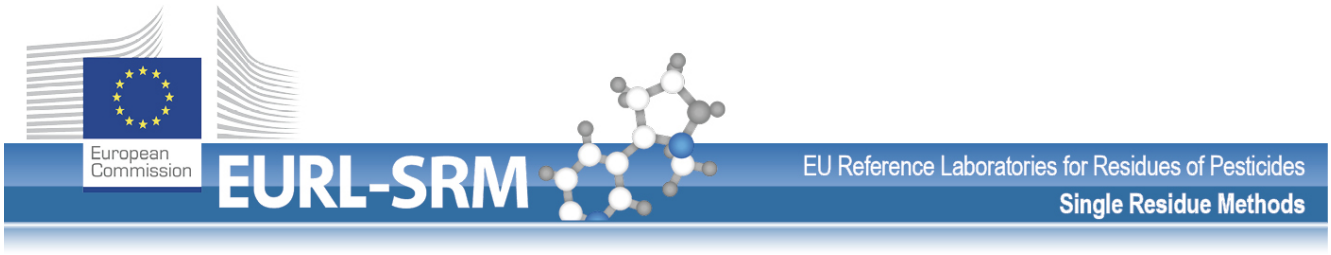
EU Reference Laboratories for Residues of Pesticides
Single Residue Methods



EU PROFICIENCY TEST
EUPT-SRM9. 2014

Residues of Pesticides
Requiring Single Residue Methods
Test Item: Cow's Milk

Preliminary Report

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General Remark

Please note that all assigned values, Qn-RSDs and z-scores, presented in the following are preliminary!
The final report of the EUPT-SRM9 will be drafted following the joint EURL/NRL-Workshop and the evaluation of the results by the EUPT-Scientific Committee scheduled towards October 2014.

Background

The proficiency test EUPT-SRM9 was conducted using cow's milk with 3.8% fat as Test Item. The Test Item was prepared by spiking UHT milk from organic production in Germany with 14 compounds dissolved in standard solutions. 8 of the compounds (2,4-D, BAC-C12, BAC-C14, chlormequat, DDAC-C10, fluazifop, maleic hydrazide and mepiquat) were classified as "compulsory" and 6 compounds (4-hydroy-chlorothalonil, chlorate, cyromazine, melamine, perchlorate and trimethyl-sulfonium) as "optional". The intention was that the "compulsory" compounds would considered in the scope-based lab classification (e.g. Categories A/B) whereas the "optional" compounds would not. This aspect will be decided during the EUPT-Scientific Committee meeting. In any case all compounds will still be evaluated as far as the quantitative and qualitative results are concerned (z-scores, false positives, false negatives). For the evaluation of the assigned values only the results of the 62 official labs from the EU member states and EFTA countries were considered.

Following spiking and mixing ca. 250 g portions of the spiked Test Item were filled into bottles and distributed to the participants on 15 April 2013. The participants were also provided with the same amount of blank material prepared from the same batch of the organic milk.

10 bottles of the Test Item were selected randomly and tested for homogeneity. Furthermore, the stability of the test material was checked over a period covering the EUPT duration.

The EUPT-materials were sent to the participants in frozen condition in insulated boxes, wherever allowed by the IATA regulations, containing dry ice. In total 69 Laboratories, including 62 OfLs from EU member states, 2 OfLs from EFTA States, 1 OfL from one EU candidate country and 4 OfLs from third countries registered for participation. Using an online submission tool the participants had the possibility to submit their results as well as the requested information about the analytical methods employed by 02 June, 2014.

Results

62 out of the 64 participating labs from EU and EFTA states and all 5 laboratories form EU candidate countries and 3rd countries submitted results.

6 false positive results were submitted (2x BAC-C10, 2x BAC-C16, 1x haloxyfop and 1x glyphosate).

4 labs reported in 5 cases false negative results („analyzed, but not detected") for compounds present in the test material. Their z-scores were calculated using the corresponding MRRL in the Target Pesticide List or the RL if this was lower. The false negative results concerned maleic hydrazide (2x), chlorate, trimethyl-sulfonium and fluazifop.

All submitted results of pesticides spiked to the test material are shown in Table 1 for compulsory compounds and Table 2 for optional compounds.

False negative results are marked in the tables with the abbreviation FN. Empty cells in the tables correspond to 'not analysed' compounds.

The table also contains the results of the participating laboratories from 3rd countries and EU candidate countries. In these cases the z-scores were calculated using the assigned values derived from the results of the EU and EFTA labs.

- **All labs are kindly asked to check their results carefully and to report any errors.**
- **Please note that only transcription errors by the Organizers can be considered at this stage.**
- **Labs with individual absolute z-scores > 2 or false positives will be asked to give a feedback about the reasons for bad performance and any corrective actions undertaken.**

Table 1a: Results for "compulsory compounds" in EUPT-SRM9 reported by OfLs from EU and EFTA countries (z-scores were calculated using preliminary assigned values)

Assigned Value [mg/kg]	2,4-D (free acid)		BAC-C12		BAC-C14		Chlormequat		DDAC-C10		Fluazifop		Maleic hydrazide		Mepiquat	
	0.088		0.284		0.279		0.179		0.268		0.168		0.342		0.333	
Qn-RSD	18.7 %		17.6%		17.9 %		19.8 %		18.9 %		26.9 %		19.4 %		19.6 %	
No. Results	50		45		45		50		44		51		30		49	
Labor No.	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score
1	0.087	0	0.326	0,6	0.318	0,6	0.199	0,4	0.320	0,8	0.094	-1,8	FN	-3,4	0.340	0,1
2	0.083	-0,2	0.543	3,7	0.330	0,7	0.158	-0,5	0.276	0,1	0.189	0,5	0.407	0,8	0.302	-0,4
3	0.0957	0,4	0.291	0,1	0.291	0,2			0.305	0,6	0.187	0,4				
4	0.0875	0					0.118	-1,4			0.175	0,2	0.327	-0,2	0.306	-0,3
5	0.0931	0,3	0.333	0,7	0.308	0,4	0.180	0	0.285	0,3	0.187	0,4	0.369	0,3	0.323	-0,1
6	0.070	-0,8	0.257	-0,4	0.281	0	0.168	-0,2	0.215	-0,8	0.116	-1,2			0.301	-0,4
7			0.327	0,6	0.219	-0,9	0.179	0	0.284	0,2					0.36	0,3
8	0.107	0,9	0.277	-0,1	0.275	-0,1	0.175	-0,1	0.254	-0,2	0.154	-0,3	0.342	0	0.335	0
9	0.0967	0,4	0.244	-0,6	0.247	-0,5	0.138	-0,9	0.239	-0,4	0.188	0,5	0.374	0,4	0.248	-1
10	0.072	-0,7	0.244	-0,6	0.309	0,4	0.298	2,7	0.289	0,3	< 0.01*	-3,8	0.343	0	0.472	1,7
11	0.066	-1	0.231	-0,7	0.205	-1,1	0.179	0	0.217	-0,8	0.154	-0,3	0.381	0,5	0.357	0,3
12	0.103	0,7	0.354	1	0.315	0,5	0.199	0,4	0.339	1,1	0.270	2,4	0.316	-0,3	0.370	0,4
13	0.095	0,3	0.325	0,6	0.320	0,6	0.205	0,6	0.301	0,5	0.203	0,8	0.251	-1,1	0.361	0,3
14																
15																
16	0.0821	-0,3	0.296	0,2	0.291	0,2	0.172	-0,2	0.301	0,5	0.190	0,5			0.349	0,2
17											0.110	-1,4				
18	0.0366	-2,3					0.116	-1,4			0.0803	-2,1	0.192	-1,8	0.196	-1,6
20																
21	0.105	0,8	0.250	-0,5	0.250	-0,4	0.240	1,4	0.250	-0,3	0.160	-0,2	0.400	0,7	0.430	1,2
22	0.084	-0,2	0.274	-0,1	0.262	-0,3	0.137	-0,9	0.278	0,1	0.175	0,2	0.918	6,7	0.255	-0,9
23	0.068	-0,9	0.110	-2,4	0.117	-2,3	0.131	-1,1	0.118	-2,2	0.157	-0,3	0.606	3,1	0.290	-0,5
24	0.0781	-0,4	0.313	0,4	0.282	0	0.195	0,4	0.321	0,8	0.194	0,6			0.368	0,4

*: result reported as < RL with the reported RL being equal to the MRRL. Following the rules in the General Protocol the z-score was calculated using RL

Table 1a: Results for "compulsory compounds" in EUPT-SRM9 reported by OfLs from EU and EFTA countries (z-scores were calculated using preliminary assigned values)

Assigned Value [mg/kg]	2,4-D (free acid)		BAC-C12		BAC-C14		Chlormequat		DDAC-C10		Fluazifop		Maleic hydrazide		Mepiquat	
	0.088		0.284		0.279		0.179		0.268		0.168		0.342		0.333	
Qn-RSD	18.7 %		17.6%		17.9 %		19.8 %		18.9 %		26.9 %		19.4 %		19.6 %	
No. Results	50		45		45		50		44		51		30		49	
Labor No.	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score
25	0.108	0,9	0.300	0,2	0.300	0,3	0.153	-0,6	0.289	0,3	0.194	0,6			0.264	-0,8
26	0.091	0,2	0.295	0,2	0.296	0,2	0.146	-0,7	0.310	0,6	0.203	0,8	0.274	-0,8	0.292	-0,5
27	0.071	-0,8	0.239	-0,6	0.2	-1,1	0.279	2,2	0.234	-0,5	0.142	-0,6			0.708	4,5
28	0.083	-0,2					0.2	0,5							0.45	1,4
30	0.113	1,2					0.242	1,4			0.218	1,2			0.429	1,2
31	0.079	-0,4	0.220	-0,9	0.223	-0,8	0.197	0,4	0.235	-0,5	0.150	-0,4	0.337	-0,1	0.375	0,5
32	0.088	0	0.066	-3,1	0.075	-2,9	0.183	0,1	0.097	-2,6	0.133	-0,8	0.250	-1,1		
34	0.109	1	0.288	0,1	0.265	-0,2			0.161	-1,6	0.137	-0,7				
35			0.300	0,2	0.302	0,3	0.180	0	0.255	-0,2					0.362	0,3
36			0.216	-1	0.240	-0,6			0.276	0,1						
37	0.078	-0,4	0.273	-0,2	0.298	0,3	0.186	0,2	0.272	0,1	0.217	1,2	0.338	0	0.301	-0,4
38	0.0746	-0,6					0.164	-0,3			0.131	-0,9	0.309	-0,4	0.311	-0,3
39	0.113	1,2					0.170	-0,2			0.208	0,9	0.261	-0,9	0.388	0,7
40			0.265	-0,3	0.285	0,1			0.249	-0,3						
41	0.065	-1	0.253	-0,4	0.192	-1,3	0.207	0,6	0.129	-2,1	0.106	-1,5			0.467	1,6
42																
43	0.0803	-0,3					0.229	1,1			0.158	-0,2			0.466	1,6
44	0.101	0,6	0.324	0,6	0.3	0,3	0.18	0	0.299	0,5	0.173	0,1			0.33	0
46	0.0961	0,4					0.197	0,4			0.0965	-1,7	0.361	0,2	0.342	0,1
47	0.390	13,8	0.326	0,6	0.297	0,3	0.216	0,8	0.253	-0,2	0.184	0,4	0.346	0	0.359	0,3
48	0.082	-0,3	0.211	-1	0.222	-0,8	0.178	0	0.190	-1,2	0.152	-0,4	0.379	0,4	0.320	-0,2
49	0.088	0	0.36	1,1	0.35	1	0.17	-0,2	0.25	-0,3	0.2	0,8	FN	-3,4	0.28	-0,6
50	0.0951	0,3	0.290	0,1	0.292	0,2	0.216	0,8	0.343	1,1	0.266	2,3			0.358	0,3
51	0.101	0,6					0.106	-1,6			0.202	0,8			0.219	-1,4

Table 1a: Results for "compulsory compounds" in EUPT-SRM9 reported by OfLs from EU and EFTA countries (z-scores were calculated using preliminary assigned values)

Assigned Value [mg/kg]	2,4-D (free acid)		BAC-C12		BAC-C14		Chlormequat		DDAC-C10		Fluazifop		Maleic hydrazide		Mepiquat	
	0.088		0.284		0.279		0.179		0.268		0.168		0.342		0.333	
Qn-RSD	18.7 %		17.6%		17.9 %		19.8 %		18.9 %		26.9 %		19.4 %		19.6 %	
No. Results	50		45		45		50		44		51		30		49	
Labor No.	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score
52	0.0881	0					0.172	-0,2			0.133	-0,8	0.416	0,9	0.324	-0,1
53	0.0778	-0,4	0.304	0,3	0.335	0,8	0.0718	-2,4	0.310	0,6	0.225	1,3	0.273	-0,8	0.147	-2,2
54	0.0880	0	0.309	0,4	0.286	0,1	0.170	-0,2	0.189	-1,2	0.141	-0,6	0.346	0	0.326	-0,1
55	0.080	-0,3					0.170	-0,2			0.132	-0,9	0.344	0	0.307	-0,3
56	0.0744	-0,6	0.278	-0,1	0.278	0	0.179	0	0.302	0,5	0.137	-0,7			0.343	0,1
57			0.282	0	0.280	0			0.264	-0,1						
58	0.071	-0,8	0.29	0,1	0.34	0,9	0.16	-0,4	0.24	-0,4	0.062	-2,5			0.30	-0,4
59	0.112	1,1					0.183	0,1			0.012	-3,7			0.273	-0,7
60	0.081	-0,3	0.362	1,1	0.358	1,1			0.349	1,2	0.212	1				
61	0.0899	0,1	0.279	-0,1	0.252	-0,4	0.211	0,7	0.267	0	0.175	0,2	0.363	0,2	0.400	0,8
62							0.15	-0,7			0.19	0,5			0.30	-0,4
63	0.108	0,9	0.244	-0,6	0.233	-0,7	0.247	1,5	0.227	-0,6	0.191	0,5	0.229	-1,3	0.334	0
64	0.0726	-0,7	0.281	0	0.286	0,1	0.177	0	0.239	-0,4	0.154	-0,3			0.377	0,5
65			0.434	2,1	0.878	8,6			0.313	0,7						
66	0.189	4,6	0.295	0,2	0.277	0	0.090	-2			0.332	3,9			0.102	-2,8
68			0.040	-3,4	0.046	-3,3			0.306	0,6						
70																

Table 1b: Results for "compulsory compounds" in EUPT-SRM9 reported by OfLs from EU candidate and 3rd countries (z-scores calculated using preliminary assigned values)

Assigned Value [mg/kg]	2,4-D (free acid)		BAC-C12		BAC-C14		Chlormequat		DDAC-C10		Fluazifop		Maleic hydrazide		Mepiquat	
	0.088		0.284		0.279		0.179		0.268		0.168		0.342		0.333	
Qn-RSD	18.7 %		17.6%		17.9 %		19.8 %		18.9 %		26.9 %		19.4 %		19.6 %	
No. Results	50		45		45		50		44		51		30		49	
Labor No.	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score
33	0.1	0.6					0.16	-0.4			0.215	1.1	0.551	2.4	0.3	-0.4
67	0.077	-0.5	0.343	0.8	0.323	0.6										
69			0.31	0.4	0.33	0.7			0.40	2						
71	0.07	-0.8	0.32	0.5	0.30	0.3	0.34		0.27	0	0.29	2.9			0.36	0.3
72	0.07	-0.8									0.202	0.8				

Table 2a: Results for "optional compounds" in EUPT-SRM9 reported by OfLs from EU and EFTA countries (z-scores were calculated using preliminary assigned values)

	4-Hydroxy-chlorothalonil		Chlorate		Cyromazine		Melamine		Perchlorate		Trimethyl-sulfonium	
Assigned Value [mg)kg]	*0.100 (uncertain due to small number of results)*		0.185		0.230		0.365		0.182		*0.382 (uncertain due to small number and broad distribution of results)*	
Qn-RSD	17.0 %		17.0 %		29.8 %		9.6 %		22.0 %		45.2 %	
No. Results	7		30		38		18		30		14	
Labor No.	Conc. [mg/kg]	*z-score (uncertain)*	Conc. [mg/kg]	z-score	Conc. [mg/kg]	*z-score*	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score
1			0.175	-0.2	0.229	0	0.324	-0.5	0.265	1.8	0.569	2
2			0.202	0.4	0.361	2.3			0.196	0.3		
3												
4			0.178	-0.2	0.224	-0.1	0.351	-0.2	0.181	0	0.304	-0.8
5	0.0916	-0.3	0.180	-0.1	0.252	0.4	0.349	-0.2	0.151	-0.7	0.914	5.6
6			0.143	-0.9	0.151	-1.4			0.127	-1.2		
7			FN	-3.6					0.132	-1.1		
8					0.172	-1	0.347	-0.2				
9			0.181	-0.1					0.184	0		
10			0.195	0.2	0.109	-2.1	0.394	0.3	0.250	1.5		
11			0.210	0.5	0.278	0.8	0.364	0	0.204	0.5	0.378	0
12			0.276	2	0.254	0.4			0.171	-0.2		
13	0.085	-0.6	0.185	0	0.280	0.9	0.340	-0.3	0.210	0.6	0.320	-0.6
14												
15												
16												
17												
18					0.145	-1.5						
20							0.396	0.3				
21	0.103	0.1	0.180	-0.1	0.250	0.4	0.500	1.5	0.170	-0.3	0.870	5.1
22												
23			0.159	-0.6	0.220	-0.2			0.126	-1.2		

Table 2a: Results for "optional compounds" in EUPT-SRM9 reported by OfLs from EU and EFTA countries (z-scores were calculated using preliminary assigned values)

	4-Hydroxy-chlorothalonil		Chlorate		Cyromazine		Melamine		Perchlorate		Trimethyl-sulfonium	
Assigned Value [mg)kg]	*0.100 (uncertain due to small number of results)*		0.185		0.230		0.365		0.182		*0.382 (uncertain due to small number and broad distribution of results)*	
Qn-RSD	17.0 %		17.0 %		29.8 %		9.6 %		22.0 %		45.2 %	
No. Results	7		30		38		18		30		14	
Labor No.	Conc. [mg/kg]	*z-score (uncertain)*	Conc. [mg/kg]	z-score	Conc. [mg/kg]	*z-score*	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score
24					0.307	1.3						
25												
26			0.162	-0.5					0.184	0	FN	-3.5
27					0.179	-0.9	< 1	-3.5§				
28					0.097	-2.3						
30			0.207	0.5	0.304	1.3			0.199	0.4		
31			0.209	0.5	0.355	2.2			0.217	0.8		
32					0.287	1			0.050	-2.9		
34					0.195	-0.6						
35			0.187	0					0.193	0.2		
36									0.076	-2.3		
37			0.135	-1.1					0.158	-0.5		
38					0.268	0.7					0.350	-0.3
39												
40												
41					0.193	-0.6						
42												
43												
44			0.16	-0.5	0.121	-1.9	0.396	0.3	0.18	0		
46					0.224	-0.1	0.399	0.4				
47	0.111	0.4	0.172	-0.3	0.214	-0.3	0.375	0.1	0.560	8.3	0.387	0.1

§: result reported as < RL with RL (1mg/kg) being much higher than the Assigned Value (0.365 mg/kg) and the MRRL (0.05 mg/kg). According to the rules in the General Protocol this result is judged as false negative.

Table 2a: Results for "optional compounds" in EUPT-SRM9 reported by OfLs from EU and EFTA countries (z-scores were calculated using preliminary assigned values)

	4-Hydroxy-chlorothalonil		Chlorate		Cyromazine		Melamine		Perchlorate		Trimethyl-sulfonium	
Assigned Value [mg)kg]	*0.100 (uncertain due to small number of results)*		0.185		0.230		0.365		0.182		*0.382 (uncertain due to small number and broad distribution of results)*	
Qn-RSD	17.0 %		17.0 %		29.8 %		9.6 %		22.0 %		45.2 %	
No. Results	7		30		38		18		30		14	
Labor No.	Conc. [mg/kg]	*z-score (uncertain)*	Conc. [mg/kg]	z-score	Conc. [mg/kg]	*z-score*	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score
48			0.203	0.4	0.196	-0.6	0.362	0	0.171	-0.2	0.387	0.1
49					0.32	1.6						
50			0.186	0	0.252	0.4			0.198	0.4		
51					0.138	-1.6	0.222	-1.6			0.210	-1.8
52					0.285	1						
53			0.152	-0.7					0.156	-0.6	0.181	-2.1
54												
55					0.221	-0.1						
56			0.235	1.1	0.305	1.3			0.226	1		
57												
58					0.17	-1						
59	0.119	0.8					0.360	-0.1				
60												
61	0.0780	-0.9	0.236	1.1	0.248	0.3	0.305	-0.7	0.208	0.6	0.480	1
62			FN	-3.6	0.19	-0.7			0.154	-0.6		
63	0.109	0.4	0.252	1.4	0.197	-0.6	0.394	0.3	0.197	0.3		
64			0.178	-0.2	0.253	0.4	0.375	0.1	0.177	-0.1	0.354	-0.3
65												
66					0.275	0.8						
68												
70												

Table 2b: Results for "optional compounds" in EUPT-SRM9 reported by EU candidate and 3rd countries (z-scores were calculated using preliminary assigned values)

	4-Hydroxy-chlorothalonil		Chlorate		Cyromazine		Melamine		Perchlorate		Trimethyl-sulfonium	
Assigned Value [mg)kg]	*0.100 (uncertain due to small number of results)*		0.185		0.230		0.365		0.182		*0.382 (uncertain due to small number and broad distribution of results)*	
Qn-RSD	17.0 %		17.0 %		29.8 %		9.6 %		22.0 %		45.2 %	
No. Results	7		30		38		18		30		14	
Labor No.	Conc. [mg/kg]	*z-score (uncertain)*	Conc. [mg/kg]	z-score	Conc. [mg/kg]	*z-score (uncertain)*	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score	Conc. [mg/kg]	z-score
33					0.186	-0.8	0.362	0				
67					0.163	-1.2	0.411	0.5				
69							0.28	-0.9				
71												
72							0.292	-0.8				