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Results from Rounds 0 to 2 from the Interlaboratory Proficiency Program for Analysis of Pesticides on Raw Wool.

By

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SUMMARY

The participating laboratories in the Wool Residue Interlaboratory Proficiency Program have returned results for Round 2, the second assessable round conducted in the current program. The results of the first assessable round, Round 1, were reported to the Raw Wool Group at the Biella meeting of IWTO in November 2005.

There was discussion that the results from the first assessable round appeared slightly poorer than for the Round 0 familiarisation round. This report presents the results from the individual laboratories that participated in Round 0 and compares them with the results from Round 1. The familiarisation round had five participating laboratories, three of which participated in the original interlaboratory proficiency program, and were considered to have significant experience in the analysis of pesticides in a wool wax matrix. The other two were relatively inexperienced in the area of multi-residue chemical analysis testing. The results of Round 0 showed 2 false negatives, 2 false positives and 13 outliers, while the Round 1 results showed 22 false negatives, 13 false positives and 23 outliers from the six participating laboratories.

Two of the more experienced laboratories that participated in Round 0 did not enrol in Round 1, while three new laboratories, two of whom were less experienced, joined the program. The results from Round 1 reflect the fact that the majority of the participating laboratories had less experience in dealing with the difficult wool matrix. In addition the average spike concentrations in Round 1 samples were closer to Limit of Reporting (LoR) concentrations than those in the Round 0 familiarisation round, and this added to the difficulty.

The outcomes from Round 2 are anticipated to improve over the Round 1 results, as laboratories have had the opportunity to refine and modify their methods and procedures in the light of the feedback provided on expected results of the preceding round. In addition, the laboratories have all been sent a selection of papers from the chemical literature, but they may not yet have had a chance to implement revised procedures.

An accompanying paper (RWG 04) provides details of a simple and robust analysis procedure that was previously used by CSIRO to achieve satisfactory results in the original proficiency program. It does not rely on sophisticated processing or extraction equipment and should be able to be implemented by most laboratories if needed. It should allow laboratories to develop a stable base method that they can then adapt and optimize to suit their needs.

The results from Round 2 were not available at the time of this report, but will be added as an appendix to the IWTO Raw Wool Group meeting at Cairo in May 2006.

INTRODUCTION

Under the sponsorship of Australian Wool Innovation Ltd, the current Wool Residue Interlaboratory Proficiency Program, being conducted by the Australian Government National Residue Survey, commenced in 2005. The initial activity was a familiarisation round in April 2005 (Round 0), followed by the first assessable round (Round 1) in August 2005, and the second in February 2006.

The program is offered to participants in two parts:

Part A	Organophosphates, organochlorines, synthetic pyrethroids, diflubenzuron and triflumuron on greasy wool
Part B	Cyromazine and dicyclanil on greasy wool

This proficiency program is important in assessing the compliance of laboratories to Draft TM 59 in two ways.

1. Draft TM 59 requires laboratories to demonstrate proficiency for the analytes they report, and
2. Draft TM 59 requires laboratories to meet the requirements of ISO/IEC 17025, and this also requires this demonstration of proficiency.

The familiarisation Round 0 was an opportunity for the participants to test their methods before the commencement of the assessable rounds. As such, Round 0 samples were spiked at higher concentrations (average spike concentrations 383% of the Limit of Reporting (LoR)) than Round 1 samples (average spike concentrations 247% of LoR). The results from Round 0 were returned to the participating laboratories, to allow them to refine or modify their procedures if necessary.

The results from the first assessable round, Round 1, were reported to the Raw Wool Group at the IWTO Biella meeting in November 2005. The results showed 22 false negatives, 13 false positives and 23 outliers from the six participating laboratories. There was some discussion around the fact that the results from Round 1 appeared poorer than for the Round 0 familiarisation round, however the results from Round 0 had not been presented. In this report, the results from Rounds 0 and 1 will be presented and discussed. Round 2 has just been completed, and when the results from Round 2 are compiled, they will be presented as an appendix at the meeting in Cairo in May 2006.

ROUND 0 RESULTS

In Round 0, Part A spiking involved 24 spikes covering 22 different analytes. Part B involved samples of wool with spiked residues of cyromazine and/or dicyclanil.

Seven laboratories enrolled in this familiarisation round, with 5 laboratories returning results for Part A, and 2 laboratories returning results for Part B. In Part A, there were 2 false positives and 2 false negatives, with 13 outliers, based on the criteria used in the assessment of the results for Round 1. Outliers are defined as results where the percentage R/S (reported result / spiked result) is either <55% or >145%. The results for the individual laboratories for Round 0 Part A are shown in Table 1.

Sample	spiked conc mg/kg	Laboratory A		Laboratory C		Laboratory E		Laboratory F		Laboratory G	
		reported mg/kg	% R / S	reported mg/kg	% R / S	reported mg/kg	% R / S	reported mg/kg	% R / S	reported mg/kg	% R / S
POT 1											
HCB	0.4301	0.28	65	0.25	58	0.36	84	0.64	149	ns	
aldrin	0.3897	0.61	157	0.26	67	0.35	90	0.50	128	nq	
diazinon	1.9148	1.1	57	2.68	140	1.9	99	2.0	104	1.6	84
deltamethrin	2.7906	1.7	61	3.14	113	4.2	151	3.5	125	4	143
POT 2											
DDT	0.1809	0.40	221	0.14	77	0.24	133	0.21	116	ns	
chlorfenvinphos	1.6989	2.2	129	1.34	79	3.0	177	2.1	124	1.4	82
dichlofenthion	0.9802	0.70	71	ns		0.99	101	1.1	112	0.7	71
diflubenzuron	3.6079	ns		ns		4.6	127	8.6	238	ns	
POT 3											
endrin	0.4121	0.42	102	0.35	85	0.45	109	0.41	99	nq	
lindane	0.3121	0.32	103	0.26	83	0.36	115	0.45	144	nq	
fenchlorphos	1.4200	0.53	37	FN		1.2	85	1.6	113	0.8	56
coumaphos	3.4111	2.7	79	ns		4.0	117	4.3	126	3.2	94
triflumuron	4.5075	ns		ns		4.0	89	4.4	98	ns	
POT 4											
dieldrin	0.5236	0.68	130	0.35	67	0.46	88	0.53	101	FN	
HCH-beta	0.2834	0.33	116	0.25	88	0.30	106	0.33	116	ns	
propetamphos	2.2945	1.4	61	1.95	85	1.8	78	3.1	135	2.4	105
fenvalerate	1.8035	1.4	78	ns		1.5	83	2.4	133	2	111
cypermethrin	not spiked	0.45	FP								
POT 5											
HCH-alpha	0.2866	0.28	98	0.14	49	0.16	56	0.36	126	ns	
cyhalothrin-lambda	2.0035	1.1	55	1.10	55	3.1	155	2.4	120	2	100
flumethrin	2.9147	0.94	32	3.05	105	2.8	96	0.56	19	ns	
POT 6											
aldrin	0.3248	1.1	339	0.19	59	0.22	68	0.46	142	nq	
HCH-delta	0.3871	0.54	139	0.27	70	0.32	83	0.38	98	ns	
chlorpyrifos	1.5928	0.86	54	1.03	65	1.70	107	1.9	119	1.1	69
fenvalerate	2.4931	2.1	84	ns		2.0	80	3.1	124	3	120
cypermethrin	not spiked	0.62	FP								

ns= not sought FN = false negative
nq = not quantified FP = false positive

Table 1. Results for Round 0 Part A test samples – organochlorines, organophosphates, synthetic pyrethroids, insect growth regulators.

Laboratory A had 2 false positives, both for the synthetic pyrethroid (SP) cypermethrin, and six outliers. Laboratory C had only one outlier, and one false negative, where the organophosphate (OP) fenchlorphos was not detected. Both Laboratories E and F had no false positives or negatives, but both Laboratory E and F had 3 outliers. Laboratory G did not seek a number of analytes, but had one false negative, where the organochlorine (OC) dieldrin was not detected.

The only false positives reported in Round 0 were cypermethrin, both from the same laboratory. Of the two false negatives, where the analyte was not reported, one was an organochlorine, and the other an organophosphate, each reported by a different laboratory. From the two laboratories that sought diflubenzuron and triflumuron, there were no false positives or negatives, but one outlier for diflubenzuron. Of the 13 outliers encountered, five were OCs, 4 SPs, 3 OPs and one for diflubenzuron. Both aldrin and flumethrin had two outliers each.

For the two laboratories that returned results for Part B, there were no false positives, false negatives or outliers. The results for Part B are shown in Table 2.

Sample	spiked conc mg/kg	Laboratory I		Laboratory J	
		reported mg/kg	% R / S	reported mg/kg	% R / S
POT 7					
cyromazine	3.1	3.9	126	3.2	103
POT 8					
cyromazine	1.8	1.5	83	1.9	106
dicyclanil	2.1	2.0	95	2.3	110
POT 9					
dicyclanil	2.5	2.8	112	2.3	92
POT 10					
cyromazine	4.9	4.9	100	5.2	106
dicyclanil	1.7	1.8	106	1.9	112

Table 2. Results for Round 0 insect growth regulators cyromazine and dicyclanil in Part B samples.

For the sake of completeness, the Round 1 results from the first assessable round that were presented at the IWTO Biella meeting in November 2005 are included.

The Part A results are found in Table 3, with the Part B results in Table 4.

Sample	spiked conc mg/kg	Laboratory A		Laboratory B		Laboratory C		Laboratory D		Laboratory E		Laboratory F	
		reported conc mg/kg	% R / S	reported conc mg/kg	% R / S	reported conc mg/kg	% R / S	reported conc mg/kg	% R / S	reported conc mg/kg	% R / S	reported conc mg/kg	% R / S
POT 11													
dieldrin	0.17	0.13	76	0.11	65	0.21	123	FN		FN		0.09	53
lindane	0.19	0.20	105	0.12	63	0.24	126	0.176	93	0.2	105	0.09	47
chlorpyrifos	0.80	0.70	88	0.53	67	0.90	113	FN		0.7	88	ns	
cypermethrin	0.89	0.26	29	0.48	54	0.81	91	1.19	134	2	225	ns	
chlorfenvinphos	not spiked							0.121	FP				
aldrin	not spiked											0.46	FP
POT 12													
DDE-p,p'	0.26	0.17	65	0.09	35	0.28	108	FN		ns		FN	
aldrin	0.22	0.36	163	0.07	32	0.42	190	0.268	121	FN		0.085	38
chlorfenvinphos	0.69	0.62	90	0.31	45	0.70	101	FN		0.9	130	ns	
chlorpyrifos	0.86	0.73	85	0.32	37	0.96	111	0.2	20	0.7	81	ns	
cyhalothrin-lambda	0.78	0.52	67	FN		0.78	100	1.09	139	1	128	ns	
dieldrin	not spiked							0.165	FP	0.2	FP	0.045	FP
POT 13													
dieldrin	0.28	0.24	85	0.32	114	0.36	128	FN		0.2	71	FN	
diazinon	0.92	0.86	93	0.62	67	0.97	105	0.196	21	0.5	54	ns	
propetamphos	1.10	1.0	91	0.64	58	1.0	91	0.231	21	0.9	82	ns	
fenvalerate	0.86	0.61	71	FN		0.84	98	0.416	48	2	232	ns	
diflubenzuron	2.50	2.4	96	ns		2.8	112	ns		ns		ns	
DDE-p,p'	not spiked							0.173	FP			0.034	FP
HCH-beta	not spiked							0.194	FP				
lindane	not spiked											0.11	FP
POT 14													
HCH-delta	0.19	0.14	73	0.19	100	0.23	121	0.215	113	ns		FN	
chlorfenvinphos	1.30	1.2	93	FN		1.4	108	FN		1.8	139	ns	
deltamethrin	0.95	0.55	58	FN		0.90	94	1.02	107	FN		ns	
flumethrin	1.99	FN		ns		2.1	105	FN		ns		ns	
dieldrin	not spiked											0.065	FP
POT 15													
HCB	0.44	0.21	48	0.27	62	0.71	163	0.241	55	ns		FN	
diazinon	2.21	2.0	90	1.6	72	2.4	109	FN		1.7	77	ns	
cyhalothrin-lambda	1.49	1.2	81	0.93	62	1.7	114	0.528	35	1	67	ns	
triflumuron	1.89	2.2	116	ns		1.7	90	ns		ns		ns	
chlorfenvinphos	not spiked							1.64	FP				
DDT-p,p'	not spiked											0.27	FP
lindane	not spiked											0.07	FP
POT 16													
HCH-beta	0.23	0.22	97	0.15	66	0.33	146	0.273	120	ns		0.13	57
propetamphos	1.71	1.8	105	1.0	59	2.3	135	0.371	22	1.7	99	ns	
coumaphos	2.51	3.0	119	FN		2.5	99	ns		2	80	ns	
fenvalerate	1.21	0.80	66	FN		1.2	99	0.7	56	2	165	ns	

ns= not sought
FN = false negative
FP = false positive

Table 3. Results for Round 1 Part A test samples – OC, OP, SP, diflubenzuron/triflumuron.

Sample	expected conc mg/kg	Laboratory G	
		reported conc mg/kg	% R / S
POT 17			
cyromazine (incurred)	2.2	2.3	105
POT 18			
dicyclanil (incurred)	7.4	7.5	101
POT 19			
cyromazine	2.2	2.1	96
dicyclanil	7.4	7.9	106
POT 20			
cyromazine (incurred)	1.5	1.5	100
dicyclanil	2.4	2	84

Table 4. Results for Round 1 insect growth regulators cyromazine and dicyclanil in Part B samples.

DISCUSSION

Wool wax is a very difficult matrix for analysis, and quite different to other lipid matrices. Of the five participating laboratories in Round 0, three were known to have significant experience in the analysis of wool wax, and the results reflect this experience. The overall outcome of Round 0 was only 2 false positives, 2 false negatives, and 13 outliers. This result appears to demonstrate the overall capability of the more experienced laboratories.

However, in the first assessable round, Round 1, two of the more experienced laboratories dropped out, and three new laboratories, two of whom were less experienced in the analysis of this matrix enrolled. Therefore, of the six participating laboratories in Round 1, four were relatively inexperienced, and the results for this round, reported at Biella in November 2005, reflect this with a higher number of false positives (13), false negatives (22) and outliers (23). The lower average spike concentration in Round 1 samples compared to Round 0 samples may have also contributed to the reporting of slightly poorer results in Round 1.

The less experienced laboratories have potentially had an opportunity to reanalyse the samples from the earlier rounds, and test any revised procedures before the current proficiency round, and an improved result from Round 2 would be anticipated. Laboratories are provided with duplicates of each test specimen, so that, in principle, they can keep one sample, now with known concentrations, to test any procedural changes. In addition they could also store excess extraction solutions so that they can repeat the analysis of the sample extracts from previous rounds.

Since completion of Round 1, all participating laboratories have been sent copies of literature methods for analysis of pesticides in wool wax and lanolin, and an accompanying paper (RWG 04) provides details of a simple and robust analysis procedure that was previously used by CSIRO to achieve satisfactory results in the original proficiency program. It does not rely on sophisticated processing or extraction equipment and should be able to be implemented by most laboratories if needed. It should allow laboratories a stable base method that they can then adapt and optimize to suit their needs.

The results from Round 2 were not available at the time of this report, but will be included as an appendix when the report is presented at Cairo in May 2006.

REFERENCES

1. IWTO Draft TM-59-02. *Method for the Determination of Chemical residues on Greasy Wool.*

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