004 005 006 028 029 031 037 046 047 048 050 054 055 056 059 061 062 067 068 072 073 075 076 077 078 080 081 082 083 084 085 086 087 090 093 094 095 097 098 099 100 101 104 105 108 110 116 118 120 121 122 123 124 125 126 127 130 132 133
no	002 011 025 039 044 049 052 064 066 069 074 079 092 096 102 109 112 113 117 129

If measured in this batch, at what stage was the spike added?	laboratory number
prior to clean up	039 075 105
prior to extraction	001 003 004 005 006 028 029 031 037 046 047 048 050 054 055 056 059 061 062 067 068 069 072 073 076 077 078 080 081 082 083 084 085 086 087 090 093 094 097 098 099 100 101 102 104 110 113 116 118 120 122 123 124 125 126 127 133
prior to instrument measurement	121 130 132

Level Of Spike (µg/kg)	laboratory number
<25	003 006 029 044 054 059 061 068 075 087 102
≥25 - <50	059 078 100 105 108 118
≥50 - <100	031 061 067 076 084 085 093 097 098 099 101 104 113 120 121 122 127
≥100 - <150	001 004 005 028 037 047 050 056 069 073 076 080 082 083 086 095 110 117 126
≥150 - <200	039 055 066 116
≥200 - <250	048 062 081 090 125
≥250 - <300	124
≥200 - <250	048 062 081 090 125
≥400 - <500	046 077
≥500	094 130 133

Composition Of Blank Commodity Used For Spiking	laboratory number
barley	078
blank provided	001 004 005 006 028 029 031 046 047 048 049 055 059 061 062 068 069 075 081 084 087 093 094 095 098 099 100 104 105 108 113 117 118 122 123 132
cucumber	002
flour	067
maize flour	120
own blank	066 073

Composition Of Blank Commodity Used For Spiking (continued)	laboratory number
prepared matrix	121
rice flour	054 133
test material provided	003 039 050 077 090 097 124 127
wheat	076 085
wheat flour	044 056 080 082 101 110 116 125

GC Column Type	laboratory number
capillary	002 003 004 006 011 025 028 029 031 037 039 040 044 046 047 048 049 050 052 054 055 056 061 062 066 068 069 072 073 075 076 079 080 081 082 084 085 086 087 090 092 094 095 096 097 098 099 101 102 104 105 108 109 110 112 113 116 117 118 120 121 122 126 127 130 132 133
megabore	065 129
narrowbore <0.53 mm id	005 059 064 067 077 078 083 093 100 123 125
packed	001
widebore	091

GC Column Packing	laboratory number
100% methyl polysiloxane	064 068 126
14% cyanopropylphenyl 86%methyl polysiloxane	031 059 091 104 105 117 120 127
65% methyl 35% phenyl polysiloxane	002 052 076 090 093
95% methyl 5% phenyl polysiloxane	001 002 003 004 005 006 011 025 028 029 037 039 040 044 046 047 048 049 050 054 055 056 061 062 065 066 067 069 072 075 076 077 079 080 081 082 083 084 085 086 087 090 092 093 094 095 096 097 098 099 100 101 102 105 108 109 110 112 113 116 117 118 120 122 123 124 125 129 130 133
CL Pesticide Specific	073
Varian VF	121

GC Injection Volume (µL)	laboratory number
≥1 - <2	002 025 028 031 037 040 044 047 048 052 054 055 059 062 066 067 069 075 078 079 080 084 085 090 091 093 100 101 105 109 112 113 116 117 118 120 123 124 125 126 127 129 130 133
≥2 - <5	003 005 006 011 029 039 046 049 050 056 061 064 065 076 081 082 086 087 092 094 095 096 097 098 099 102 104 108 110 122
≥5 - <10	068 073 121
≥10	001 004 077 083 132

GC Injection Mode	laboratory number
on-column	073 091 121 129
PTV	001 004 068 076 083 124 127 130
split	002 025 037 064 105 117 132
splitless	003 005 006 011 028 029 031 039 044 047 048 050 052 054 055 056 059 061 062 065 066 069 075 077 078 079 080 081 082 084 085 086 087 090 092 093 094 095 097 098 099 100 102 104 108 109 110 112 113 116 118 120 122 123 125 126 133
CAS	067
pulsed splitless	096 101

GC Detector	laboratory number
ECD	002 011 025 029 031 037 039 040 044 052 054 055 062 064 073 075 076 077 079 082 085 087 090 091 093 100 101 104 105 108 112 117 118 120 123 125 126 129
FPD	076 093 108 118 120 133
HR-MS	044 113
ITD	046 056 066
MS	001 003 004 005 006 028 047 048 049 050 059 061 062 065 067 069 075 077 078 080 081 083 084 086 090 093 094 095 096 097 098 099 101 102 109 110 116 118 122 124 126 127 130 133
MS-MS	068 075 081 092 121 132
NPD	044 076 077 079 100 101 126

HPLC Column Packing	laboratory number
C18	074 121

HPLC Guard Column Used?	laboratory number
yes	046 074 121
no	006 029 087 130

Mobile Phase Programme	laboratory number
gradient	006 046 074 121 130

Mobile Phase Components	laboratory number
acetic acid	121
acetonitrile	121
ammonium acetate 25 mM	074
methanol	074 121

HPLC Column Temperature (°C)	laboratory number
>ambient - <50	074 121

HPLC Injection Volume (µL)	laboratory number
≥10 - <25	074
≥50 - <100	121

Mobile Phase Flow Rate (mL/min)	laboratory number
<0.25	074 121

HPLC Detector Type	laboratory number
MS-MS	074 121

Permethrin (Sum Isomers)

Is the Method used Accredited?	laboratory number
yes	001 002 003 004 005 010 025 026 028 031 034 035 037 039 044 046 047 048 049 050 051 052 055 056 057 062 063 064 066 067 068 069 070 073 075 076 077 082 083 084 090 091 093 095 096 097 098 099 100 101 102 104 105 106 108 110 112 116 117 120 122 123 124 125 126 128 129 130
no	006 011 029 054 058 060 072 074 079 080 081 085 086 087 092 109 115 118 119 121 133

Sample Weight (g)	laboratory number
≥1 - <2	063
≥2 - <5	003 004 006 010 028 029 034 040 046 060 062 070 106 123
≥5 - <10	031 035 047 048 056 061 067 068 081 082 090 102 109 113 120 121 127 128 130
≥10 - <25	001 011 037 039 049 050 052 054 055 057 059 064 065 066 069 073 074 075 077 079 080 083 084 086 087 088 091 092 093 095 097 098 099 100 101 105 108 110 112 115 116 118 119 122 124 129 133
≥25 - <50	005 025 058 076 096 104 125
≥50	002 044 051 072 085 126

Extraction Solvent	laboratory number
acetone	002 003 005 010 025 034 035 039 044 046 047 048 050 054 057 064 069 070 072 074 082 087 088 096 105 108 109 110 112 116 117 119 120 124 126 129 130
acetonitrile	001 004 006 029 037 040 049 051 065 066 067 079 080 081 083 084 085 086 092 095 097 098 099 102 121 126 127 133
cyclohexane	002 025 044 064 068 076 077 096 105 108 112
dichloromethane	005 046 047 050 054 062 115 117 119 123
diethyl ether	060
ethyl acetate	002 011 025 028 044 052 055 056 058 059 061 064 068 075 076 090 091 096 100 101 104 105 108 112 113 118 122 125 128
hexane	026 034 070 073 106
methanol	080 087
petroleum ether / spirit	031 035 046 050 063
water	010 046 079 086 112

Extraction pH Adjusted?	laboratory number
yes	028 049 095 105 116 121 124
no	001 002 003 004 005 006 010 011 025 026 029 031 034 035 037 039 040 044 046 047 048 050 051 052 054 055 056 057 058 059 060 061 062 063 064 065 066 067 068 069 070 072 073 074 075 076 077 079 080 081 082 083 084 085 086 087 088 090 091 092 093 096 097 098 099 100 101 102 104 106 108 109 110 112 113 115 117 118 119 120 122 123 125 126 127 128 129 130 133

Sample Clean-up Technique	laboratory number
Additional Cleanup with Charcoal & Alumina Acidic	087
alumina column	026 087
carbon based column	006 065 082 084
dispersive SPE with PSA	075

Sample Clean-up Technique (continued)	laboratory number
extraction	072 087 112
Extrelut	039 086 128
filter	051 058 113 119 122
florisil column	031 034 035 047 060 062 063 070 082 090 109 110 123 126
GPC	105
GPC/HPGPC	002 005 010 025 040 044 050 052 055 056 058 064 066 068 069 076 077 088 090 091 100 101 104 106 108 112 116 117 118 125
liquid / liquid extraction	055 057 069 074 082 084 087 096 097 098 099 110 112 115 120 124 129
NH_2 / aminopropyl column	001 049 085 097 098 099 127
PSA	066 067
QuEChERS	121
silica column	037 064 126
solid phase extraction (SPE)	003 004 011 028 048 054 059 061 073 080 081 084 085 092 095 097 098 099 102 133
none	046 079 083

SPE Column Type	laboratory number
alumina	029
C18	037 085 097 098 099 133
C18 / Envicarb / NH_2	081 086
C18 / GCB-PSA	095
C18 / NH_2	080
C18 / Envicarb / PSA	004
Envicarb / GCB	006 028 048 049 059 069
florisil	051

SPE Column Type (continued)	laboratory number
GCB / PSA	065
NH_2	001 003 039 092
PSA	084 102
silica	011 054 061 073 077 126

Were Certified Standards Used?	laboratory number
yes	001 002 003 004 005 010 011 025 026 028 029 031 034 035 037 039 040 044 046 047 048 049 050 051 054 055 056 057 058 059 060 061 062 063 064 065 066 067 068 069 070 072 073 074 075 076 077 079 080 084 085 086 087 091 093 095 096 097 098 099 100 101 102 104 105 106 108 109 112 113 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 133
no	006 052 081 082 083 088 090 092 110

MS Confirmation?	laboratory number
yes	001 002 003 004 005 006 025 028 037 040 044 046 047 048 049 050 051 052 054 055 056 058 059 060 061 062 065 066 067 068 069 072 073 074 075 077 080 081 083 084 085 086 088 090 093 095 097 098 099 100 101 102 104 105 109 110 113 115 116 117 118 120 121 122 124 125 126 127 128 130 133
no	010 011 026 029 031 034 035 039 057 063 064 070 076 079 082 087 091 092 096 106 108 112 119 123 129

Calibrations	laboratory number
matrix-matched	002 005 026 028 046 050 052 055 056 059 061 065 066 068 075 080 081 084 085 093 095 097 098 099 101 104 105 116 118 123 125 126 130
multi-level	001 002 025 028 029 031 034 044 046 047 048 049 050 054 055 056 060 061 063 068 069 070 072 074 077 079 080 082 084 085 086 090 091 097 098 099 102 105 106 108 109 110 113 115 116 118 121 122 123 125 127 128 129 133

Calibrations (continued)	laboratory number
single-level	004 005 006 011 035 037 039 051 057 058 062 064 067 076 081 083 088 090 093 100 112 117 130
solvent	003 010 025 044 057 058 064 067 069 073 076 082 091 096 100 112 117 120 122 127
standard addition	087 124

Is quoted percentage recovery measured in same analytical batch as test material?	laboratory number
yes	001 003 004 005 006 010 028 029 031 034 035 037 046 047 048 050 051 052 054 055 056 059 061 062 063 067 068 072 073 075 076 077 080 081 082 083 084 085 086 087 088 090 093 095 097 098 099 100 101 104 105 108 110 115 116 118 119 120 121 122 123 124 125 126 127 128 130 133
no	002 011 025 026 039 044 049 057 058 060 064 066 069 070 074 079 092 096 102 106 109 112 113 117 129

If measured in this batch, at what stage was the spike added?	laboratory number
prior to clean up	039 075 105 119
prior to extraction	001 003 004 005 006 010 028 029 031 034 035 037 046 047 048 050 051 052 054 055 056 059 061 062 063 067 068 069 072 073 076 077 080 081 082 083 084 085 086 087 088 090 093 097 098 099 100 101 102 104 110 113 115 116 118 120 122 123 124 125 126 127 128 133
prior to instrument measurement	121 130

Level Of Spike (µg/kg)	laboratory number
<25	003 006 029 044 054 059 061 068 075 087 102 128
≥25 - <50	059 063 088 100 105 108 118
≥50 - <100	051 061 076 084 085 093 097 098 099 101 104 113 120 121 122 127

Level Of Spike (µg/kg) (continued)	laboratory number
≥100 - <150	001 004 005 010 028 031 035 037 047 050 056 067 069 073 076 080 082 083 086 095 110 115 117 119 126
≥150 - <200	034 039 055 066 116
≥200 - <250	048 081 090
≥250 - <300	124
≥400 - <500	046 052 062 077
≥500	057 125 130 133

Composition Of Blank Commodity Used For Spiking	laboratory number
blank provided	001 004 005 006 010 028 029 031 035 046 047 048 049 051 055 057 059 061 062 068 069 075 081 084 087 088 093 095 098 099 100 104 105 108 113 115 117 118 122 123 128
cucumber	002
flour	067
maize flour	120
own blank	066 073
prepared matrix	121
rice flour	133 054
test material provided	003 034 039 050 063 077 090 097 119 124 127
wheat	076 085
wheat flour	044 052 056 080 082 101 110 116 125

GC Column Type	laboratory number
capillary	002 003 004 006 010 011 025 026 028 029 031 035 037 039 040 044 046 047 048 049 050 051 052 054 055 056 057 058 060 061 062 063 066 068 070 072 073 075 076 079 080 081 082 084 085 086 087 088 090 092 095 096 097 098 099 101 102 104 105 106 108 109 110 112 113 115 116 117 118 119 120 121 122 126 127 128 130 133
megabore	065 069 129
narrowbore <0.53 mm id	005 034 059 064 067 077 083 093 100 123 125
packed	001
widebore	091

GC Column Packing	laboratory number
100% methyl polysiloxane	058 068 070 126
14% cyanopropylphenyl 86%methyl polysiloxane	031 034 056 059 091 104 105 117 120 127
50% methyl 50% phenyl polysiloxane	035 057 060 069
65% methyl 35% phenyl polysiloxane	002 052 076 090 093
95% methyl 5% phenyl polysiloxane	001 002 003 004 005 006 010 011 025 028 029 037 039 040 044 046 047 048 049 050 051 054 055 056 057 061 062 063 064 065 066 067 072 075 076 077 079 080 081 082 083 084 085 086 087 088 090 092 093 095 096 097 098 099 100 101 102 105 106 108 109 110 112 113 115 116 117 118 120 122 123 124 125 128 129 130 133
CL Pesticide Specific	073
Varian VF	121

GC Injection Volume (µL)	laboratory number
<1	026
≥1 - <2	002 010 025 028 031 034 035 037 040 044 047 048 052 054 055 057 059 060 062 063 066 067 069 070 075 079 080 084 085 088 090 091 093 100 101 105 109 112 113 115 116 117 118 119 120 123 124 125 126 127 128 129 130 133
≥2 - <5	003 005 006 011 029 039 046 049 050 051 056 058 061 064 065 076 081 082 086 087 092 095 096 097 098 099 102 104 106 108 110 122
≥5 - <10	068 073 121
≥10	001 004 077 083

GC Injection Mode	laboratory number
headspace	119
on-column	010 069 073 091 121 129
PTV	001 004 058 068 076 083 124 127 128 130
split	002 025 037 051 064 105 117
splitless	003 005 006 011 028 029 031 034 035 039 044 047 048 050 052 054 055 056 057 059 060 061 062 063 065 066 070 075 077 079 080 081 082 084 085 086 087 088 090 092 093 095 097 098 099 100 102 104 106 108 109 110 112 113 115 116 118 120 122 123 125 126 133
CAS	067
pulsed splitless	096 101

GC Detector	laboratory number
ECD	002 010 011 025 026 029 031 034 035 037 039 040 044 052 054 055 056 057 062 063 064 069 070 073 075 076 077 079 082 085 087 090 091 093 100 101 104 105 106 108 112 117 118 119 120 123 125 126 129
FPD	010 076 093 108 118 120
HR-MS	044 113
ITD	046 058 066

GC Detector (continued)	laboratory number
MS	001 003 004 005 006 025 028 047 048 049 050 051 059 061 062 065 067 075 077 080 081 083 084 086 090 093 096 097 098 099 101 109 110 115 116 118 122 124 126 127 128 130 133
MS-MS	060 068 075 081 088 092 095 102 121
NPD	044 057 076 077 079 100 101 126
FPD	133

HPLC Column Packing	laboratory number
C18	074 121

HPLC Guard Column Used?	laboratory number
yes	046 074 121
no	006 029 087 128 130

Mobile Phase Programme	laboratory number
gradient	006 046 074 121 130

Mobile Phase Components	laboratory number
acetic acid	121
acetonitrile	121
methanol	074 121
ammonium acetate 25 mM	074

HPLC Column Temperature (°C)	laboratory number
>ambient - <50	074 121

HPLC Injection Volume (µL)	laboratory number
≥10 - <25	074
≥50 - <100	121

Mobile Phase Flow Rate (mL/min)	laboratory number
<0.25	074 121

HPLC Detector Type	laboratory number
MS-MS	074 121

APPENDIX III: FAPAS® Secure Web, Reports and Protocol

1. FAPAS® SECUREWEB

Access to the secure area of our web site is only available to participants in our proficiency tests. Please contact us if you require a UserID and Password. FAPAS® SecureWeb allows participants to:

- Obtain their laboratory numbers for the proficiency tests in which they have participated.
- View the results they submitted in past and current proficiency tests.
- Submit their results and methods for current tests.
- Review future tests they have ordered.
- Order proficiency tests and quality control materials, *including surplus test materials from the batch used in this proficiency test*.
- Freely download copies of reports, in Acrobat PDF format, of proficiency tests in which they have participated.

2. FAPAS® REPORTS

The Acrobat PDF version of this report is available to all participants as a free download from FAPAS® SecureWeb.

A printed and bound version of this report is priced £35 if ordered at the same time as the proficiency test or £50 if ordered subsequently.

3. FAPAS® PROTOCOL

The Protocol [1] sets out how FAPAS® is organised. It gives full details of the statistical procedures used and includes worked examples. Copies can be downloaded from our website.

4. CONTACT DETAILS

FAPAS®

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