



## SUMMARY

1. The test material for FAPAS<sup>®</sup> proficiency test 1997 was dispatched in September 2009. Each participant received an orange oil test material to be analysed for pesticide residues. In total, 26 sets of test materials were distributed to participants in 12 countries. Of these, 20 participants, i.e. 77%, returned results for some combination of the analytes within the time-scale demanded by the Scheme.
2. From a list of 9 possible pesticide residues, participants were requested to identify and quantify those present in the orange oil. The test material contained azoxystrobin, carbendazim, pyraclostrobin and trifloxystrobin.
3. The assigned value ( $\hat{X}$ ) was calculated from the most appropriate measure of central tendency of participants' results [1, 2].
4. The target standard deviation ( $\sigma_p$ ) for each analyte was calculated using the appropriate form of the Horwitz equation [3] and in conjunction with the assigned value ( $\hat{X}$ ) was used to derive a z-score for participants' results. z-Scores are considered satisfactory if  $|z| \leq 2$ .
5. For pyraclostrobin, the results were widespread, with no consensus, so it was not possible to set an assigned value. For trifloxystrobin, the assigned value had a high uncertainty that could affect participants' z-scores; consequently, the assigned value and z-scores are *given for information only*.
6. Results for this proficiency test are summarised as follows:

analyte	assigned value, $\hat{X}$ , $\mu\text{g/kg}$	number of satisfactory scores, $ z  \leq 2$	total number of scores	satisfactory %
azoxystrobin	108	8	13	62
carbendazim	47.0	8	13	62
trifloxystrobin	39.0	4	11	36

*figures in italics are shown for information only*

7. Surplus test materials are available for sale, see APPENDIX III.
8. Whereas this Report has been produced in good faith and in accordance with best industry practice, neither the Food and Environment Research Agency 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.

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## **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 [4] 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 [5] 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<sup>®</sup> 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<sup>®</sup> 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.

Full details of the FAPAS<sup>®</sup> proficiency testing scheme are available via our protocols [6, 7].

## **2. TEST MATERIAL**

### **2.1. Preparation**

Sample preparation was carried out by a laboratory contracted to do so by FAPAS<sup>®</sup>.

Commercially available orange oil was obtained from a health food supplier. A portion was screened and found to contain incurred residues of azoxystrobin, carbendazim, pyraclostrobin and trifloxystrobin. Consequently, no residues were spiked into the test material.

Bottles of orange oil were emptied into a large glass beaker and the oil stirred for one hour on a magnetic stirrer.

Individual portions of at least 25mL were dispensed into clean glass bottles, which were sealed, labelled and stored at +4°C until distribution.

## 2.2. Homogeneity

Ten randomly selected test materials were analysed in duplicate for all analytes by a laboratory contracted to do so by FAPAS<sup>®</sup>. The results, together with their statistical evaluation [8], are given in APPENDIX I. Statistical tests initially check the data for any widely discrepant pairs using Cochran's test and if found, such data are removed. Thereafter, the remaining data are subject to analysis of variance (ANOVA) to estimate the sampling and analytical variances.

These data show sufficient homogeneity, and are not included in the subsequent calculation of the assigned values.

## 2.3. Distribution

The dispatch date was 11 September 2009. Each participant received an individually numbered orange oil test material in a padded envelope, together with a covering letter, instructions for electronic submission of results and methods and the results form for participants with no internet access.

## 3. RESULTS

From a list of ten pesticide residues participants were required to report which residues the orange oil had been analysed for, together with a limit of quantification (LoQ). For all pesticides found, the amount present (in µg/kg, uncorrected for recovery) together with the percentage recovery was requested. Most pesticides were to be reported as the parent compound only, but some were to be reported as the parent compound plus one or more metabolites or the sum of all isomers. Such pesticides were indicated in the results form.

Results were submitted by 20 participants before the closing date for this test, 22 October 2009.

Each participant was given a laboratory number, assigned in order of receipt of results. The reported analyte concentrations are given in Table 1.

The analytical methods used by each participant are summarised in APPENDIX II.

If a participant failed to identify the presence of azoxystrobin, carbendazim, pyraclostrobin and/or trifloxystrobin and their LoQ was *below* the level needed for a satisfactory z-score, then as required by the FAPAS<sup>®</sup> Protocol [6, 7], the reported result was assigned a zero value.

If a participant failed to identify the presence of azoxystrobin, carbendazim, pyraclostrobin and/or trifloxystrobin and their LoQ was *above* the level needed for a satisfactory z-score, then the result was recorded as <LoQ.

None of the pesticides on the results form, other than azoxystrobin, carbendazim, pyraclostrobin and/or trifloxystrobin at levels >30 µg/kg were reported by participants; however, some pesticides not on the results form were reported. These are listed in Table 1.

## 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. The procedure follows that recommended in the IUPAC/ISO/AOAC International Harmonised Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories [9].

### 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) results from participants *not* reporting a percentage recovery,
  - ii) results from participants whose recovery is outside the range 70–120% [10],
  - iii) results from participants not reporting an LoQ (limit of quantification),
  - iv) results reported as approximately 10, 100 or 1000 x greater or smaller than the majority of submitted results (as these were considered to be reporting errors).
- Considering the normality (Kolmogorov-Smirnov test), or otherwise, of the distribution of results.
- Minimising the influence of outliers by the use of a robust statistical procedure to derive the mean [2].
- Considering the median of participants' results.
- Comparing the identified mode(s) with the mean derived from a robust statistical procedure [2].
- Assessing the standard uncertainty ( $u$ ) of the mode(s), median and robust mean. For the mode(s)  $u$  was taken to be directly equivalent to the standard error of the mode. For the robust mean and median:

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

where  $\hat{\sigma}$  = the standard deviation of the robust mean or the scaled median absolute deviation (sMAD).

NB this is NOT the target standard deviation for the test ( $\sigma_p$ )

and  $n$  = the number of data points used to calculate the robust mean or median.

For all four pesticide residues there were few results and the robust means had a high uncertainty. For azoxystrobin, carbendazim and trifloxystrobin the median had a lower uncertainty and was chosen as the assigned value. For trifloxystrobin, however, the median still had an uncertainty high enough to affect participants' z-scores. Consequently, the assigned value and z-scores are given *for information only, i.e. NOT for evaluative purposes*.

For pyraclostrobin, the range of results was wide, with no clear consensus; therefore, no assigned value was set and no z-scores were calculated.

The assigned values for all azoxystrobin, carbendazim and trifloxystrobin, together with  $u$ ,  $n$  and sMAD are shown in Table 3. Those for trifloxystrobin are shown *for information only*.

#### 4.2. Target Standard Deviation for the Test, $\sigma_p$

The value of  $\sigma_p$  determines the limits of satisfactory performance in a FAPAS<sup>®</sup> 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 [3] are valuable indicators of best practice.

For all four analytes  $\sigma_p$  was derived from the appropriate form of the Horwitz equation [3]. 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  $\equiv 10^{-6}$  or %  $\equiv 10^{-2}$ . 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  $\geq 120$  ppb and  $\leq 13.8\%$

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

- 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  $\equiv 10^{-6}$  or %  $\equiv 10^{-2}$

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

The values for  $\sigma_p$  used to calculate z-scores from the reported results of 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  $\sigma_p$  = the target standard deviation.

Participants' z-scores for azoxystrobin, carbendazim and trifloxystrobin are given in Table 1 and shown as histograms in Figures 1 - 3. Those for trifloxystrobin are shown *for information only*. 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 values and target standard deviations prior to their publication in Table 3.

The number and percentage of z-scores in the satisfactory range,  $|z| \leq 2$ , for azoxystrobin, carbendazim and trifloxystrobin are given in Table 4. Again, those for trifloxystrobin are shown *for information only*.

The number and percentage of participants correctly identifying all four pesticides, and the number and percentage of participants obtaining satisfactory z-scores for azoxystrobin and carbendazim are shown in Table 5. In this case, participants identifying additional pesticides  $>30 \mu\text{g}/\text{kg}$  are not considered satisfactory. This information is given for interest only and is not a measure of satisfactory performance in the proficiency test. Satisfactory performance is indicated in Table 1 and summarised in Table 4.

## 5. REFERENCES

- 1 Lowthian, P.J. and Thompson, M., 2002, Bump-hunting for the proficiency tester-searching for multimodality, *Analyst*, **127**, 1359-1364.
- 2 Analytical Methods Committee, 1989, Robust Statistics – How not to reject outliers Part 1. Basic Concepts, *Analyst*, **114**, 1693-1697.
- 3 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.
- 4 ISO/IEC 17025:2005, General requirements for the competence of testing and calibration laboratories.
- 5 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.
- 6 FAPAS<sup>®</sup>, 2009, Protocol for Proficiency Testing Schemes, Part 1 – Common Principles, Revision 2009, Version 1, Issued November 2009.
- 7 FAPAS<sup>®</sup>, 2009, Protocol for Proficiency Testing Schemes, Part 2 – FAPAS<sup>®</sup>, Revision 2009, Version 1, Issued November 2009.
- 8 Fearn, T. and Thompson, M., 2001, A new test for sufficient homogeneity, *Analyst*, **126**, 1414-1417.
- 9 Thompson, M., Ellison, S.L.R. and Wood, R., 2006, The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, *Pure Appl. Chem.*, **78**, No. 1, 145–196.
- 10 31 October 2007, *Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed*. Document No SANCO/2007/3131.

Table 1: Results and z-Scores for Orange Oil Test Material

laboratory number	analyte															
	azoxystrobin assigned value 108 µg/kg				carbendazim assigned value 47.0 µg/kg				pyraclostrobin assigned value not set				trifloxystrobin assigned value 39.0 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	result µg/kg	recovery %	LoQ µg/kg	z-score	
001	<LoQ		500		82		10	<b>3.4</b>	840		10	36		10	<i>-0.3</i>	
002	121	104.2	10	0.5	31	97.4	10	-1.5	898	103.9	10	39	115.7	10	<i>0.0</i>	
003	#				#				#			#				
004	156	100	10	2.0	#				341	100	100	68	100	10	3.4	
005	<LoQ		100		35	80	30	-1.2	293	80	30	<LoQ		100		
006	#				#				#			#				
007	#				#				#			#				
008	103	105	10	-0.2	42	100	10	-0.5	575	97	10	24	94	10	-1.7	
009	125	78	20	0.7	47	88	20	0.0	#			<LoQ	79	100		
010	132		50	1.0	47		20	0.0	535		20	29		20	-1.2	
011	#				23.0	65	1.0	<b>-2.3</b>	#			#				
012	107	93	25	0.0	50	100	25	0.3	460	100	25	59	100	25	2.3	

LoQ = limit of quantification

z-scores outside the satisfactory range, i.e.  $|z| > 2$ , are shown in **bold**

# = pesticide not analysed for

*figures in italics are shown for information only*

Table 1 (continued): Results and z-Scores for Orange Oil Test Material

laboratory number	analyte															
	azoxystrobin assigned value 108 µg/kg				carbendazim assigned value 47.0 µg/kg				pyraclostrobin assigned value not set				trifloxystrobin assigned value 39.0 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	z-score µg/kg	result µg/kg	recovery %	LoQ µg/kg	z-score	
013	0		20	<b>-4.5</b>	49	100	20	0.2	#			0		20	-4.5	
014	56.0	95	10	<b>-2.2</b>	20.8	98	10	<b>-2.5</b>	105.4	101	10	0		10	-4.5	
015	♥	109	80-120	50	0.0	NQ	80-120	50	335	80-120	50	<LoQ		50		
016	69	105	10	-1.6	49	112	10	0.2	288	94	10	15	88	10	-2.8	
017	0	93	10	<b>-4.5</b>	86	90	10	<b>3.8</b>	781	95	10	0	94	10	-4.5	
018	0		0.4	<b>-4.5</b>	0		0.02	<b>-4.5</b>	#			0		0.2	-4.5	
019	#				#				#			#				
020	0	89.75	20	<b>-4.5</b>	#				#			#				

LoQ = limit of quantification

NQ = identified but not quantified

z-scores outside the satisfactory range, i.e.  $|z| > 2$ , are shown in **bold**

# = pesticide not analysed for

♥ = participants comment: there are many compounds positive not included in the list

*figures in italics are shown for information only*

Table 2: Additional Pesticide Residues Reported

laboratory number	pesticide residue >30 µg/kg	result µg/kg
010	flufenoxuron	80
010	methidathion	1840
010	propargite	1030
016	methidathion	1600
016	propargite	present

Table 3: Assigned Values and Target Standard Deviations

analyte	assigned value, µg/kg				target standard deviation, µg/kg	
	data points <i>n</i>	median	sMAD	uncertainty <i>u</i>	derived from	$\sigma_p$
azoxystrobin	8	108	22.2	7.86	Horwitz*	23.8
carbendazim	9	47.0	7.4	2.47	Horwitz*	10.34
trifloxystrobin	5	39.0	29.7	13.3	Horwitz*	8.60

\* see page 7 for appropriate form of the Horwitz equation  
*figures in italics are shown for information only*

Table 4: Number and Percentage of Satisfactory z-Scores

analyte	number of satisfactory scores $ z  \leq 2$	total number of scores	satisfactory %
azoxystrobin	8	13	62
carbendazim	8	13	62
trifloxystrobin	4	11	36

*figures in italics are shown for information only*

Table 5: Number and Percentage of Participants Correctly Identifying and Obtaining Satisfactory z-Scores for all Pesticides Present >30 µg/kg

criteria	number of satisfactory participants	total number of participants	satisfactory %
correctly identified all four pesticides	5	20	25
correctly identified all four pesticides and obtained satisfactory z-scores for azoxystrobin and carbendazim	5	20	25

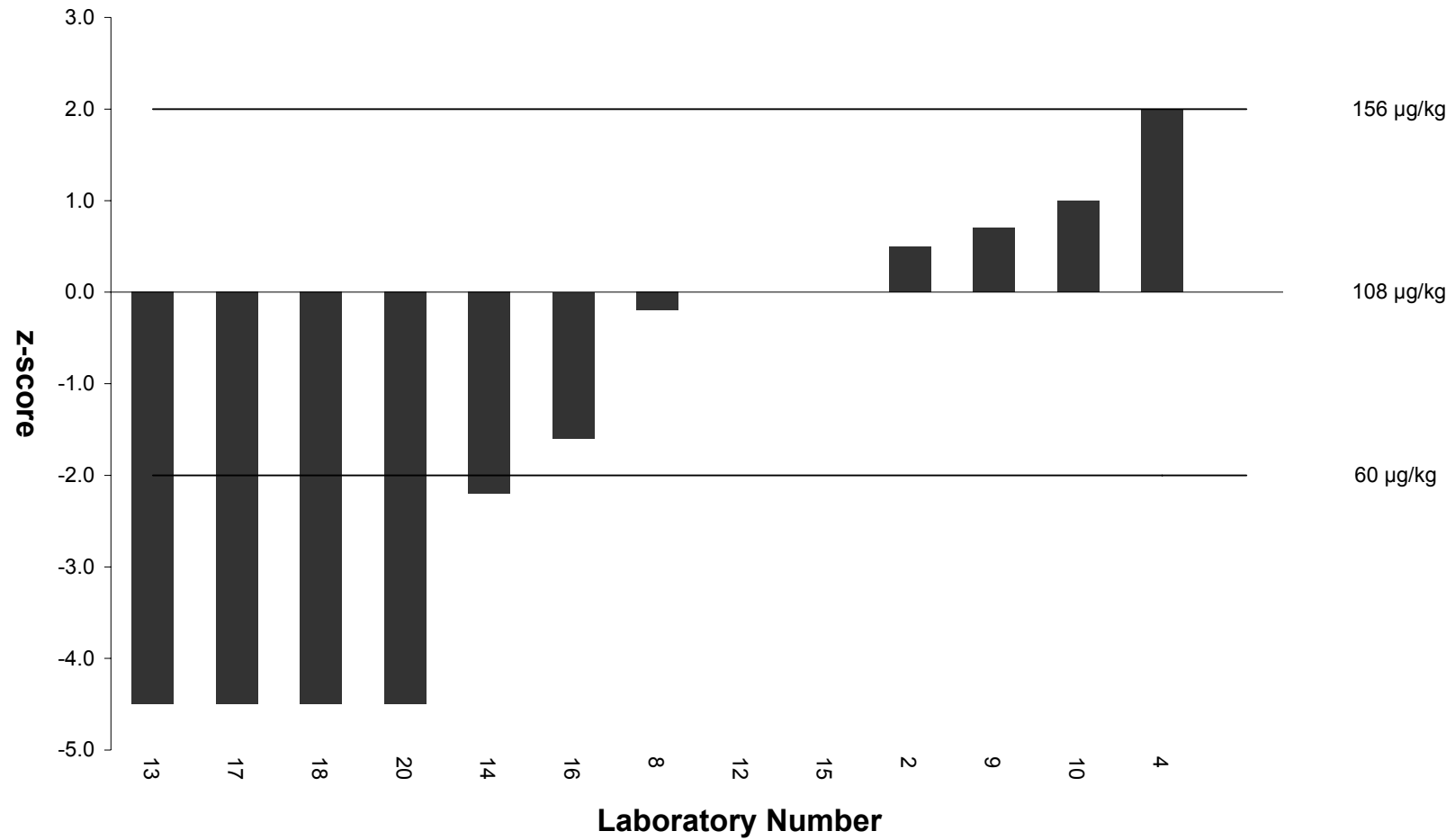


Figure 1: z-Scores for Azoxystrobin (108 µg/kg) in Orange Oil Test Material  
participants assigned a result of 0 µg/kg for azoxystrobin obtain a z-score of -4.5

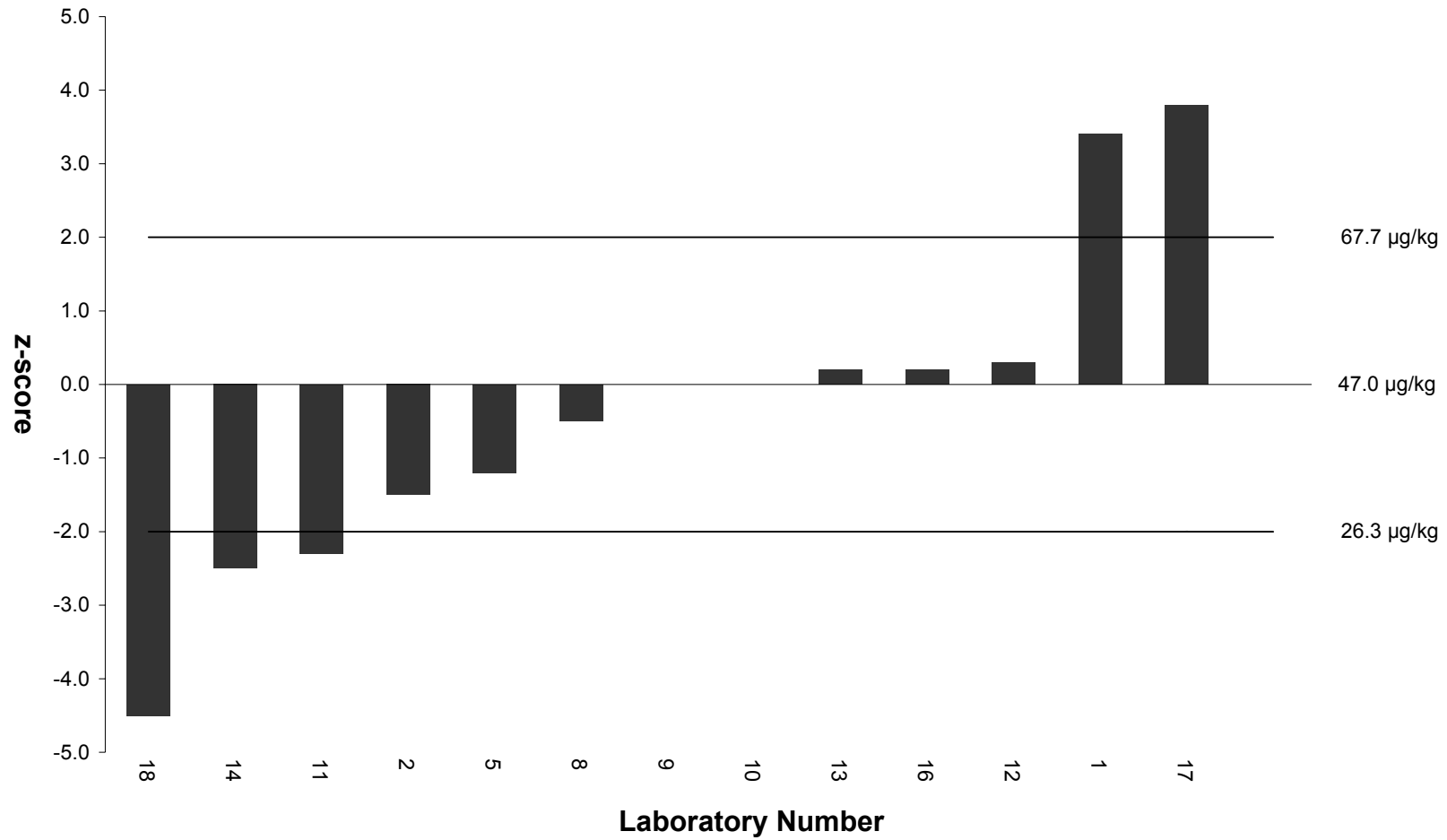


Figure 2: z-Scores for Carbendazim (47.0 µg/kg) in Orange Oil Test Material  
participants assigned a result of 0 µg/kg for carbendazim obtain a z-score of -4.5

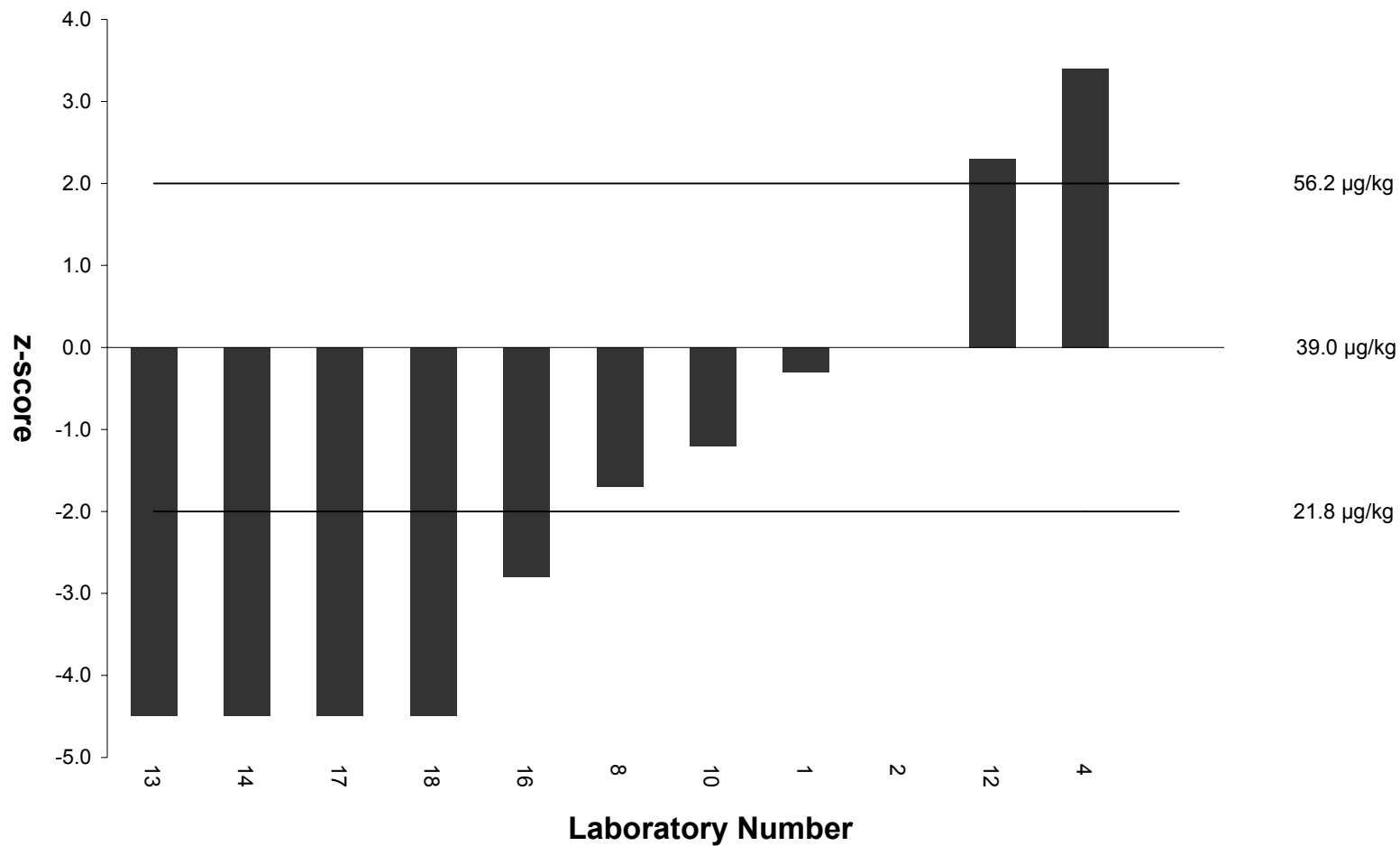


Figure 3: z-Scores for Trifloxystrobin ( $39.0 \mu\text{g}/\text{kg}$ ) in Orange Oil Test Material  
participants assigned a result of  $0 \mu\text{g}/\text{kg}$  for trifloxystrobin obtain a z-score of  $-4.5$   
*this histogram is shown for information only*

**APPENDIX I: Homogeneity Data for Orange Oil Test Material**

sample identity	analyte							
	azoxystrobin µg/kg		carbendazim µg/kg		pyraclostrobin µg/kg		trifloxystrobin µg/kg	
	replicate 1	replicate 2	replicate 1	replicate 2	replicate 1	replicate 2	replicate 1	replicate 2
1	98	114	12.7	14.1	691	681	19.6	30.2
2	124	130	14.9	13.3	656	664	32.1	31.7
3	108	106	10.0	11.7	648	678	24.4	26.9
4	124	125	14.4	12.8	674	662	29.2	31.9
5	130	112	13.7	14.0	692	678	33.0	27.9
6	125	141	13.2	13.6	679	665	31.6	37.9
7	136	121	11.9	12.6	681	662	29.6	35.9
8	149	135	13.6	12.8	668	674	35.7	35.3
9	112	150	12.6	5.6	r 683	657	27.1	36.6
10	128	143	9.2	12.8	656	648	33.0	32.3
mean, <i>n</i>	126	20	12.9	18	670	20	31.1	20
origin of target sd ( $\sigma_p$ )	Horwitz*		Horwitz*		Horwitz*		Horwitz*	
abs. target sd ( $\sigma_p$ ) & as RSD%	27.4	21.9	2.83	22.0	113.8	17.0	6.84	22.0
$s_{an}$	12.1		1.16		11.7		4.01	
$s_{sam}^2$	60.4		0.78		38.8		3.93	
$\sigma_{all}^2$	67.8		0.72		1165.8		4.21	
<i>critical</i>	275.6		2.89		2330.0		24.20	
$s_{sam}^2 < \text{critical?}$	<b>ACCEPT</b>		<b>ACCEPT</b>		<b>ACCEPT</b>		<b>ACCEPT</b>	

r = pair removed as Cochran's outlier

## APPENDIX II: Analytical Methods Used by Participants

Notes:

- 1) Participants' methods are tabulated according to the information supplied by electronic submission of methods entry. Some responses have been combined or edited for clarity.

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### Azoxystrobin

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Accredited Method Used	laboratory number
yes	004 009 010 012
no	002 008 014 016

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Sample Weight (g)	laboratory number
≥1 - <2	004 008 012 016
≥2 - <5	002 010 014

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Extraction Solvent	laboratory number
hexane	016
cyclohexane	012
acetone	004
ethyl acetate	010 012
acetonitrile	002 008 014

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Extraction Technique Used	laboratory number
cold solvent extraction at atmospheric pressure	008 009 010 014 016
dilution	004

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Extraction pH Adjusted	laboratory number
no	002 004 008 009 010 012 014 016

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<b>Sample Clean-up Technique</b>	<b>laboratory number</b>
GPC/HPGPC	012
solid phase extraction (SPE) (column/cartridge)	002 008
silica column	012
florisil column	014
liquid/liquid extraction with Extrelut	016
liquid/liquid extraction	008 009 012
none	004

<b>SPE Column Type</b>	<b>laboratory number</b>
Florisil	014
NH <sub>2</sub>	008
SAX/PSA	002

<b>Certified Standards Were Used</b>	<b>laboratory number</b>
yes	004 008 009 010 012 014 016
no	002

<b>MS Confirmation</b>	<b>laboratory number</b>
yes	002 004 008 009 010 014 016
no	012


<b>Calibrations</b>	<b>laboratory number</b>
solvent	010 012 016
matrix-matched	008 009
single-level	010
multi-level	004 008 009 012 016
standard addition	002 009 014


<b>Source of Standards</b>	<b>laboratory number</b>
Dr Ehrenstorfer	004 009 010 012 016
Fluka	008
Sigma/Aldrich	014
Wako	002

<b>Quoted percentage recovery was measured in same analytical batch as test material</b>	<b>laboratory number</b>
yes	002 004 008 009 010 012 014 016

<b>If measured in this batch, at what stage was the spike added</b>	<b>laboratory number</b>
prior to clean up	009
prior to extraction	002 008 012 014 016
prior to instrument measurement	004

<b>Level of Spike (µg/kg)</b>	<b>laboratory number</b>
≥25 - <50	002
≥100 - <150	004 009
≥200 - <250	014
≥250 - <300	008
≥400 - <500	016
≥500	004 009 012

<b>Composition of Blank Commodity used for Spiking</b>	<b>laboratory number</b>
orange oil blank provided 	009
orange oil test material provided	002 008 014
orange oil	012
purified orange terpenes	016
oil	004

 NB: a blank test material was not provided for this proficiency test

<b>GC Column Type</b>	<b>laboratory number</b>
capillary	004 012 014
narrowbore	010

<b>GC Column Packing</b>	<b>laboratory number</b>
100% methyl polysiloxane	004
95% methyl 5% phenyl polysiloxane	010 012 014

<b>GC Injection Volume (µL)</b>	<b>laboratory number</b>
≥2 - <5	004 010 012 014

<b>GC Injection Mode</b>	<b>laboratory number</b>
KAS	012
PTV	010
splitless	004 014

<b>GC Detector</b>	<b>laboratory number</b>
ECD	012
MSD	004 010 014

<b>HPLC Column Packing</b>	<b>laboratory number</b>
C18	002 008 009 016
endcapped	016

<b>Used HPLC Guard Column</b>	<b>laboratory number</b>
yes	002 009 016
no	008

<b>Mobile Phase Programme</b>	<b>laboratory number</b>
gradient	002 008 009 016

<b>Mobile Phase Components</b>	<b>laboratory number</b>
methanol	002 008 009 016
formic acid	008
ammonium formate	016
water	008 009 016

<b>HPLC Column Temperature (°C)</b>	<b>laboratory number</b>
ambient	009 016
>ambient - <50	002 008

<b>HPLC Injection Volume (µL)</b>	<b>laboratory number</b>
<5	016
≥5 - <10	008 009
≥10 - <25	002

<b>Mobile Phase Flow Rate (mL/min)</b>	<b>laboratory number</b>
<0.25	002 009 016
≥0.25 - <0.75	008

<b>HPLC Detector Type</b>	<b>laboratory number</b>
MS-MS	002 008 009 016

## **Carbendazim**

<b>Accredited Method Used</b>	<b>laboratory number</b>
yes	005 009 017
no	001 002 008 010 011 012 013 014 016

<b>Sample Weight (g)</b>	<b>laboratory number</b>
<1	001
≥1 - <2	008 011 012 014 016
≥2 - <5	002 010 013

≥5 - <10 005 017

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**Extraction Solvent** laboratory number

hexane	016
dichloromethane	013
acetonitrile	002 005 008 010 011 012 017
methanol	001 014

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**Extraction Technique Used** laboratory number

cold solvent extraction at atmospheric pressure	001 005 008 009 010 011 012 014 016 017
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**Extraction pH Adjusted** laboratory number

no	001 002 005 008 009 010 011 012 014 016 017
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**Sample Clean-up Technique** laboratory number

GPC/HPGPC	013
solid phase extraction (SPE) (column/cartridge)	002 008
solid phase extraction (SPE) (dispersive)	010 012
PSA and C18 material	010
NH <sub>2</sub> /aminopropyl column	017
florisil column	011
liquid/liquid extraction	008 009
liquid/liquid extraction with Extrelut	016
filter	001 014

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**SPE Column Type** laboratory number

NH <sub>2</sub>	008
SAX/PSA	002

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**Certified Standards Were Used** laboratory number

yes	001 005 008 009 010 011 012 013 014 016 017
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no 002

<b>MS Confirmation</b>	<b>laboratory number</b>
yes	001 002 005 008 009 010 011 012 013 014 016 017

<b>Calibrations</b>	<b>laboratory number</b>
solvent	010 016
matrix-matched	008 009 012 013
multi-level	002 005 008 009 010 011 012 016 017
standard addition	001 009 014

<b>Source of Standards</b>	<b>laboratory number</b>
Accu Standard	001
Dr Ehrenstorfer	005 009 010 012 013 016 017
Sigma/Aldrich	014
Wako	002 008

<b>Quoted percentage recovery was measured in same analytical batch as test material</b>	<b>laboratory number</b>
yes	002 005 008 009 010 011 012 013 014 016 017
no	001

<b>If measured in this batch, at what stage was the spike added</b>	<b>laboratory number</b>
prior to clean up	009
prior to extraction	002 005 008 011 012 013 014 016 017

<b>Level of Spike (µg/kg)</b>	<b>laboratory number</b>
<25	001 011 012
≥25 - <50	002 012 013
≥50 - <100	001 013
≥100 - <150	009 013 014

<b>Level of Spike (µg/kg) (continued)</b>	<b>laboratory number</b>
≥200 - <250	005 008
≥250 - <300	017
≥300 - <400	013
≥400 - <500	016
≥500	001 009

<b>Composition of Blank Commodity used for Spiking</b>	<b>laboratory number</b>
orange oil blank provided ☹️	009
orange oil test material provided	002 008 014
orange oil	012
purified orange terpenes	016
orange extract	013
cucumber	005

☹️ NB: a blank test material was not provided for this proficiency test

<b>GC Column Type</b>	<b>laboratory number</b>
capillary	017

<b>HPLC Column Packing</b>	<b>laboratory number</b>
C18	001 002 005 008 009 010 011 012 014 016 017
endcapped	010 016
BEH	013

<b>Used HPLC Guard Column</b>	<b>laboratory number</b>
yes	002 005 009 010 014 016
no	001 008 011 012 013 017

<b>Mobile Phase Programme</b>	<b>laboratory number</b>
gradient	001 002 005 008 009 010 011 012 013 014 016 017

016 017

<b>Mobile Phase Components</b>	<b>laboratory number</b>
acetonitrile	001 005 017
methanol	001 002 008 009 010 012 013 014 016
ethanol	001
acetic acid	010
formic acid	008 012
ammonium formate	016
water	001 005 008 009 010 012 013 014 016

<b>HPLC Column Temperature (°C)</b>	<b>laboratory number</b>
ambient	005 009 011 016 017
>ambient - <50	002 008 010 012 013 014
≥50	001

<b>HPLC Injection Volume (µL)</b>	<b>laboratory number</b>
<5	001 005 016
≥5 - <10	008 009 011 012 013 014
≥10 - <25	002 010 017

<b>Mobile Phase Flow Rate (mL/min)</b>	<b>laboratory number</b>
<0.25	002 009 011 016
≥0.25 - <0.75	001 005 008 010 012 013 014 017

<b>HPLC Detector Type</b>	<b>laboratory number</b>
MS-MS	001 002 005 008 009 010 011 012 013 014 016 017

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## Pyraclostrobin

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Accredited Method Used	laboratory number
yes	004 005 017
no	001 002 008 010 012 014 016

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Sample Weight (g)	laboratory number
<1	001
≥1 - <2	004 008 012 014 016
≥2 - <5	002 010
≥5 - <10	005 017

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Extraction Solvent	laboratory number
acetone	004
acetonitrile	002 005 008 010 012 017
hexane	016
methanol	001 014

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Extraction Technique Used	laboratory number
cold solvent extraction at atmospheric pressure	001 005 008 010 012 014 016 017
dilution	004

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Extraction pH Adjusted	laboratory number
no	001 002 004 005 008 010 012 014 016 017

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Sample Clean-up Technique	laboratory number
solid phase extraction (SPE) (column/cartridge)	002 008
solid phase extraction (SPE) (dispersive)	010 012
PSA and C18 material	010
NH <sub>2</sub> aminopropyl column	017

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<b>Sample Clean-up Technique (continued)</b>	<b>laboratory number</b>
liquid/liquid extraction with Extrelut	016
liquid/liquid extraction	008
filter	001 014
none	004

<b>SPE Column Type</b>	<b>laboratory number</b>
NH <sub>2</sub>	008
SAX/PSA	002

<b>Certified Standards Were Used</b>	<b>laboratory number</b>
yes	001 004 005 008 010 012 014 016 017
no	002

<b>MS Confirmation</b>	<b>laboratory number</b>
yes	001 002 004 005 008 010 012 014 016 017

<b>Calibrations</b>	<b>laboratory number</b>
solvent	010 016
matrix-matched	008 012
multi-level	004 005 008 010 012 016 017
standard addition	001 002 014

<b>Source of Standards</b>	<b>laboratory number</b>
Accu Standard	001
Dr Ehrenstorfer	004 005 010 012 016 017
Fluka	008
Sigma/Aldrich	014
Wako	002

<b>Quoted percentage recovery was measured in same analytical batch as test material</b>	<b>laboratory number</b>
yes	002 004 005 008 010 012 014 016 017
no	001

<b>If measured in this batch, at what stage was the spike added</b>	<b>laboratory number</b>
prior to extraction	002 005 008 012 014 016 017
prior to instrument measurement	004

<b>Level of Spike (µg/kg)</b>	<b>laboratory number</b>
<25	001
≥50 - <100	001
≥100 - <150	004 012
≥150 - <200	014
≥200 - <250	005
≥250 - <300	017
≥400 - <500	012 016
≥500	001 002 004 008 012

<b>Composition of Blank Commodity used for Spiking</b>	<b>laboratory number</b>
orange oil test material provided	002 008 014
orange oil	012
purified orange terpenes	016
blank oil	004
cucumber	005

<b>GC Column Type</b>	<b>laboratory number</b>
capillary	002 017

<b>GC Column Packing</b>	<b>laboratory number</b>
5% methylpolysiloxane	002
<b>GC Injection Volume (µL)</b>	<b>laboratory number</b>
≥2 - <5	002
<b>GC Injection Mode</b>	<b>laboratory number</b>
splitless	002
<b>GC Detector</b>	<b>laboratory number</b>
MS	002
<b>HPLC Column Packing</b>	<b>laboratory number</b>
C18	001 004 005 008 010 012 014 016 017
endcapped	010 016
<b>Used HPLC Guard Column</b>	<b>laboratory number</b>
yes	004 005 010 014 016
no	001 008 012 017
<b>Mobile Phase Programme</b>	<b>laboratory number</b>
gradient	001 004 005 008 010 012 014 016 017
<b>Mobile Phase Components</b>	<b>laboratory number</b>
acetic acid	004 010
acetonitrile	001 004 005 017
ammonium formate	016
ethanol	001
formic acid	008 012
methanol	001 008 010 012 014 016
water	001 004 005 008 010 012 014 016

HPLC Column Temperature (°C)	laboratory number
ambient	005 016 017
>ambient - <50	004 008 010 012 014
≥50	001

HPLC Injection Volume (µL)	laboratory number
<5	001 005 016
≥5 - <10	004 008 012 014
≥10 - <25	010 017

Mobile Phase Flow Rate (mL/min)	laboratory number
<0.25	016
≥0.25 - <0.75	001 005 008 010 012 014 017

HPLC Detector Type	laboratory number
MS-MS	001 004 005 008 010 012 014 016 017

## Trifloxystrobin

Accredited Method Used	laboratory number
yes	004
no	001 002 008 010 012 016

Sample Weight (g)	laboratory number
<1	001
≥1 - <2	004 008 012 016
≥2 - <5	002 010

<b>Extraction Solvent</b>	<b>laboratory number</b>
hexane	016
acetone	004
acetonitrile	002 008 010 012
methanol	001

<b>Extraction Technique Used</b>	<b>laboratory number</b>
cold solvent extraction at atmospheric pressure	001 008 010 012 016
dilution	004

<b>Extraction pH Adjusted</b>	<b>laboratory number</b>
no	001 002 004 008 010 012 016

<b>Sample Clean-up Technique</b>	<b>laboratory number</b>
solid phase extraction (SPE) (column/cartridge)	002 008
solid phase extraction (SPE) (dispersive)	010 012
PSA and C18 material	010
liquid/liquid extraction with Extrelut	016
liquid/liquid extraction	008
filter	001
none	004

<b>SPE Column Type</b>	<b>laboratory number</b>
NH <sub>2</sub>	008
SAX/PSA	002

<b>Certified Standards Were Used</b>	<b>laboratory number</b>
yes	001 004 008 010 012 016
no	002

<b>MS Confirmation</b>	<b>laboratory number</b>
yes	001 002 004 008 010 012 016

<b>Calibrations</b>	<b>laboratory number</b>
solvent	010 016
matrix-matched	008 012
multi-level	004 008 010 012 016
standard addition	001 002

<b>Source of Standards</b>	<b>laboratory number</b>
Accu Standard	001
Dr Ehrenstorfer	004 010 012 016
Fluka	008
Wako	002

<b>Quoted percentage recovery was measured in same analytical batch as test material</b>	<b>laboratory number</b>
yes	002 004 008 010 012 016
no	001

<b>If measured in this batch, at what stage was the spike added</b>	<b>laboratory number</b>
prior to extraction	002 008 012 016
prior to instrument measurement	004

<b>Level of Spike (µg/kg)</b>	<b>laboratory number</b>
<25	001 012
≥25 - <50	002 012
≥50 - <100	001
≥100 - <150	004 008
≥400 - <500	016
≥500	001 004

<b>Composition of Blank Commodity used for Spiking</b>	<b>laboratory number</b>
orange oil test material provided	002 008
orange oil	012
purified orange terpenes	016
oil	004

<b>GC Column Type</b>	<b>laboratory number</b>
capillary	004

<b>GC Column Packing</b>	<b>laboratory number</b>
100% methyl polysiloxane	004

<b>GC Injection Volume (µL)</b>	<b>laboratory number</b>
≥2 - <5	004

<b>GC Injection Mode</b>	<b>laboratory number</b>
splitless	004

<b>GC Detector</b>	<b>laboratory number</b>
MSD	004

<b>HPLC Column Packing</b>	<b>laboratory number</b>
C18	001 002 008 010 012 016
endcapped	010 016

<b>Used HPLC Guard Column</b>	<b>laboratory number</b>
yes	002 010 016
no	001 008 012

<b>Mobile Phase Programme</b>	<b>laboratory number</b>
gradient	001 002 008 010 012 016

<b>Mobile Phase Components</b>	<b>laboratory number</b>
acetonitrile	001
methanol	001 002 008 010 012 016
ethanol	001
acetic acid	010
formic acid	008 012
ammonium formate	016
water	001 008 010 012 016

<b>HPLC Column Temperature (°C)</b>	<b>laboratory number</b>
ambient	016
>ambient - <50	002 008 010 012
≥50	001

<b>HPLC Injection Volume (µL)</b>	<b>laboratory number</b>
<5	001 016
≥5 - <10	008 012
≥10 - <25	002 010

<b>Mobile Phase Flow Rate (mL/min)</b>	<b>laboratory number</b>
<0.25	002 016
≥0.25 - <0.75	001 008 010 012

<b>HPLC Detector Type</b>	<b>laboratory number</b>
MS-MS	001 002 008 010 012 016

## APPENDIX III: FAPAS<sup>®</sup> SecureWeb, Reports and Protocol

### 1. FAPAS<sup>®</sup> 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<sup>®</sup> 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. REPORTS

The Acrobat PDF version of this report is available to all participants as a free download from FAPAS<sup>®</sup> 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. PROTOCOL

The Protocol [6, 7] sets out how FAPAS<sup>®</sup> 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

Participants with any comments or concerns about this proficiency test should contact:

FAPAS<sup>®</sup>  
Food and Environment Research Agency  
Sand Hutton, York  
YO41 1LZ  
UK

Tel: +44 (0)1904 462100  
Fax: +44 (0)1904 462040  
e-mail: [info@fapas.com](mailto:info@fapas.com)  
[testmaterials@fapas.com](mailto:testmaterials@fapas.com)  
web: [www.fapas.com](http://www.fapas.com)

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