EUROPEAN COMMISSION PROFICIENCY TEST FOR PESTICIDES IN FRUITS AND VEGETABLES SCREENING METHODS 01 (EUPT-FV-SM-01) 2009

Pesticide Residues in Orange Extract Homogenate

Final Report

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2009

BACKGROUND

According to Article 28 of Regulation 396/2005/EC of the European Parliament and European Council regarding maximum residue levels of pesticides in, or on, food and feed of plant and animal origin[1]: all laboratories analysing samples for the official control on pesticide residues shall participate in the European Community Proficiency Tests (EUPTs) for pesticide residues, facilitated by the Commission. These proficiency tests are carried out on an annual basis in order to ensure the quality, accuracy and comparability of the residue data reported by EU Member States to the European Commission, as well as by other Member States within the framework of co-ordinated and national monitoring and surveillance programmes.

Regulation (EC) No 882/2004[2] lays down the general tasks, duties and requirements for Community Reference Laboratories (CRLs) for Food, Feed and Animal Health. Among these tasks is the provision of independently-organised comparative tests. This year the CRL for pesticides in Fruit and Vegetables at the University of Almería, Spain[3] initiated for the first time a proficiency test on qualitative/semi-quantitative screening methods for pesticides in vegetable/fruit commodities. This test was organised because many laboratories have recently invested in new higher mass accuracy MS systems that allows them to greatly increase the scope by using screening methods.

Because the use of such screening methods is not yet common practise amongst all EU laboratories involved in official monitoring, participation in this PT was on a purely voluntary basis. Another reason for not making this PT mandatory was that a PT for quantitative pesticide multi-residue analysis (EUPT-FV11) had been organised in the same time period. Nevertheless, all FV-NRLs and FV-Official laboratories involved in the determination of pesticide residues in fruit and vegetables for the EU-coordinated monitoring programme or for their own national programmes were invited to take part. Countries such as Egypt and Turkey were also invited to participate.

This report will be presented to the European Commission Standing Committee for Animal Health and the Food Chain. Furthermore, DG-SANCO has full access to all data of EUPTs including the individual lab-codes/lab-name keys.

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[1] Regulation (EC) No 396/2005, published at OJ of the EU L70 of 16.03.2005, as last amended by Regulation 839/2008 published at OJ of the EU L234 of 30.08.2008.

[2] Regulation (EC) No 882/2004 of the European Parliament and of the Council on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules. Published at OJ of the EU L191 of 28.05.2004

[3] Commission Regulation (EC) No 776/2006 of 23 May 2006 - amending Annex VII to Regulation (EC) No 882/2004 of the European Parliament and of the Council as regards Community Reference Laboratories.

1. INTRODUCTION

Over the last 10 years, the operation of the European Proficiency Test for pesticide residues in fruit and vegetables using multi-residue methods has provided a great deal of useful information. As well as this wealth of residue data, the year-on-year increase in the scope of the participating laboratories can be seen.

Nowadays, there is an even stronger demand to greatly enlarge the number of compounds covered by each multi-residue analysis. However this is a very costly task for many laboratories utilising conventional GC-MS and LC-MS/MS based methods, and too often cannot be fulfilled. As a consequence, "not analysed" (NA) is reported for a high percentage of the pesticides from the EUPT-target lists. For example, in last years PT (EUPT-FV10), 22% of the results were reported as 'NA'.

Mass spectrometry plays an essential role in everyday work carried out by laboratories. It is used typically for target analysis purposes and the scope of many official laboratories is around 150 pesticides. Technological improvements in modern MS systems (and the accompanying software) offers new possibilities for increasing the scope of MRM analysis. Whereas full-scan measurement is theoretically the best approach for MS screening, developments in targeted measurement also enables substantially increased scope of analysis. In GC-MS, Time-of-Flight and the new quadrupole mass spectrometers allow more sensitive full-scan measurement. In addition, improvements in software (automated peak deconvolution/identification) have made wide-scope screening a more feasible option for routine analysis. In LC-MS, tandem-MS detectors allow faster measurement of MS/MS transitions (or even MS/MS spectra), which can be used to increase the number of pesticides determined within a single chromatographic run. Furthermore, single stage TOF-MS systems, which enable sensitive full-scan acquisition with high mass accuracy, have been shown to provide a practical alternative. These new tools are options that complement existing multi-residue methods and can be used to increase identification capabilities, providing efficient ways to perform a more comprehensive monitoring programme.

The CRL-FV aim is to be able to use mass spectrometry screening methods in routine practice. To this end, we organised this explorative proficiency test for laboratories that have instruments and methods available to allow a wide-scope MS screening of pesticides. By means of this test, the effectiveness of the laboratory using such procedures can be evaluated in order to help develop the quality control systems necessary for the screening results to have a harmonized consistency.

From the results of this proficiency test, participating laboratories could be provided with an assessment of both their identification capabilities, as well as the reliability of their MS screening methods – as compared to the other participating laboratories.

2. TEST MATERIALS

The pesticides used to spike the orange extract were decided on the basis not only of the EU Coordinated Monitoring Programme, as in other EUPT-FVs, but also with regard to recent positive findings in oranges together with some pesticides where approvals have been withdrawn.

2.1 Analytical methods

The two analytical methods described briefly below were used by the Organiser for the homogeneity and stability tests performed by the CRL-FV. These were:

- GC method [1]: gas chromatography/mass spectrometry (GC–MS) using electron impact (EI) ionisation and full-scan acquisition.
- LC method [2]: HPLC-TOF-MS using electrospray ionisation and operating in the positive ion mode

2.2 Preparation of spiked and 'blank' orange extract test material.

This proficiency test was performed in 2009 using orange extract homogenate. The oranges were provided by an organic grower in Almería.

The oranges were extracted using an acetonitrile-based procedure in the following way:
A representative 10 g portion of previously-homogenized sample was weighed in a 200 mL PTFE centrifuge tube. 10 mL of acetonitrile was added, and the tube vigorously shaken for 1 min. After this time, 1 g of NaCl, 4 g of $MgSO_4$, 1 g of trisodium citrate dihydrate and 0.5 g of disodium hydrogencitrate sesquihydrate were added, and the shaking process repeated for 1 min. The tube was then centrifuged at 3500 rpm for 5 min. A 5 mL aliquot of the supernatant (acetonitrile phase) was transferred to a 15 mL graduated centrifuge tube containing 125 mg of PSA, 750 mg of $MgSO_4$ and 125 mg C_{18}, and energetically mixed using a vortex mixer for 30 s. Following this, it was centrifuged again (3500 rpm) for 5 min. After centrifugation, the cleaned up extract was pH adjusted to 5 by the addition a 5 % formic acid solution in acetonitrile (vol/vol) (40 µL).

The method was repeated as many times as necessary to obtain 1000 mL of extract, which was separated into two parts: 500 mL to act as the 'blank' or non-spiked extract, and the other 500 mL was spiked with three different mixtures of pesticides from the target pesticide list. Each of the three mixtures was prepared at a different concentration.

5 mL of treated extract were measured out into a screw-capped topaz vials and stored in a freezer at about -20ºC prior to distribution to participants. The same procedure was performed on the 'blank' extract.

2.3 Check analyses for the presence of the pesticides in the spiked orange extract

As this was a 'qualitative' PT the organiser decided that the homogeneity and stability tests associated with 'quantitative' PTs were not necessary. Hence the PT extract was only analysed in order to detect the presence of all the spiked pesticides.

Ten vials of spiked extract were randomly chosen from those stored in the freezer and analysed in order to check the presence of the pesticides. The injection sequence of the 10 extract analyses by GC and LC were determined from a table of randomly generated numbers.

Further analyses were also performed on two more occasions. On each occasion, a single vial stored in the freezer at -20°C was randomly chosen and analysed.

The two occasions were:

- Day 1: coinciding with the sample shipment, which took place on 15th June 2009.
- Day 2: soon after the deadline for reporting results, on 22nd June 2009.

For all the analysis, the two analytical methods described briefly above (in section 2.1) were used.

The aim of these tests was to demonstrate the detectability of all the pesticides added to the treated extracts at shipment, and then again shortly after the deadline for submission of results once the PT had passed. All the pesticides that had been spiked into the extract were detected on both occasions.

2.4 Distribution of test extract and protocol to participants

The test extract, approximately 5 mL of orange extract homogenate containing residues of pesticides, together with another 5 mL of 'blank' orange extract homogenate, were shipped to participants on the 15th June 2009. The deadline for the submission of results to the Organiser was 48 hours after receipt of the test extract. Participants were provided with a target list of two hundred and twenty-seven pesticides (Annex 1), which could be present in the spiked test extract and they were asked to report all the pesticide residues that they detected. Previously, when applying for the test, the laboratories were asked for their analytical scope.

Laboratories were asked to screen the extracts using the wide-scope screening methods they normally apply, or anticipate applying, for official monitoring purposes. This typically involves full-scan techniques like GC-MS (full-scan quadrupole, ion trap, ToF) and/or LC-ToF-MS and Orbitrap. However, extended targeted methods using LC tandem MS (triple quadrupole, Q-trap, Q-ToF) or GC-MS/MS could also be used.

Before shipment, the laboratories had received full instructions (Annex 1) for the receipt and analysis of the spiked test extract although they were encouraged to use their own screening methods. These instructions, laid out as Protocol, were uploaded onto the EUPT-FV-SM01 web page, designed especially for this Proficiency Test, together with the Target Pesticide List. This information was also sent by e-mail to all participant laboratories. The Application Form was uploaded onto this same web site; together with Forms 2 and 3 to be used to send back results – these allowed the evaluation of the mass-spectrometric screening methods that each of the participants used.

3. STATISTICAL METHODS

3.1 False positives and negatives

3.1.1 False positives

These are considered as those results that show the apparent presence of pesticides that were listed in the Target Pesticide List, but which were (i) not used to spike the extract and/or (ii) not detected by the Organiser, even after repeated analyses. However, if a number of participants had detected the same additional pesticide, then a decision as to whether, or not, this should be considered to be a false positive result was made on a case-by-case basis.

> *Organiser Note:* not all screening methods immediately provide sufficient information to allow full identification. In such cases, in real-life, laboratories normally do a follow-up confirmatory analysis when they detect a pesticide with e.g. using LC-MS/MS and based on only one transition. In future PTs of this nature, there will be a need to distinguish between suspect or tentative detects and full identifications.

3.1.2 False negatives

These are results for pesticides reported by the laboratories as "analysed" but their presence was not reported, although they were used by the Organiser to spike the extract and were detected by the majority of participants.

4. RESULTS

4.1 Summary of reported results

Forty-five laboratories agreed to participate in this first proficiency test on screening methods. Forty-four laboratories submitted results. All results reported by the participants are given in Appendix 1. Graphical representations of the results reported are shown in Appendix 2. Details on the screening methods used are provided in Appendix 3. The laboratories that agreed to participate are listed in Annex 2.

A summary of the results reported by pesticide can be seen in Table 4.1.

Table 4.1 Summary of Results Reported.

Pesticides	No. of Reported Results	No. of Not Analysed Results	No. of False Negatives	% of Laboratories that Reported Results *
Acrinathrin	34	3	7	77
Atrazine	38	5	1	86
Azoxystrobin	40	0	4	91
Bifenthrin	42	1	1	95
Bromuconazole	28	12	4	64
Buprofezin	40	1	3	91
Chlorotoluron	16	26	2	36
Chlorpyrifos	41	1	2	93
Chlorpyrifos-methyl	43	1	0	98
Chromafenozide	5	37	2	11
Cyproconazole	40	2	2	91
Cyprodinil	44	0	0	100
Dimethoate	37	2	5	84
Diuron	26	15	3	59
Endosulfan alpha	36	2	6	82
Endosulfan beta	37	2	5	84
Fenazaquin	31	10	3	70
Fenhexamid	33	5	6	75
Fenuron	9	32	3	20
Fluometuron	11	30	3	25
Imidacloprid	33	8	3	75
Indoxacarb sum	34	6	4	77
Isoprocarb	15	26	3	34
Isoproturon	21	20	3	48
Lenacil	14	21	9	32

Pesticides	No. of Reported Results	No. of Not Analysed Results	No. of False Negatives	% of Laboratories that Reported Results *
Malathion	42	0	2	95
Mepanipyrim	39	3	2	89
Metolachlor	33	10	1	75
Omethoate	35	5	4	80
Penconazole	41	1	2	93
Pirimicarb	43	1	0	98
Procymidone	38	2	4	86
Promecarb	24	16	4	55
Prometryn	34	9	1	77
Propazine	24	19	1	55
Pyridaphenthion	32	11	1	73
Pyrimethanil	38	2	4	86
Pyriproxyfen	43	0	1	98
Quinoxyfen	40	4	0	91
Spiroxamine	38	5	1	86
Terbuthylazine	34	9	1	77
Terbutrin	27	14	3	61
Thiacloprid	34	10	0	77
Tolfenpyrad	12	29	3	27
Tolylfluanid	25	7	12	57
Triflumizol	26	16	2	59
Vinclozolin	41	2	1	93

* The % of Laboratories that Reported Results is calculated relative to the total number of laboratories submitting results (44).

4.1.1 False positives

Many laboratories reported additional pesticides to those spiked into the extract. These pesticides and their deviation in RT reported are presented in Table 4.2.

Table 4.2. Laboratories that reported false positives in the spiked extract.

Laboratory Code	Pesticide	Deviation in Rt
Lab 5	Desethylterbutylazine	5 -10%
	Endosulfan sulfate	
	Fenobucarb	
Lab 6	Tebufenpyrad	-10.8 sec

Laboratory Code	Pesticide	Deviation in Rt
Lab 7	Diazinon	1.62
	Metobromuron	
Lab 8	Chlorfenvinphos	0.1
Lab 14	Methamidophos	<2.5%
Lab 17	Endosulfan sulfate	
Lab 18	Bromopropylate	
	Chlorfenvinphos	
	Cyflutrin	
	Deltametrin	
	Fenarimol	
	Hexaconazole	
	Lambda Cyhalothrin	
	Myclobutanil	
	Pirimiphos-Methyl	
	Prochloraz	
Lab 22	Lambda Cyhalothrin	0.20%
Lab 26	Diazinon	
	Difenconazole	
Lab 29	Lambda Cyhalothrin	
Lab 32	Endosulfan sulfate	
	Malaoxon	
	Metobromuron	
	Paclobutrazole	
	Prochloraz	
Lab 33	Aclonifen	2.50%
	Boscalid	2.50%
	Malaoxon	0.50%
	Oxydemeton-methyl	0.50%
Lab 35	Carbaryl	
Lab 36	Dimetomorph	
	Isocarbofos	
Lab 38	Anilofos	
	Chloroxuron	
	Fenobucarb	
Lab 41	Dimethylvinphos	

Simazine Case: this pesticide was not used to spike the extract although twelve laboratories reported it as having been detected at a very low concentration. Therefore Simazine was not assigned as a false positive. Table 4.3 shows the laboratories that reported the presence of this pesticide and the concentrations that they reported.

Table 4.3 Laboratories that detected Simazine and the concentration.

Laboratory Code	Concentration (mg/Kg)
Lab 4	0.01
Lab 5	Above 0.01
Lab 6	
Lab 7	0.01
Lab 9	
Lab 10	<0.01
Lab 22	<0.01
Lab 26	<0.01
Lab 29	Above 0.05
Lab 35	0.004
Lab 38	
Lab 44	<0.01

4.1.2 False negatives

Table 4.4 summarizes how many laboratories reported false negatives for each pesticide. A graphical representation of Table 4.4 can be seen in Appendix 2.

Table 4.4 Laboratories that failed to report pesticides that were present in the spiked extract.

Pesticide	Lab Code																	
	1	2*	4	5	6	7*	8	9	11*	12*	13*	14	15	17*	18*	19	20*	21
Acrinathrin			ND							ND			ND					ND
Atrazine																		ND
Azoxystrobin						ND					ND							ND
Bifenthrin																		ND
Bromuconazole					ND							ND						ND
Buprofezin											ND	ND						
Chlorotoluron	ND																	
Chlorpyrifos												ND						ND
Chromafenozide																		
Cyproconazole												ND						
Dimethoate		ND		ND														
Diuron														ND				ND
Endosulphan α							ND					ND	ND					ND
Endosulphan β							ND					ND						ND
Fenazaquin											ND							ND
Fenhexamid									ND			ND						ND
Fenuron																		
Fluometuron																		
Imidaloprid											ND		ND					
Indoxacarb													ND	ND				
Isoprocarb																		
Isoproturon																		
Lenacil		ND			ND		ND										ND	ND
Malathion															ND			ND
Mepanipyrim							ND											
Metolachlor																		ND
Omethoate		ND	ND															ND
Penconazole																ND		
Procymidone		ND				ND												ND
Promecarb								ND										
Prometryn																		ND
Propazine																		ND
Pyridaphention																		ND
Pyrimethanil												ND						ND
Pyriproxyfen																		
Spiroxamine																		
Terbuthylazine																		ND
Terbutrin																		ND
Tolfenpyrad				ND														
Tolyfluanid		ND			ND		ND					ND			ND	ND		
Triflumizol				ND														ND
Vinclozolin																		ND

* NRL in Fruits and Vegetables

Pesticide	Lab Code																	
	24*	25	27	28*	29	30	31	32	34	36	37	38*	39*	40	41	42	43	45
Acrinathrin										ND	ND						ND	
Atrazine																		
Azoxystrobin														ND				
Bifenthrin																		
Bromuconazole								ND										
Buprofezin																		ND
Chlorotoluron									ND									
Chlorpyrifos																		
Chromafenozide		ND												ND				
Cyproconazole				ND														
Dimethoate			ND				ND	ND										
Diuron									ND									
Endosulphan α													ND					ND
Endosulphan β													ND					ND
Fenazaquin			ND															
Fenhexamid	ND												ND	ND				
Fenuron		ND							ND								ND	
Fluometuron									ND					ND			ND	
Imidaloprid																		ND
Indoxacarb						ND												
Isoprocarb											ND	ND		ND				
Isoproturon						ND					ND						ND	
Lenacil		ND				ND										ND	ND	
Malathion																		
Mepanipyrim			ND															
Metolachlor																		
Omethoate					ND													
Penconazole																		ND
Procymidone																		ND
Promecarb			ND							ND	ND							
Prometryn																		
Propazine																		
Pyridaphention																		
Pyrimethanil					ND								ND					
Pyriproxyfen																	ND	
Spiroxamine													ND					
Terbuthylazine																		
Terbutrin				ND						ND								
Tolfenpyrad														ND			ND	
Tolyfluanid			ND			ND			ND	ND				ND	ND			
Triflumizol																		
Vinclozolin																		

* NRL in Fruits and Vegetables

4.2 Concentration levels.

Forty-seven pesticides were used to spike the orange extract at three different levels. The aim was not to quantify them but to evaluate if the laboratories were able to detect and report them at the three concentration ranges. Table 4.5 gives the pesticides added for each of the concentrations range.

Table 4.5 Pesticides and Concentration Range present in the extract.

High concentration (2 -1 mg/Kg)	Medium concentration (1 - 0.1 mg/Kg)	Low concentration (0.1 - 0.05 mg/Kg)
Atrazine	Bifenthrin	**Acrinathrin (17%)**
Diuron (10%)	Bromuconazole	Azoxystrobin
Chlorpyrifos-methyl	Chlorpyrifos	Buprofezin
Malathion)	Cyproconazole	Chlorotoluron
Metolachlor	Endosulfan beta	**Chromafenozide (29%)**
Omethoate	Fenazaquin	Cyprodinil
Pirimicarb	Imidacloprid	Dimethoate
Promecarb	Indoxacarb	Endosulfan alpha
Pyridaphenthion	Isoproturon	**Fenhexamid (15%)**
Terbuthylazine	**Lenacil (39%)**	**Fenuron (25%)**
Tolfenpyrad (20%)	Mepanipyrim	**Fluometuron (21%)**
Triflumizol	Penconazole	**Isoprocarb (17%)**
Vinclozolin	Procymidone	Pyrimethanil
	Prometryn	Pyriproxyfen
	Propazine	Quinoxyfen
	Spiroxamine	Terbutrin
	Thiacloprid	**Tolylfluanid (32%)**

In bold there are the pesticides that gave a higher number of false negative reported results; above 15%. The percentage is calculated from the total number of laboratories reporting that particular pesticide.

4.3 Assessment of laboratory performance.

No z-score values, or any other statistical calculations, have been performed as no numerical results were reported by the participants. However, a classification has been considered of importance, based on the number of detected results each laboratory reported and also according to the methods used.

Table 4.6 Classification of laboratories according to the number of pesticides reported.

Laboratory Code	Detected	Not Detected (ND)	Not Analysed (NA)	False Positives
Lab 38*	46	0	1	3
Lab 10	45	0	2	
Lab 9	44	1	2	
Lab 41	44	1	2	1
Lab 25	44	3	0	
Lab 20*	43	1	3	
Lab 42	42	1	4	
Lab 32	42	2	3	5
Lab 26	40	0	7	2
Lab 5	40	3	4	3
Lab 40	40	7	0	
Lab1	39	1	7	
Lab 28*	39	2	6	
Lab 6	39	3	5	1
Lab 8	39	5	3	1
Lab 36	39	6	2	2
Lab 34	38	5	4	
Lab 12*	37	1	9	
Lab 4	37	2	8	
Lab 30	37	4	6	
Lab 3	36	0	11	
Lab 43	36	7	4	
Lab 24*	35	1	11	
Lab 2*	35	5	7	
Lab 31	34	1	12	
Lab 17*	34	2	11	1
Lab 29	34	2	11	1
Lab 11*	33	1	13	
Lab 7*	33	2	12	2
Lab 37	33	3	11	
Lab 22	31	0	16	1
Lab 44	30	0	17	
Lab 27	30	5	12	
Lab 13*	29	4	14	
Lab 33	28	0	19	4
Lab 19	28	2	17	
Lab 16	26	0	21	

Laboratory Code	Detected	Not Detected (ND)	Not Analysed (NA)	False Positives
Lab 35	23	0	24	1
Lab 14	23	9	15	1
Lab 15	21	4	22	
Lab 45	21	6	20	
Lab 39*	20	6	21	
Lab 21	13	24	10	
Lab 18*	11	2	34	10
Lab 23	No Results Reported			

* National Reference Laboratories in Fruit and Vegetables participating in this test.

The classification of laboratories is complemented using the information coming from their reporting methods.

Table 4.7 Methods given by participating laboratories.

Method(s) used and number of compounds in the method									
Lab Code	GC-MS (/MS)				GC-specific			LC-MS (/MS)	
	Full Scan	SIM	NCI	MS/MS	FPD	ECD	NPD	Full Scan	MS/MS
38*	100**			100				Not specified	160
10	590	82	51		34				273
9	410							472	
25	500		350			700		500	
41	216								111+24
20*	90								170
32	90								170
42				170					170
5	70**							320	
26	100**								200
40	No method information provided								
1	No method information provided								
6	930								130
8	566								188
28*	160**								90
36	250								360
34	624								159
4	68**								257
12*	No method information provided								
30	529								423+213

Method(s) used and number of compounds in the method									
Lab Code	GC-MS (/MS)				GC-specific			LC-MS (/MS)	
	Full Scan	SIM	NCI	MS/MS	FPD	ECD	NPD	Full Scan	MS/MS
3	146**								232
43	250				100				50
2*	200**								150
24*	927								
17*	525			123		Not specified			174+188
29	Not specified								Not specified
31	543								
7*	150**								200
11*	70**		18	122					23+27
37	210								84
22				40					100
27	927							104	
44	200								
13*				206					38
19	160								
33				Not specified					Not specified
16	Not specified								
14	215								63
35								150	
15	91								68
45	21**								21
39*	132								
21	Not specified								Not specified
18*	13**								
23	No Results Reported								

* NRL-FV ** Full Scan or SIM (not specified)

5. CONCLUSIONS

Forty-five laboratories applied to participate in this test and forty-four laboratories submitted results. Taking into account that this PT was announced at very short notice, an adequate number of participants responded. Twelve participating laboratories were National Reference Laboratories for Fruits and Vegetables (marked with an asterisk on the graphs and tables).

Most laboratories analysed the extract using methods based on both gas and liquid chromatography, combined with mass spectrometric detection. In the case of GC-MS analysis, full scan acquisition, with a target-library (covering a large number of pesticides), was used by the majority of the laboratories. In contrast where LC-MS analysis was used, targeted acquisition methods using triple quadrupole instruments was favoured. Only 6 laboratories used LC combined with full scan measurement (high resolution instruments). Most of the laboratories indicated that they could cover a scope above 400 pesticides, which was well beyond the target list provided by the organiser.

None of the laboratories was able to detect all 47 pesticides spiked into the orange extract. More than 50% of the participants failed to detect 10 or more pesticides. This was partly due to a miss-match in the scope of the participant's method and the target list of the organiser. For laboratories with a high number of compounds in their scope, this was a less serious issue, but it might be worth reconsidering the choice of the pesticides included in the scope of the participant's screening method(s). Much more serious was the reporting of false negatives for pesticides claimed to be within the scope of the laboratory. Such cases of false negatives should be investigated by the participants.

A number of participants reported pesticides that were not spiked into the orange extract. Whether or not this should be judged as poor performance depends on how the participant would act on these results in routine analysis. If the detected pesticide would be reported as positive without any further confirmation of identity, then the result would be a false positive and erroneous monitoring data would be reported. If the detected pesticide would be regarded as only 'suspect' or 'indicatively present' and followed up by additional analysis to confirm identity before reporting the result, then the pesticide indicated as false positive in this report and is not really an issue

This first interlaboratory test on wide-scope screening methods showed that such an approach can substantially expand the scope of pesticide residue analysis. This is especially useful for pesticides not frequently found in food and, therefore, not included in current quantitative methods. The use of screening methods greatly increases the chance of detecting less commonly found pesticides. However, the test also revealed that improvements in scope (both in number and the choice of pesticides included) and verification of the performance of screening methods (i.e. validation) are necessary to improve reliability of such methods.

6. SUGGESTIONS FOR FUTURE WORK

The Organiser and the Scientific Committee of the first proficiency comparison test on screening methods for pesticide residues considers that such methods have added value in addition to the quantitative multiresidue methods currently routinely used for monitoring purposes. The results of this first test are very encouraging, but also indicate the need for continued evaluation of screening methods. Therefore, further proficiency tests will be organised to provide support to those laboratories using screening methods in order to extend their use and improve their reliability. These methods will be used more and more as screens/filters, to make routine laboratory work easier and faster. The need for validation of screening methods has been recognised and guidelines for such validation have been prepared and included in the update of the SANCO document for "Method validation and quality control procedures for pesticide residue analysis in food and feed" (SANCO/10684/2009).

For next year, a new matrix extract will be used. If there is an interest from laboratories for specific matrices, they should inform the CRL-FV as soon as possible. The timing of delivery of the test extract will be April, and as this year, 48 hours will be allowed for submission of results (given that this should be time enough to undertake screening methods). There will be no target list, as was in this first test.

7. REFERENCES

1. Mezcua M., Martinez-Uroz M. A., Wylie P. L. and Fernandez-Alba A.R. Simultaneous screening and target analytical approach by GC-q-MS for pesticide residues in fruits and vegetables. Journal of AOAC Int., 2009, 92 (6).

2. Mezcua M., Malato O., Garcia-Reyes J. F., Molina-Diaz A., and Fernandez-Alba A. R. Accurate-Mass Databases for Comprehensive Screening of Pesticide Residues in Food by Fast Liquid Chromatography Time-of-Flight Mass Spectrometry. Anal. Chem. 2009, 81, 913–929

3. DG SANCO/10684/2009 of the European Quality Control Guidelines.

4. ILAC G-13:2000 Guidelines for the Requirements for the Competence of Providers of Proficiency Testing Schemes.

5. UNE 66543 Proficiency testing by inter-laboratory comparisons – Part 1 and Part 2.

8. ACKNOWLEDGEMENTS

The Organiser is grateful to the European Commission for funding this 1st European Proficiency Test in Fruit and Vegetables for Screening Methods.

The Organiser wishes to thank the members of the Scientific Committee for their invaluable and knowledgeable advice.

The Organiser wishes to give a special thank-you to Almeria University for the use of their facilities.

APPENDIX 1. Results

Lab Code	Pesticides Present in the Extract																				
	Acrinathrin	Atrazine	Azoxystrobin	Bifenthrin	Bromuconazole	Buprofezin	Chlorofoluron	Chlorpyrifos	Chlorpyrifos-methyl	Chromafenozide	Cyproconazole	Cyprodinil	Dimethoate	Diuron	Endosulfan alpha	Endosulfan beta	Fenazaquin	Fenhexamid	Fenuron	Fluometuron	Imidacloprid
1	YES	YES	YES	YES	YES	YES	NO	YES	YES	NA	YES	YES	YES	NA	YES	YES	YES	YES	NA	NA	NA
2	YES	YES	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	NO	YES	YES	YES	YES	YES	NA	NA	YES
3	YES	YES	YES	YES	NA	YES	NA	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	NA	NA	YES
4	NO	YES	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES
5	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	NO	YES	YES	YES	NA	YES	YES	YES	YES
6	YES	YES	YES	YES	NO	YES	NA	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	NA	NA	YES
7	YES	YES	NO	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	NA	YES	YES	NA	YES	NA	NA	YES
8	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	NO	NO	YES	YES	NA	NA	YES
9	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES
10	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
11	YES	YES	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	YES	NA	YES	YES	NA	NO	NA	NA	YES
12	NO	YES	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	NA	NA	YES
13	YES	YES	NO	YES	YES	NO	NA	YES	YES	NA	YES	YES	YES	YES	YES	YES	NO	YES	NA	NA	NO
14	YES	NA	YES	YES	NO	NO	NA	NO	YES	NA	NO	YES	YES	NA	NO	NO	YES	NO	NA	NA	YES
15	NO	NA	YES	YES	NA	YES	NA	YES	YES	NA	NA	YES	YES	NA	NO	YES	NA	YES	NA	NA	NO
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17	YES	NA	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	YES	NO	YES	YES	YES	YES	NA	NA	YES
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20	YES	YES	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES
21	NO	NO	NO	NO	NO	YES	NA	NO	YES	NA	YES	YES	YES	NO	NO	NO	NO	NO	NA	NA	YES
22	NA	YES	YES	YES	NA	YES	NA	YES	YES	NA	YES	YES	YES	NA	YES	YES	NA	YES	NA	NA	YES
23	No Results Given																				
24	YES	YES	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	YES	NA	YES	YES	YES	NO	NA	NA	NA
25	YES	YES	YES	YES	YES	YES	YES	YES	YES	NO	YES	YES	YES	YES	YES	YES	YES	YES	NO	YES	YES
26	YES	YES	YES	YES	NA	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	NA	NA	YES
27	YES	NA	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	NO	YES	YES	YES	NO	YES	NA	NA	YES
28	YES	YES	YES	YES	NA	YES	YES	YES	YES	NA	NO	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES
29	YES	YES	YES	YES	NA	YES	NA	YES	YES	NA	YES	YES	YES	YES	YES	YES	NA	YES	NA	YES	YES

APPENDIX 1. Results

Lab Code	Pesticides Present in the Extract																				
	Acrinathrin	Atrazine	Azoxystrobin	Bifenthrin	Bromuconazole	Buprofezin	Chlorofoluron	Chlorpyrifos	Chlorpyrifos-methyl	Chromafenozide	Cyproconazole	Cyprodinil	Dimethoate	Diuron	Endosulfan alpha	Endosulfan beta	Fenazaquin	Fenhexamid	Fenuron	Fluometuron	Imidacloprid
30	YES	YES	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	NA	NA	YES
31	YES	YES	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	NO	NA	YES	YES	YES	YES	NA	NA	NA
32	YES	YES	YES	YES	NO	YES	YES	YES	YES	YES	YES	YES	NO	NA	YES	YES	YES	YES	YES	YES	YES
33	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	NA	NA	YES	NA	YES
34	YES	YES	YES	YES	NA	YES	NO	YES	YES	NA	YES	YES	YES	NO	YES	YES	YES	YES	NO	NO	YES
35	NA	YES	YES	NA	YES	NA	YES	NA	NA	NA	YES	YES	YES	YES	NA	NA	YES	YES	NA	NA	YES
36	NO	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
37	NO	YES	YES	YES	NA	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	NA	NA	YES
38	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES
39	YES	YES	YES	YES	NA	YES	NA	YES	YES	NA	YES	YES	YES	NA	NO	NO	NA	NO	NA	NA	NA
40	YES	YES	NO	YES	YES	YES	YES	YES	YES	NO	YES	YES	YES	YES	YES	YES	YES	NO	YES	NO	YES
41	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
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43	NO	YES	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	NO	NO	YES
44	YES	YES	YES	YES	NA	YES	NA	YES	YES	NA	YES	YES	YES	NA	YES	YES	YES	NA	NA	NA	NA
45	YES	YES	YES	YES	NA	NO	NA	YES	YES	NA	YES	YES	YES	NA	NO	NO	YES	NA	NA	NA	NO

YES: detected pesticide; NO: not detected; NA: not analysed

APPENDIX 1. Results

Lab Code	Pesticides Present in the Extract																				
	Indoxacarb sum	Isoprocarb	Isoproturon	Lenacil	Malathion	Mepanipyrim	Metolachlor	Omethoate	Penconazole	Pirimicarb	Procymidone	Promecarb	Prometryn	Propazine	Pyridaphenthion	Pyrimethanil	Pyriproxyfen	Quinoxyfen	Spiroxamine	Terbuthylazine	Terbutrin
1	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
2	YES	NA	YES	NO	YES	YES	YES	NO	YES	YES	NO	YES	YES	NA	YES	YES	YES	YES	YES	YES	NA
3	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	NA	NA	YES	YES	YES	YES	YES	YES
4	YES	NA	YES	NA	YES	YES	YES	NO	YES	YES	YES	YES	YES	NA	YES	NA	YES	YES	YES	YES	YES
5	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES
6	YES	NA	YES	NO	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
7	YES	YES	NA	NA	YES	YES	YES	YES	YES	YES	NO	NA	YES	NA	NA	YES	YES	YES	YES	YES	YES
8	YES	YES	NA	NO	YES	NO	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
9	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	NO	YES	YES	YES	YES	YES	YES	YES	YES	YES
10	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
11	NA	NA	NA	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES
12	YES	NA	NA	NA	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES
13	YES	NA	NA	NA	YES	YES	NA	YES	YES	YES	YES	NA	YES	NA	YES	YES	YES	YES	YES	NA	NA
14	YES	NA	NA	NA	YES	YES	YES	YES	YES	YES	YES	YES	NA	NA	YES	NO	YES	YES	YES	NA	NA
15	NO	NA	NA	NA	YES	YES	NA	YES	YES	YES	YES	NA	NA	NA	NA	YES	YES	YES	YES	NA	NA
16	YES	YES	NA	NA	YES	YES	NA	NA	YES	YES	YES	NA	NA	NA	YES	YES	YES	YES	NA	NA	NA
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20	YES	YES	YES	NO	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
21	YES	NA	NA	NO	NO	NA	NO	NO	YES	YES	NO	NA	NO	NO	NO	NO	YES	NA	YES	NO	NO
22	YES	NA	NA	NA	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	NA	YES	YES	YES	YES	YES	NA
23	No Results Given																				
24	NA	YES	NA	NA	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
25	YES	YES	YES	NO	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
26	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES
27	YES	NA	YES	NA	YES	NO	NA	YES	YES	YES	YES	NO	YES	NA	YES	YES	YES	YES	NA	NA	YES
28	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	NO

APPENDIX 1. Results

Lab Code	Pesticides Present in the Extract																				
	Indoxacarb sum	Isoprocarb	Isoproturon	Lenacil	Malathion	Mepanipyrim	Metolachlor	Omethoate	Penconazole	Pirimicarb	Procymidone	Promecarb	Prometryn	Propazine	Pyridaphenthion	Pyrimethanil	Pyriproxyfen	Quinoxyfen	Spiroxamine	Terbuthylazine	Terbutrin
29	YES	NA	NA	NA	YES	YES	YES	NO	YES	YES	YES	NA	NA	YES	YES	NO	YES	YES	YES	YES	YES
30	NO	YES	NO	NO	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES
31	YES	YES	NA	NA	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA
32	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES
33	NA	NA	YES	NA	YES	YES	YES	NA	NA	YES	NA	NA	NA	NA	NA	YES	YES	YES	YES	YES	NA
34	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	NA
35	YES	NA	YES	NA	YES	YES	NA	YES	YES	YES	NA	NA	NA	NA	NA	YES	YES	YES	YES	NA	NA
36	YES	NO	NO	YES	YES	YES	YES	YES	YES	YES	YES	NO	YES	YES	YES	YES	YES	YES	YES	YES	NO
37	YES	NO	YES	NA	YES	YES	NA	YES	YES	YES	YES	NO	YES	NA	YES	YES	YES	YES	YES	NA	NA
38	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
39	NO	NA	NA	NA	YES	YES	NA	YES	YES	NA	YES	NA	NA	NA	YES	NO	YES	YES	NO	NA	NA
40	YES	NO	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
41	YES	NA	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
42	YES	NA	YES	NO	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
43	YES	NA	NO	NO	YES	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	NO	YES	YES	YES	YES
44	NA	NA	NA	NA	YES	YES	NA	YES	YES	YES	YES	YES	YES	NA	YES	YES	YES	YES	YES	YES	YES
45	YES	NA	NA	NA	YES	NA	YES	YES	NO	YES	NO	YES	NA	NA	NA	YES	YES	YES	NA	YES	NA

YES: detected pesticide; NO: not detected; NA: not analysed

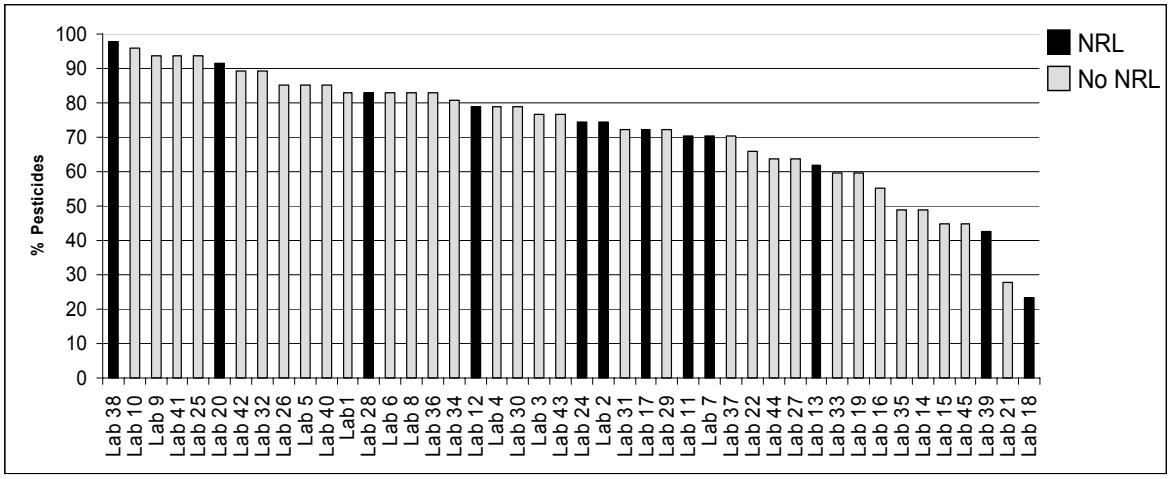
APPENDIX 1. Results

Lab Code	Pesticides Present in the Extract				
	Thiacloprid	Tolfenpyrad	Tolylfluanid	Triflumizol	Vinclozolin
1	NA	YES	YES	YES	YES
2	YES	YES	NO	YES	YES
3	YES	NA	YES	NA	YES
4	YES	NA	YES	YES	YES
5	YES	NO	NA	NO	YES
6	YES	YES	NO	YES	YES
7	YES	NA	YES	NA	YES
8	YES	YES	NO	YES	YES
9	YES	YES	YES	YES	YES
10	YES	NA	YES	YES	YES
11	YES	NA	YES	NA	YES
12	YES	NA	YES	YES	YES
13	YES	NA	YES	NA	YES
14	YES	NA	NO	NA	YES
15	NA	NA	YES	NA	YES
16	NA	NA	YES	NA	YES
17	YES	NA	YES	YES	YES
18	NA	NA	NO	NA	YES
19	NA	NA	NO	NA	YES
20	YES	YES	YES	YES	YES
21	YES	NA	YES	NO	NO
22	YES	NA	NA	YES	YES
23	No Results Given				
24	NA	YES	YES	YES	
25	YES	YES	YES	YES	YES
26	YES	NA	YES	NA	YES
27	YES	NA	NO	YES	YES
28	YES	NA	YES	YES	YES
29	YES	NA	YES	YES	YES
30	YES	NA	NO	YES	YES
31	NA	YES	NA	YES	YES
32	YES	YES	NA	YES	YES
33	NA	NA	NA	NA	YES
34	YES	NA	NO	YES	YES
35	YES	NA	NA	NA	NA
36	YES	NA	NO	YES	YES
37	YES	NA	YES	NA	YES
38	YES	YES	YES	YES	YES
39	NA	NA	YES	NA	YES
40	YES	NO	NO	YES	YES
41	YES	YES	NO	YES	YES
42	YES	NA	YES	YES	YES
43	YES	NO	YES	YES	YES
44	NA	NA	YES	NA	YES
45	YES	NA	NA	NA	NA

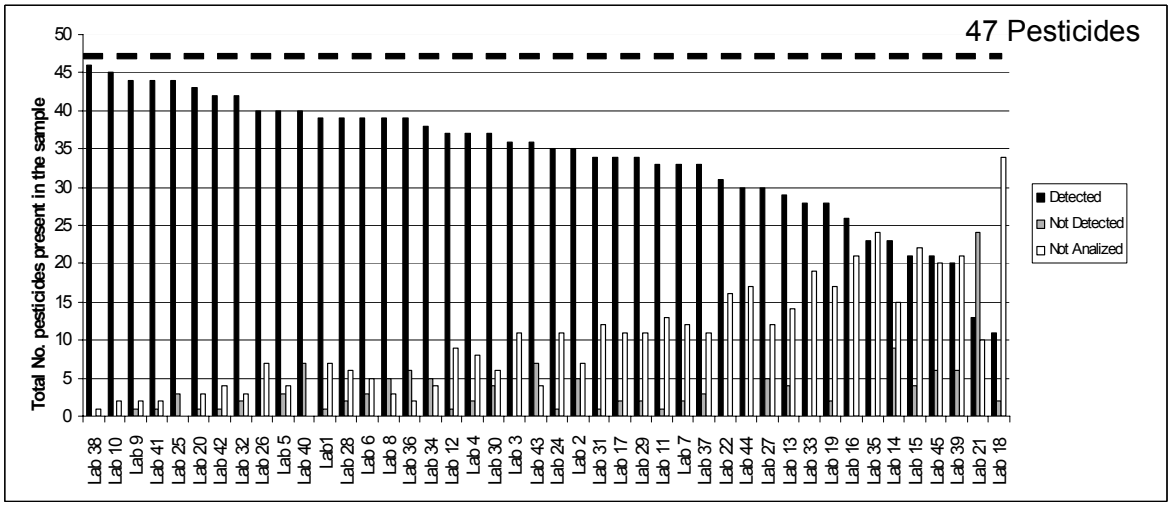
YES: detected pesticide; NO: not detected; NA: not analysed.

APPENDIX 2. Graphical Representations

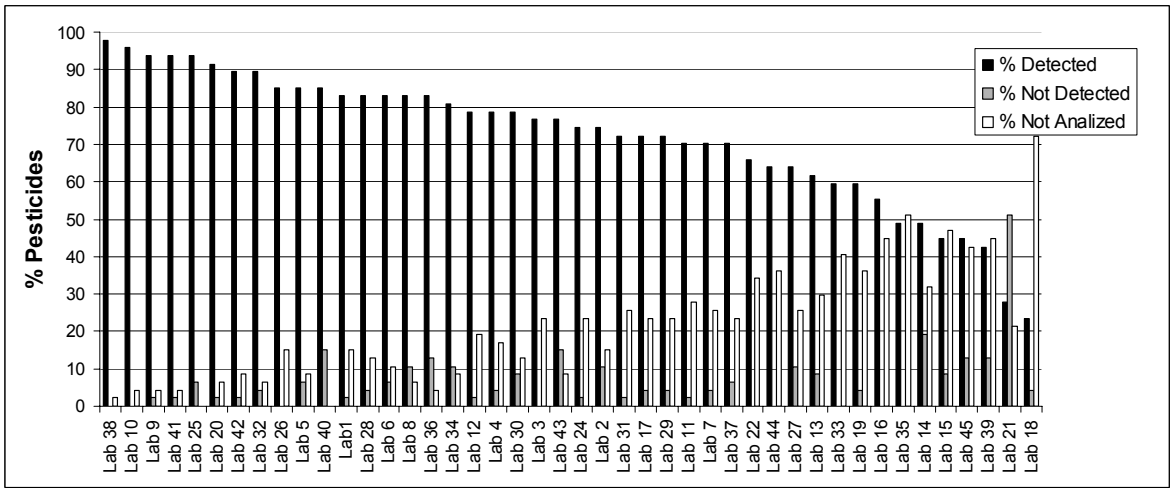
Total % of pesticides reported by the participant laboratories



No. of pesticides detected, not detected and not analysed by the participant laboratories

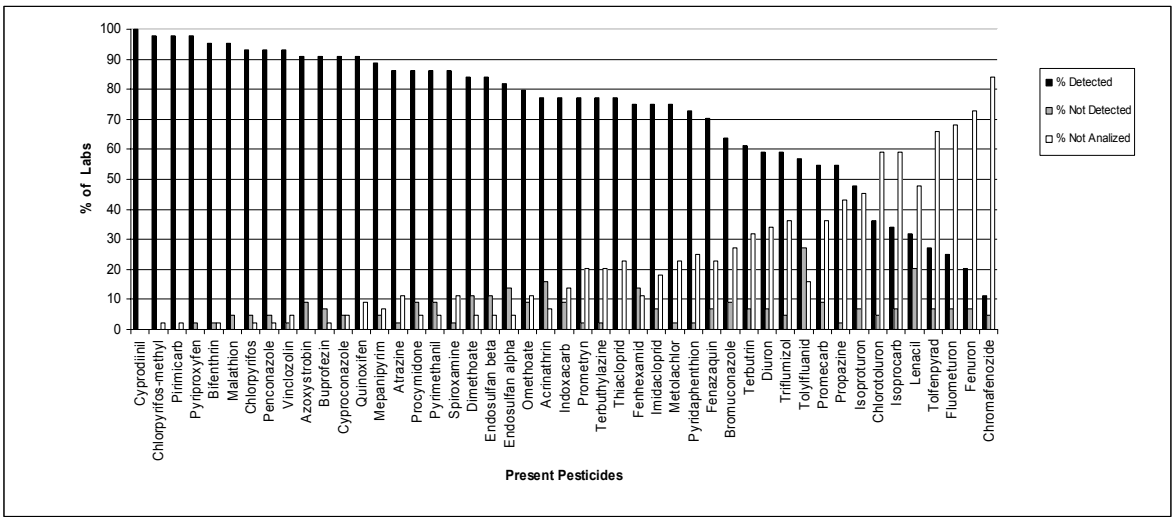


% of pesticides detected, not detected and not analysed by the participant laboratories

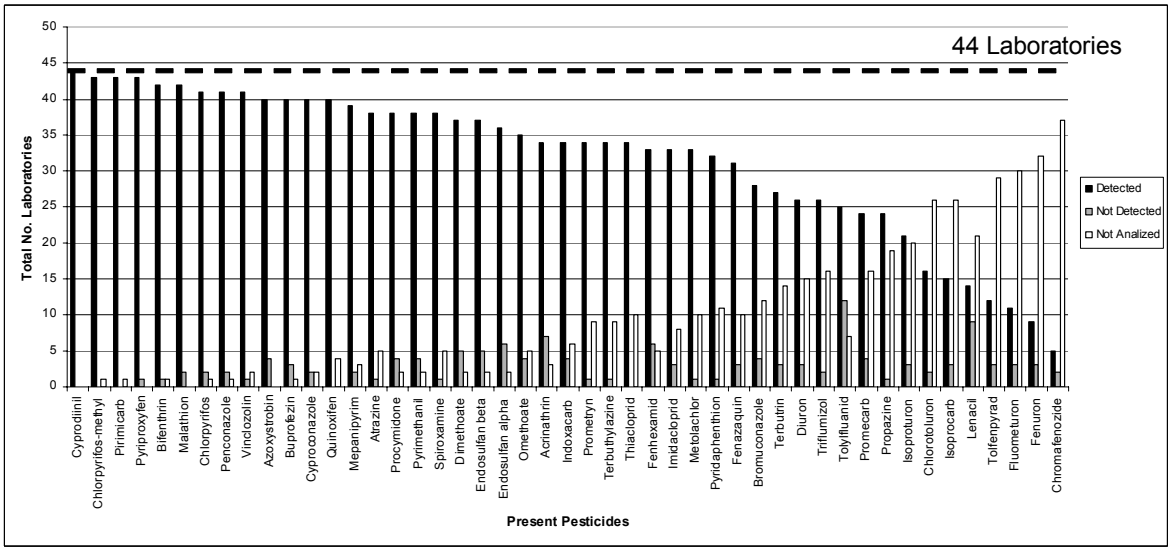


APPENDIX 2. Graphical Representations

% of laboratories reporting detected, not detected and not analysed by pesticides



Total No. of laboratories reporting detected, not detected and not analysed by pesticides



APPENDIX 3. Methods used by participants for detecting pesticides.

Lab Code	Extract Adjustment for GC(if any)				Extract Adjustment for LC(if any)				Instrument Used	Chromatographic Conditions		Software automated or manual or both	No. of compounds in method or library	Were standard solution analysed together with sample extract? (Yes or No)
	Dilution factor	Solvent Switch	Final extract composition	Final concentration	Dilution factor	Solvent Switch	Final extract composition	Final concentration		Column Type	Injection Volume (µL)			
001	NO INFORMATION PROVIDED													
002	None	None	Neat	No Deviation	None	None	Neat	No Deviation	Agilent 6890 GC with 5973N MS Q	HP5MS	2	Chemstation	200	YES
									Applied Biosystems API400 QQQ	SppedRod	10	Analyst 1.5	150	YES
003	5	To toluene	Toluene/Acetonitrile 4/1	0.2g/ml					GC-MS (quad) GC 6890-MSD 5973 (Agilent)	DB5-MS	1	manual	146	YES
									LC-MS/MS Alliance 2695-Quattro Premier XE, (Waters)	reversed phase	5	Both	232	YES
004	1	Hexane/acetone 9/1			No	No			LC-MSMS	C18	5	Automated	257	YES
									GC-MSD	HP-5	1	Automated	68	YES
005		Ciclohexan				MeOH/water050/50			TOF	C18	5	AUTOMATED	320	YES
									GC-MS	DB5.MS	10	AUTOMATED	70	YES
006		Isooctan/ Toluol 9+1		1g/ml		Methanol	Methanol	5g/ml	API 2000 Triple quadrupole mass spectrometer	ODS	5	Both	130	YES
									Agilent MSD 5975C	HP5-MS	2	Both	195 in method - 930 in library	YES
007		isooctane-toluene 9:1	isooctane-toluene 9:1			methanol-water 3:7	methanol-water 3:7		GC	DB5	1	automated	150	NO
									LC-MS/MS	C-18	5	automated	200	YES

APPENDIX 3. Results (mg/Kg) and z-scores for FFP RSD (25%).

Lab Code	Extract Adjustment for GC(if any)				Extract Adjustment for LC(if any)				Instrument Used	Chromatographic Conditions		Software automated or manual or both	No. of compounds in method or library	Were standard solution analysed together with sample extract? (Yes or No)
	Dilution factor	Solvent Switch	Final extract composition	Final concentration	Dilution factor	Solvent Switch	Final extract composition	Final concentration		Column Type	Injection Volume (µL)			
008	No	No			No	No			GC-MS	DB-5 MS	2	automated	566	NO
									LC-MS/MS	C-18-3m	10	manual	188	NO
009	none	none	Acetonitrile		2	None	Acn:water 1:1	0.5g/ml	Leco Pegasus GCxGCTOF	Rtx-ClPesticides	10	both	410	YES (not all compounds)
									Thermo Exactive LC-hrMS	Waters Atlantis T3	10	both	472	YES (not all compounds)
010	1;1:10	No	Acetonitrile	1 g/ml; 0.1 g/ml	No	No			LC-qqq-MS/MS	C18 3µ 50x2mm	10	both	273	YES
									GC-q-MS	HP-5MS	3	automated	590	No
									GC-q-MS (EI)	HP-5MS	3	both	82	YES
									GC-q-MS (NCI)	HP-5MS	3	both	51	YES
									GC-FPD	DB5 / DB1701	2	both	34	YES
011					2		Acetonitril:mobile phase 1/1	0.5g/ml	LC MSMS ITD	c18	5	both	23	YES
									LC MSMS quad*	c18	5	automated	27	
									GC MSMS itd	5% phenyl metyl siloxan	5ul	both	122	YES
									GC MS quad	5% phenyl metyl siloxan	1	manual	70	NO
									GC NCI	5% phenyl metyl siloxan	1	both	18	YES

APPENDIX 3. Methods used by participants for detecting pesticides.

Lab Code	Extract Adjustment for GC(if any)				Extract Adjustment for LC(if any)				Instrument Used	Chromatographic Conditions		Software automated or manual or both	No. of compounds in method or library	Were standard solution analysed together with sample extract? (Yes or No)
	Dilution factor	Solvent Switch	Final extract composition	Final concentration	Dilution factor	Solvent Switch	Final extract composition	Final concentration		Column Type	Injection Volume (µL)			
012	NO INFORMATION PROVIDED													
013	Yes	Yes	Hexane	2g/ml	No	No	Acetonitrile	1g/ml	GC-MS-MS Varian 4000	Rxi 5ms 30mx0,25mm	2	both	206	YES
									LC-MS-MS Agilent 1100-Bruker esquire3000	UP3 ODB-10QS	10	both	38	YES
014									GC-MS full-scan quadrupole	HP-5MS 0,25 ID 30m	1	both	215	YES
									LC- MS triple quadrupole	C18 150*2 3µm	10	both	63	YES
015					2		50%ACN - 50% eluant (80%water/20%MeOH)		GC/MS ion trap	DB 5	5	both	91	YES
									triple quad LC/MS/MS	C18	5	both	68	YES
016									GC-TOF-MS	DB5-MS	2	Automated		YES
017	2 (1 + 1 with acetonitrile)	No	Acetonitrile	0.5g/ml	2 (1+1 with methanol)	No	acetonitrile:methanol (1:1)	0.5g/ml	GC-ITD	VF-5MS	5	automated	525	YES
									GC-ECD	VF-5MS	5	automated		YES
									GC-MS/MS	VF-5MS	5	automated	123	YES
									LC-MS/MS (ESI+ and ESI-)	RP18	2	automated	174	YES
									UPLC-MS/MS (ESI+)	BEH-C18	2	automated	188	YES
018									GC Agilent 6890N /MS Agilent5975	HP-5MS	2	automated	13	YES
019	No	Yes	Acetone						GC-MS	HP5	1	both	160	NO

APPENDIX 3. Results (mg/Kg) and z-scores for FFP RSD (25%).

Lab Code	Extract Adjustment for GC(if any)				Extract Adjustment for LC(if any)				Instrument Used	Chromatographic Conditions		Software automated or manual or both	No. of compounds in method or library	Were standard solution analysed together with sample extract? (Yes or No)
	Dilution factor	Solvent Switch	Final extract composition	Final concentration	Dilution factor	Solvent Switch	Final extract composition	Final concentration		Column Type	Injection Volume (µL)			
020*	1:04	AcOet:ciclohexano 1:9	AcOet:ciclohexano 1:9		1:04	ACN:H2O 1:3	ACN:H2O 1:3		Varian GC-ITD 4000	Varian Factor four VF-5ms	10	both	90	YES
									Waters Acquity UPLC-Quattro Premier XE	Acquity UPLC HSS T3	7	both	170	YES
021			Acetonitril				Acetonitril		GC-MS	Rtx-CLPII	1	automated		YES
									LC-MS/MS	Synergi 4u Fusion-RP 80 A	10	automated		YES
022					5	ACN:H2O 1:5			ThermoFinnigan TSQ Quantum Ultra LC-MS/MS	Xterra	20	both	100	YES
									ThermoFinnigan POLARISQ GC-MS/MS	DB-5ms	1	both	40	NO
023	NOT RESULTS REPORTED													
024	2	No	acetonitrile + acetone						Agilent 6890N (5973 MSD)	HP-5ms	1	DRS	927	YES
025	No	No	addition of ISTD-solution in ACN	No	No	addition of ISTD-solution in ACN			LC-QToF	BEH C18	2	Both	500	
									GC-ToF	DB5-MS	5	Both	500	YES
									GC-CI neg	DB5-MS	3	Both	350	
									GC-ECD/NPD	DB5-MS	3	Both	700	YES
									LC-MS/MS					
026	No	No	Acetonitril		undiluted (and factor 10)	No	Acetonitril	1 g/ml (and 0.1 g/ml)	HPLC Perkin Elmer 200 API 4000 (AB)	C-18 Zorbax Eclipse	5	Analyst	~ 200	YES
									GC - MSD 5973 (Agilent)	DB-17 MS	1	ChemStation	~ 100	YES
027	1	No			1	No			GC-MS (quad.)	HP-5	10	automated	927	NO
									LC-HRMS	C18	10	both	104	NO

APPENDIX 3. Methods used by participants for detecting pesticides.

Lab Code	Extract Adjustment for GC(if any)				Extract Adjustment for LC(if any)				Instrument Used	Chromatographic Conditions		Software automated or manual or both	No. of compounds in method or library	Were standard solution analysed together with sample extract? (Yes or No)
	Dilution factor	Solvent Switch	Final extract composition	Final concentration	Dilution factor	Solvent Switch	Final extract composition	Final concentration		Column Type	Injection Volume (µL)			
028									CG/MS-Q	PB5	1	BOTH	160	ONLY REPRESENTATIVE STANDARDS
									LC/MS/MS QQQ	C18	5	BOTH	90	ONLY REPRESENTATIVE STANDARDS
029									GC-MS (ION TRAP)	FV5	10	BOTH		YES
									LC-MS		10	BOTH		YES
030					2	Acetonitril+5mmol NH4-formiat in Water	Acetonitril+5mmol NH4-formiat in Water	0.5 g	GC6890 with MSD 5973 by Agilent	DB 5 ms 30 m x 0,25 mm x 0,25 µm	4	both	529	YES
									UPLC with MSMS Quattro Premier XE by Waters	Acquity UPLC BEH C18, 2,1x50 mm, 17 µm	5 or 10	5 or 10	423	YES
									UPLC API 2000 by Applied Biosystems	Phenomenex Aqua 150x2 mm, 3 µm	20	both	213	YES
031	5	Yes	Acetonitrile + analyte protectants						GC-MS Single Q	HP5MS	2	A	543	NO
032	4		AcOet/ciclohexane		4		ACN:H2O		Varian GC-ITD 4000	Varian Factor four VF-5ms	10	Both	90	YES
									Waters Acquit UPLC-Quattro Premier XE	Acquity UPLC HSS T3	7	Both	170	YES
033			Heptane/acetone						GC-MS/MS thermo		1	automated		YES
									LC-MS/MS thermo ultra		20	automated		YES

APPENDIX 3. Results (mg/Kg) and z-scores for FFP RSD (25%).

Lab Code	Extract Adjustment for GC(if any)				Extract Adjustment for LC(if any)				Instrument Used	Chromatographic Conditions		Software automated or manual or both	No. of compounds in method or library	Were standard solution analysed together with sample extract? (Yes or No)
	Dilution factor	Solvent Switch	Final extract composition	Final concentration	Dilution factor	Solvent Switch	Final extract composition	Final concentration		Column Type	Injection Volume (µL)			
034			Acetonitrile		Mixing injection on-line 1:10 with water		Acetonitrile		Agilent GC-MS (5973N) with PTV and EI full-scan	HP-5MS(I)	20	AMDIS	204 / 624	YES, for pesticides in method
									Agilent LC-MS/MS 6410B	C18, 1.8 um	2	both	159	YES
035									Waters Xevo QTOF	UPLC BEH C18	3	both	150	YES
036	None	None	Internal standard added	1 g / 1.12 ml	None	Extract : 4mM Ammonium formate = 1:1	Internal standard added	0.5 g / 1.12 ml	GC-MS (LVI)	HP-5MS (15m)	10	manual	250	YES
									LC-MS/MS	C18	0.03	manual	360	YES
037	0.1	Ethyl Acetate		10g/mL	10	None	10% ACN, 90% HPLC H2O	0.1 g/mL	Agilent 6890 - 5973 GC-MSD	DB35ms	2	both	210	YES
									Waters Acquity - Quattro Premier XE LC-MS/MS	BEH C18 1.7um	10	both	84	YES
038		Ethyl acetate	100%Ethyl acetate		10	diluted with water	10:90 Acetonitrile: water	0.1g/ml	Agilent 6890/5973 MSD	DB-5 MS	2	both	100	YES
									Thermo scientific GC-MS/MS	TR pesticide	2	both	100	NO
									Waters Premier XE UPLC-MS/MS	C18	20	both	160	YES
									Agilent 6220 UPLC-TOF-MS	C18	20	both		NO

APPENDIX 3. Methods used by participants for detecting pesticides.

Lab Code	Extract Adjustment for GC(if any)				Extract Adjustment for LC(if any)				Instrument Used	Chromatographic Conditions		Software automated or manual or both	No. of compounds in method or library	Were standard solution analysed together with sample extract? (Yes or No)
	Dilution factor	Solvent Switch	Final extract composition	Final concentration	Dilution factor	Solvent Switch	Final extract composition	Final concentration		Column Type	Injection Volume (µL)			
039		Ethyl a acetate	orange extract in ethyl acetate						GC-TOF-MS	VF-5 ms; 30m*25mm ; DF=0.25	1	both	132	YES
040	NO INFORMATION PROVIDED													
041									API 2000	C18 Synergi Fusion 4mm 80A 100*2mm	7	both	24	YES
									API 4000QTrap	Pursuit XRs Ultra 2,8 C18 50x2mm	6	both	111	YES
									GC TOF	Phenomenex ZB 5 -MS	3	both	216	YES
042		Yes	Hexane		5		ACN / H2O	0.2g/ml	Waters QPXE MSMS	C18	5	both	170	YES
									Waters GCMSMS quattro	DB5-MS	1	both	170	YES
043							ACN/H2O		Varian 4000 ion trap		1	both	250	NO
									Varian 3800 (ECD/PFPD)		1	a	100	YES
									HP 1100 LC system	Chromasil	20	a	50	YES
044	Concentration: 5 ml to 1 ml	Acetate ethyl: ciclohexane 1:9	Acetate ethyl: ciclohexane 1:9	5 g/ml					GC-MS (quad)	HP-5 MS	2	Manual	200	YES
045	1000	isottane			1000				GC MS	DB5	2	Automated	21	YES
									LC/MS/MS	C18	5	Automated	21	YES

Protocol

Introduction:
Over the last 10 years, the operation of the European Proficiency Test for pesticide residues in fruit and vegetables by multi-residue methods has provided a great deal of information. As well as this wealth of gathered data, a further additional and very important aspect which can be drawn from this information is the increased year-on-year scope of the participating laboratories.
Nowadays, there is a clear need in many cases to enlarge the number of compounds covered in each multi-residue analysis. But this is a very costly task for many laboratories, one which too often cannot be fulfilled. As a consequence, "not analysed" (NA) is reported for a high percentage of the pesticides from the EUPT-target lists. As an example of this, in last year EUPT-Fv10, 22% of the reported results were 'NA'.
Mass spectrometry plays an essential role in the everyday work carried out by laboratories. It is used typically for target analysis purposes and the scope of official laboratories is generally in the range of 150 pesticides. Improvements in MS systems (and the accompanying software) offer several possibilities for increasing the scope of analysis. Full-scan working mode is theoretically the best approach for MS Screening although other possibilities developed by the laboratories will also be considered. GC-MS, Time-of-Flight and the new quadrupole mass spectrometers allow more sensitive full-scan measurement. In addition, improvements in software (automated deconvolution/identification) have made wide-scope screening a more feasible option for routine practice. LC-MS, tandem-MS detectors allow faster measurement of MS/MS transitions (or even MS/MS spectra) which can be used to increase the number of pesticides determined within one run. Furthermore, single stage TOF-MS systems, which enable sensitive full-scan acquisition with high mass accuracy, have been shown to be an interesting alternative. These new tools are options to complement existing multi-residue methods and can be used to increase identification capabilities offering adequate quality control in a fast and cheap way. Our aim now is to evaluate how effectively we can work using such procedures in order to develop the quality control systems necessary to give the screening results enough harmonized consistency.
The CRL-FV aim is to be able to use mass spectrometry screening methods in routine practice. To make this possible, we have organised this explorative proficiency test for those laboratories that have instruments and methods available to allow wide-scope MS screening of pesticides. Participating laboratories will be provided with an assessment of their identification capabilities and the reliability of their MS screening methods – as compared to the other participating laboratories.
This ring test will have a protocol containing general steps to evaluate the mass spectrometric screening method that each of the participants use. This might be their own in-house developed method or commercial products.

Main Characteristics:
This ring test will be performed for a citrus matrix (**orange**). Sample preparation will be done using an acetonitrile-based extraction method (Quechers). The initial extract will be spiked with between 40 to 60 pesticides and will be distributed to the labs that have previously sent the application form and which the Organiser has accepted into the test and given a lab code.
Laboratories are asked to screen the extracts using the wide-scope screening methods they would apply or foresee using in routine practice. This typically involves full-scan techniques like GC-MS (full-scan quadrupole, ion trap, ToF) and/or LC-ToF-MS but extended targeted methods using LC tandem MS (triple quadrupole, Q-trap, Q-ToF) or GC-MS/MS may also be used. The laboratory is requested to report the list of pesticides detected within 48 hours after receipt of the extracts.

Sample Extract Preparation:
Oranges will be purchased from an organic grower in Almeria.
The extract will be obtained using the Quechers method, as follows:
A representative 10 g portion of previously homogenized sample will be weighed in a 200 mL PTFE centrifuge tube. Then 10 mL of acetonitrile will be added, and the tube will be vigorously shaken for 1 min. After this time, 1 g of NaCl, 4 g of $MgSO_4$, 1 g of trisodium citrate dihydrate and 0.5 g of disodium hydrogen citrate sesquihydrate will be added, and the shaking process will be repeated for 1 min. The tube will then be centrifuged at 3500 rpm for 5 min. A 5 mL amount of the supernatant (acetonitrile phase) will be transferred to a 15 mL graduated centrifuge tube containing 125 mg of PSA, 750 mg of $MgSO_4$ and 125 mg C18 and energetically shaken using a vortex mixer for 30 s. Following this, it will be centrifuged again (3500 rpm) for 5 min. After centrifugation, the cleaned extract is pH adjusted to 5 by adding a 5 % formic acid solution in acetonitrile (vol/vol) (40 µL). Finally, the extract, is transferred into a screw cap vial containing the equivalent of 1 g of sample per mL in acetonitrile.
The method will be repeated as many times as necessary to obtain enough extract to be separated into two parts: one as a 'blank', or non-treated extract, and the other as the treated extract. The treated extract will be spiked with a mixture of pesticides from the target pesticide list.
Laboratories will receive two extracts, one spiked and one 'blank'.

Advice on sample handling:
As soon as you receive the extracts put them in the refrigerator until you are ready to inject.

Laboratories are allowed to adjust the solvent composition of the extracts by dilution or by evaporation/reconstitution in an appropriate solvent if considered necessary for injection.

Calendar:

Activity	Date
Receipt of Application Forms from invited laboratories.	29th May 2009
Extract matrix distribution.	15th June 2009
Deadline for receipt of extract matrix acceptance: Form 1	As soon as received
Deadline for receipt of results: Form 2	48 hours after receiving
Preliminary Report	July 2009
Final Report distributed to the Laboratories.	December 2009

Application Form:
The laboratory name, contact person and the laboratory delivery address should be indicated clearly on the Application Form, which should be sent not later than 29th May 2009. On the application form you should include information regarding your equipment, and your scope.

Shipping of the sample extract:
The shipment of the sample extract will be carried out in two days (Monday – Tuesday), so laboratories will have 48 hours for analysis before the week ends. A warning message will be sent out a week before the shipment. Laboratories must make their own arrangements for the reception of the sample extract. They must inform the Organiser of any public holidays in their country/city during the delivery period given in the calendar as well as make the necessary arrangements to receive the shipment even if the laboratory is closed.

Form 1:
Once the laboratory has received the sample extract, they must complete Form 1 and send it off right away after filling in the date and the hour of receipt, the condition of the sample extract (for example, whether the vial has been broken or there are any losses) and confirm its acceptance. If Form 1 is not received, the laboratory results will not be accepted. If any laboratory has not received the test material by 17th June, it must inform the Organiser immediately via e-mail (pmedina@ual.es).

Form 2:
Once the laboratory has run the sample extract on each of the MS screening methods they have available at their lab (on each of the equipment types listed on their application form), they have **48 hours** to fill in Form 2: marking which pesticide they have detected from the target pesticide list and other parameters their library may have. A semi-quantification may be done which will be optional and using the same MS system used for the screening (e.g. below 50 µg/Kg, between 50 – 500 µg/Kg or above 500 µg/Kg). This Form must be sent by e-mail to pmedina@ual.es

Confidentiality:
The results arising from this ring test will be known by the participants and the Organiser. Each participating laboratory will be presented as a lab code to the Commission or at a Workshop.

Communication:
The official language used will be English.
Communication between participating laboratories during the test on matters concerning the test is not permitted.

Evaluation of the Results:
The procedures used for the evaluation of results will be based mainly on false negatives and false positives. After receiving the results, the Organiser may consider further evaluation that will highlight important information received. Therefore:
- *False Positives*: these will be considered as those results that show the apparent presence of pesticides that were listed in the Target Pesticide List, but which were (i) not used in the sample treatment, and (ii) not detected by the Organiser, even after repeated analyses. However, if a number of participants do detect the same additional pesticide, then a decision as to whether, or not, this should be considered to be a false positive result will be made on a case-by-case basis.
- *False Negatives*: these will be considered as the absence of any "detected" result reported by the lab after the Organiser has treated the sample extract and it has been detected by the majority of participants.
- *Semi-quantification analysis*: an optional semi-quantification evaluation of the compounds found will be considered at three levels of concentration

A final report will be sent after the results have been submitted with all the conclusions raised from this test.

Application Form

PLEASE, ALWAYS save a copy of this document in your computer before sending it

The Laboratory agrees to participate in the interlaboratory test pesticide screening methods.

Please, fill in this form and send it back by e-mail (pmedina@ual.es) before 29th May 2009.

Laboratory Name					
Contact Name					
E-mail					
Tel.		**Fax.**			
Laboratory Delivery Address					
Postal Code		**City**		**Country**	

EQUIPMENTS / TECHNIQUES YOU WILL USE

For GC:

For LC:

☑ **I agree to be responsible for completing and returning this document to the Organiser. In the case of no e-mail reception confirmation by the Organiser for this document (within 3 to 4 days), I will contact them as soon as possible.**

CLICK HERE!!!

Together with this Application Form, please include the scope of each of the screening methods you will use to analyse the extracts. Fill in the second Data Sheet in this document.

CLICK HERE!!!

Please, fill in this form and send it back by e-mail (pmedina@ual.es) before 29th May 2009.

PLEASE, ALWAYS save a copy of this document in your computer before sending it

Please, ALWAYS save a copy of this document in your computer before sending it

FORM 1

Sample delivery - Reception Form

Please, fill in this form and send it back by e-mail to pmedina@ual.es

Laboratory Code:	
Sample extract code	
Blank extract code	
Date of receipt	
Hour of receipt	

Observation: - Write in the box below **Yes** or **No**

	Sample	Blank
Loses		
Frozen		
Broken		

Other Comments	

☑ **I accept the extract test material. I do not need more**

Date _____ **Responsible** _____

Please, fill in this form and send it back by e-mail (pmedina@ual.es) as soon as you have received the test material.

If no Form 1 is received by the Organiser, the laboratory results will not be accepted.

EUPT-FV-SM-01

European Proficiency Test in Fruits and Vegetables
Screening Method 01

FORM 2 - Sample Extract

Please, ALWAYS save a copy of this document in your computer before sending it

Lab. Code

To be fill up by the participant		
Sample Code	**Date**	**Hour**

Sample Results

Please, fill in this form and send it back by mail

Pesticides	Detected (1)	Determination Technique (2)	Deviation in Rt (3)	Mass Confirmatory Information (4)	Semi-Quantitative Concentration (mg/kg) (5)
2,4-dimethylaniline					
3,5-Xylylmethylcarbamate					
3-hydroxy-carbofuran					
Acephate					
Acetamiprid					
Aclonifen					
Acrinathrin					
Alachlor					
Alanycarb					
Albendazole					
Aldicarb					
Aldicarb Sulfone					
Aldicarb Sulfoxide					
Amitraz					
Anilofos					
Atrazine					
Azinphos-methyl					
Azoxystrobin					
Benalaxyl					
Bendiocarb					
Bifenthrin					
Bitertanol					
Boscalid					
Bromacil					
Bromopropylate					
Bromuconazole					
Bupirimate					
Buprofezin					
Butocarboxin					
Butoxycarboxin					
Cadusafos					
Cambendazole					
Captan					
Carbaryl					
Carbendazim (sum of benomyl and carbendazim expressed as carbendazim)					
Carbofuran					
Chlorbromuron					
Chlorfenapyr					
Chlorfenvinphos					
Chloridazon					
Chlorothalonil					
Chlorotoluron					
Chloroxuron					
Chlorpropham					
Chlorpyrifos					

Chlorpyrifos-methyl					
Chromafenozide					
Clofentezine					
Clothianidin					
Cyfluthrin					
Cymoxanil					
Cypermethrin					
Cyproconazole					
Cyprodinil					
Cyromazine					
Deet					
Deltamethrin					
Demeton-S-methyl					
Demeton-S-methylsulfone					
Desethylterbutylazine					
Desmethyl-pirimicarb					
Diafenthiuron					
Diazinon					
Dichlofluanid					
Dichlorvos					
Dicloran					
Dicofol					
Diethofencarb					
Difenoconazole					
Difenoxuron					
Diflubenzuron					
Dimethoate					
Dimethomorph					
Dimethylvinphos					
Dinotefuran					
Diphenylamine					
Diuron					
Edifenphos					
Emamectin benzoate					
Endosulfan alpha					
Endosulfan beta					
Endosulfan sulphate					
Epoxiconazole					
Ethiofencarb					
Ethion					
Ethiprole					
Ethoprophos					
Ethoxyquin					
Fenamiphos					
Fenamiphos sulphone					
Fenamiphos sulphoxide					
Fenarimol					
Fenazaquin					
Fenbuconazole					
Fenhexamid					
Fenitrothion					
Fenobucarb					
Fenoxycarb					
Fenpropathrin					
Fenpropimorph					
Fenuron					
Fipronil					
Fipronil sulfone					
Flazasulfuron					
Fluacrypyrim					
Fluazifop					
Fludioxonil					
Flufenoxuron					
Fluometuron					
Fluquiconazole					
Fluroxypyr					
Flusilazole					
Flutriafol					
Folpet					
Fosthiazate					
Hexaconazole					
Hexaflumuron					
Hexythiazox					
Imazalil					
Imidacloprid					
Indoxacarb (Indoxacarb as sum of the isomers S and R)					
Iprodione					
Iprovalicarb					
Isocarbofos					
Isofenphos-methyl					
Isoprocarb					
Isoproturon					
Kresoxim-methyl					
Lambda-Cyhalothrin					
Lenacil					
Linuron					
Lufenuron					
Malaoxon					
Malathion					
Mebendazole					
Mepanipyrim					
Metalaxyl and metalaxyl-M					
Metamitron					
Metconazole					
Methamidophos					
Methidathion					
Methiocarb					
Methiocarb sulfone					

Methiocarb sulfoxide					
Methomyl					
Methoxyfenozide					
Metobromuron					
Metolachlor					
Metolcarb					
Miconazole					
Monocrotophos					
Monolinuron					
Monuron					
Myclobutanil					
Neburon					
Nitempyram					
Omethoate					
Oxadixyl					
Oxamyl					
Oxfendazole					
Oxydemeton-methyl					
Paclobutrazole					
Paraoxon-methyl					
Parathion					
Parathion-methyl					
Penconazole					
Pendimethalin					
Phenthoate					
Phosalone					
Phosmet					
Phosmet oxon					
Phoxim					
Pirimicarb					
Pirimicarb					
Pirimiphos-methyl					
Prochloraz					
Procymidone					
Profenofos					
Promecarb					
Prometryn					
Propamocarb					
Propaphos					
Propargite					
Propazine					
Propiconazole					
Propyzamide					
Prothioconazole					
Pyridaben					
Pyridaphenthion					
Pyrimethanil					
Pyrimidifen					
Pyriproxyfen					
Quinalphos					
Quinoxifen					
Simazine					
Spinosad A					
Spinosyn D					
Spiromesifen					
Spiroxamine					
Tebuconazole					
Tebufenozide					
Tebufenpyrad					
Teflubenzuron					
Tefluthrin					
Terbuthylazine					
Terbutrin					
Tetraconazole					
Tetradifon					
Thiabendazole					
Thiacloprid					
Thiamethoxam					
Thiocyclam					
Thiodicarb					
Thiophanate-ethyl					
Tolclofos-methyl					
Tolfenpyrad					
Tolylfluanid					
Triadimefon					
Triadimenol					
Triazophos					
Trichlorfon					
Triclocarban					
Trifloxystrobin					
Triflumizol					
Triflumuron					
Trifluralin					
Triticonazole					
Vinclozolin					

(1) If the pesticide was detected using the mass spectrometry method fill in Yes; if not, fill in No and if the pesticide is not included in your scope, put NA. This information must be sent within 48 hours of receipt.
(2) Give the determination technique used e.g. LC-TOF-MS, GC-MS (quad), GC-MS (ion trap), GC-TOF-MS, LC-MS/MS etc. This information must be sent within 48 hours of receipt.
(3) Deviation in Retention time (%) differences between the Rt of the analysis and the library Rt (if available) used to compare the screening method. This information must be sent within 48 hours of receipt.
(4) Mass Confirmatory Information: write how MS identification was done: EI-spectrum, ion ratio x ions; exact mass (specify mass accuracy and number of ions used); MS/MS transition(s); etc. This information must be sent within 48 hours of receipt.
(5) Semi-quantitative concentration: report approximately the concentration for each of the pesticides detected (e.g. above or below 10 ppb).

I agree to be responsible for completing and returning this form to the Organiser within 48 hours of sample extract receipt. In the case that no e-mail reception confirmation for this document arrives (in 3 or 4 days), I will contact the Organiser as soon as possible.

DATE	
RESPONSIBLE	

Laboratories should fill in this form and send it to the following e-mail address: pmedina@ual.es

FORM 2 - Method Description

Please,
ALWAYS save a copy of this document in your computer before sending it

Lab. Code

To be fill up by the participant	
Date	**Hour**

Extract Adjustment for GC (if any):	
Dilution factor (if any):	
Solvent switch (if any):	
Final extract composition:	
Final concentration (if deviates from 1 g/mL):	

Extract Adjustment for LC (if any):	
Dilution factor (if any):	
Solvent switch (if any):	
Final extract composition:	
Final concentration (if deviates from 1 g/mL):	

EQUIPMENT USED (fill in one row for each one)

Instrument Used	Chromatographic Conditions		Software: automated or manual or both	No. of Compounds in method or library	Were standard solution analysed together with sample extract? (Yes or No)
	Column Type	Injection Volume (µL)			

☑ **I agree to be responsible for completing and returning this form to the Organiser within 48 hours of sample extract receipt. In the case that no e-mail reception confirmation for this document arrives (in 3 or 4 days), I will contact the Organiser as soon as possible.**

DATE

RESPONSIBLE

Laboratories should fill in this form and send it to the following e-mail address: pmedina@ual.es

EUPT-FV-SM-01 TARGET PESTICIDE LIST

2,4-dimethylaniline
3,5-Xylylmethylcarbamate
3-hydroxy-carbofuran
Acephate
Acetamiprid
Aclonifen
Acrinathrin
Alachlor
Alanycarb
Albendazole
Aldicarb
Aldicarb Sulfone
Aldicarb Sulfoxide
Amitraz
Anilofos
Atrazine
Azinphos-methyl
Azoxystrobin
Benalaxyl
Bendiocarb
Bifenthrin
Bitertanol
Boscalid
Bromacil
Bromopropylate
Bromuconazole
Bupirimate
Buprofezin
Butocarboxin
Butoxycarboxin
Cadusafos
Cambendazole
Captan
Carbaryl
Carbendazim (sum)
Carbofuran
Chlorbromuron
Chlorfenapyr
Chlorfenvinphos
Chloridazon
Chlorothalonil
Chlorotoluron
Chloroxuron
Chlorpropham
Chlorpyrifos
Chlorpyrifos-methyl
Chromafenozide
Clofentezine
Clothianidin
Cyfluthrin
Cymoxanil
Cypermethrin
Cyproconazole
Cyprodinil
Cyromazine
Deet
Deltamethrin
Demeton-S-methyl
Demeton-S-methylsulfone
Desethylterbutylazine
Desmethyl-pirimicarb
Diafenthiuron
Diazinon
Dichlofluanid
Dichlorvos
Dicloran
Dicofol
Diethofencarb
Difenoconazole
Difenoxuron
Diflubenzuron
Dimethoate
Dimethomorph
Dimethylvinphos
Dinotefuran
Diphenylamine
Diuron
Edifenphos
Emamectin benzoate
Endosulfan alpha
Endosulfan beta
Endosulfan sulphate
Epoxiconazole
Ethiofencarb
Ethion
Ethiprole
Ethoprophos
Ethoxyquin
Fenamiphos
Fenamiphos sulphone
Fenamiphos sulphoxide
Fenarimol
Fenazaquin
Fenbuconazole
Fenhexamid
Fenitrothion
Fenobucarb
Fenoxycarb
Fenpropathrin
Fenpropimorph
Fenuron
Fipronil
Fipronil sulfone
Flazasulfuron
Fluacrypyrim
Fluazifop
Fludioxonil
Flufenoxuron
Fluometuron
Fluquiconazole
Fluroxypyr
Flusilazole
Flutriafol
Folpet
Fosthiazate
Hexaconazole
Hexaflumuron
Hexythiazox
Imazalil
Imidacloprid
Indoxacarb (Indoxacarb as sum of the isomers S and R)
Iprodione
Iprovalicarb
Isocarbofos
Isofenphos-methyl
Isoprocarb
Isoproturon
Kresoxim-methyl
Lambda-Cyhalothrin
Lenacil
Linuron
Lufenuron
Malaoxon
Malathion
Mebendazole
Mepanipyrim
Metalaxyl and metalaxyl-M
Metamitron
Metconazole
Methamidophos
Methidathion
Methiocarb
Methiocarb sulfone
Methiocarb sulfoxide
Methomyl
Methoxyfenozide
Metobromuron
Metolachlor
Metolcarb
Miconazole
Monocrotophos
Monolinuron
Monuron
Myclobutanil
Neburon
Nitempyram
Omethoate
Oxadixyl
Oxamyl
Oxfendazole
Oxydemeton-methyl
Paclobutrazole
Paraoxon-methyl
Parathion
Parathion-methyl
Penconazole
Pendimethalin
Phenthoate
Phosalone
Phosmet
Phosmet oxon
Phoxim
Pirimicarb
Pirimicarb
Pirimiphos-methyl
Prochloraz
Procymidone
Profenofos
Promecarb
Prometryn
Propamocarb
Propaphos
Propargite
Propazine
Propiconazole
Propyzamide
Prothioconazole
Pyridaben
Pyridaphenthion
Pyrimethanil
Pyrimidifen
Pyriproxyfen
Quinalphos
Quinoxifen
Simazine
Spinosad A
Spinosyn D
Spiromesifen
Spiroxamine
Tebuconazole
Tebufenozide
Tebufenpyrad
Teflubenzuron
Tefluthrin
Terbuthylazine
Terbutrin
Tetraconazole
Tetradifon
Thiabendazole
Thiacloprid
Thiamethoxam
Thiocyclam
Thiodicarb
Thiophanate-ethyl
Tolclofos-methyl
Tolfenpyrad
Tolylfluanid
Triadimefon
Triadimenol
Triazophos
Trichlorfon
Triclocarban
Trifloxystrobin
Triflumizol
Triflumuron
Trifluralin
Triticonazole
Vinclozolin

ANNEX 2. List of laboratories that participate in EUPT-FV-SM-01.

COUNTRY	CITY	LABORATORY NAME	REPORTED RESULTS
AUSTRIA	WIEN	COMPETENCE CENTRE FOR RESIDUE ANALYSIS, AUSTRIAN AGENCY FOR HEALTH AND FOOD SAFETY	YES
AUSTRIA	INNSBRUCK	AGES COMPETENCE CENTER FOR RESIDUES OF PLANT PROTECTION PRODUCTS, INNSBRUCK, AUSTRIA	YES
BELGIUM	ZWIJNAARDE	FYTOLAB	YES
BULGARIA	BURGAS	RIOKOZ - BURGAS	YES
CZECH REPUBLIC	PRAGUE	INSTITUTE OF CHEMICAL TECHNOLOGY, PRAGUE	YES
EGYPT	GIZA	CENTRAL LAB OF RESIDUE ANALYSIS OF PESTICIDES AND HEAVY METALS IN FOODS	YES
FRANCE	MONTPELLIER	LABORATOIRE DU SCL DE MONTPELLIER	YES
FRANCE	ILLKIRCH	SCL STRASBOURG	YES
FRANCE	RENNES	SCL - RENNES	YES
FRANCE	LE MANS	LABORATOIRE DÉPARTEMANTAL DE LA SARTHE	YES
GERMANY	ERLANGEN	BAYERISCHES LANDESAMT FÜR GESUNDHEIT UND LEBENSMITTELSICHERHEIT	YES
GERMANY	FELLBACH	CVUA STUTTGART	YES
GERMANY	MUENSTER	CHEMISCHES LANDES- UND STAATLICHES VETERNIAER UNTERSUCHUNGSAMT MUENSTER	YES
GERMANY	ROSTOCK	LANDESAMT FÜR LANDWIRTSCHAFT, LEBENSMITTELSICHERHEIT UND FISCHEREI MECKLENBURG-VORPOMMERN	YES
GERMANY	KIEL	LUFA-ITL GMBH	YES
GERMANY	OLDENBURG	NIEDERSAECHSISCHES LANDESAMT FÜR VERBRAUCHERSCHUTZ UND LEBENSMITTELSICHERHEIT	YES
GREECE	KIFISSIA	BENAKI PHYTOPATHOLOGICAL INSTITUTE	YES
GREECE	ATHENS	GENERAL CHEMICAL STATE LABORATORY, PESTICIDE RESIDUES LABORATORY	YES
HUNGARY	MISKOLC	AGRICULTURAL OFFICE OF B.-A.-Z. COUNTY PLANT PROTECTION AND SOIL CONSERVATION DIRECTORATE PESTICIDE RESIDUE ANALYTICAL LABORATORY	YES
HUNGARY	KAPOSVÁR	AGRICULTURAL OFFICE OF SOMOGY COUNTY; PESTICIDE RESIDUE ANALYTICAL LABORATORY	YES
IRELAND	CELBRIDGE, CO. KILDARE	PESTICIDE CONTROL LABORATORY	YES
ITALY	AREZZO	A.R.P.A.T.-DIPARTIMENTO DI AREZZO	YES
ITALY	BOZEN	AGENTUR FÜR UMWELT - LABOR FÜR LUFT- UND LÄRMANALYSEN	YES
ITALY	PORDENONE	ARPA FRIULI VENEZIA GIULIA DIPARTIMENTO DI PORDENONE	YES
ITALY	FERRARA	ARPA EMILIA-ROMAGNA RAR FITOFARMACI (EX. ECCELLENZA FITOFARMACI)	YES

ANNEX 2. List of laboratories that participate in EUPT-FV-SM-01.

COUNTRY	CITY	LABORATORY NAME	REPORTED RESULTS
NORWAY	AAS	BIOFORSK, PLANT HEALTH AND PLANT PROTECTION, PESTICIDE CHEMISTRY	YES
POLAND	OLSZTYN	WOJEWODZKA STACJA SANITARNO-EPIDEMIOLOGICZNA OLSZTYN	NO
PORTUGAL	OEIRAS	L-INIA - LABORATÓRIO DE RESÍDUOS DE PESTICIDAS	YES
SLOVAKIA	BRATISLAVA	STATE VETERINARY AND FOOD INSTITUTE BRATISLAVA	YES
SLOVENIA	MARIBOR	INSTITUTE OF PUBLIC HEALTH MARIBOR	YES
SLOVENIA	KRANJ	INSTITUTE OF PUBLIC HEALTH KRANJ	YES
SPAIN	SANTA FE, GRANADA	LABORATORIO AGROALIMENTARIO DE GRANADA	YES
SPAIN	BURJASSOT	LABORATORIO AGROALIMENTARIO DE LA GENERALITAT VALENCIANA	YES
SPAIN	MADRID	LABORATORIO ARBITRAL AGROALIMENTARIO	YES
SPAIN	JAEN	LABORATORIO DE PRODUCCIÓN Y SANIDAD VEGETAL	YES
SPAIN	LA MOJONERA	LABORATORIO DE PRODUCCIÓN Y SANIDAD VEGETAL DE ALMERÍA	YES
SPAIN	EL PALMAR (MURCIA)	LABORATORIO AGROALIMENTARIO Y DE SANIDAD ANIMAL	YES
THE NETHERLANDS	WAGENINGEN	RIKILT - INSTITUTE OF FOOD SAFETY	YES
THE NETHERLANDS	AMSTERDAM	VWA - FOOD AND CONSUMER PRODUCT SAFETY AUTHORITY	YES
TURKEY	ADANA	THE MINISTRY OF AGRICULTURE AND RURAL AFFAIRS DIRECTORATE OF ADANA PROVINCIAL CONTROL LABORATORY	YES
TURKEY	MERSIN	MSM FOOD CONTROL LABORATORIES INC	YES
UNITED KINGDOM	TEDDINGTON	LABORATORY OF THE GOVERNMENT CHEMIST	YES
UNITED KINGDOM	EDINBURGH	SASA	YES
UNITED KINGDOM	WOLVERHAMPTON	EUROFINS LABORATORIES LTD.	YES
UNITED KINGDOM	YORK	THE FOOD AND ENVIRONMENT RESEARCH AGENCY	YES