

Table S1: Preparation of matrix-matched calibration solutions.

Group A includes MPA, cyanuric acid, ethephon, fosetyl Al, glyphosate, HEPA, Maleic hydrazide, N-acetyl- glyphosate; Group B includes glufosinate ammonium, MPP and NAG;

ILIS group A includes AMPA-<sup>13</sup>C,<sup>15</sup>N cyanuric acid <sup>3</sup>C<sub>3</sub>, ethephon D<sub>4</sub>, fosetyl al D<sub>15</sub>, glyphosate 2-<sup>13</sup>C,<sup>15</sup>N, HEPA D<sub>4</sub>, N-Acetyl-glifosate <sup>13</sup>C<sub>2</sub>,<sup>15</sup>N and maleic hydrazide D<sub>2</sub>

ILIS group A includes glufosinate ammonium D<sub>3</sub>, MPP D<sub>3</sub> and NAG D<sub>3</sub>

Matrix	Name	Volume of extract (μL)	Volume of working solution to add to extract (μL)				Final volume (μL)	[C] group A [mg/kg]	[C] group B [mg/kg]	[C] ILIS group A [mg/kg]	[C] ILIS group B [mg/kg]
			WS5	WS4	WSIS2	H <sub>2</sub> O					
Chicken eggs	MP1	470	10		20		500	0.0010	0.0002	0.006	0.0012
	MP2	455	25		20		500	0.0025	0.0005	0.006	0.0012
	MP3	430	50		20		500	0.0050	0.0010	0.006	0.0012
	MP4	455		25	20		500	0.0100	0.0020	0.006	0.0012
	MP5	430		50	20		500	0.0200	0.0040	0.006	0.0012
Cow milk	MP1	250	10		20	220	500	0.0010	0.0002	0.006	0.0012
	MP2	250	25		20	205	500	0.0025	0.0005	0.006	0.0012
	MP3	250	50		20	180	500	0.0050	0.0010	0.006	0.0012
	MP4	250		25	20	205	500	0.0100	0.0020	0.006	0.0012
	MP5	250		50	20	180	500	0.0200	0.0040	0.006	0.0012
	MP6	250		100	20	130	500	0.0400	0.0080	0.006	0.0012
Bovine fat	MP1	250	10		20	220	500	0.0010	0.0002	0.006	0.0012
	MP2	250	25		20	205	500	0.0025	0.0005	0.006	0.0012
	MP3	250	50		20	180	500	0.0050	0.0010	0.006	0.0012
	MP4	250		25	20	205	500	0.0100	0.0020	0.006	0.0012
	MP5	250		50	20	180	500	0.0200	0.0040	0.006	0.0012
	MP6	250		100	20	130	500	0.0400	0.0080	0.006	0.0012

Table S2: MS parameters for pesticides quantification, DP: declustering potential, CE: collision energy

Molecule	Scan type	Product of	Fragment ion (Da)	Accumulation time (sec)	Tof MS range (da)	DP	CE
All	TOF MS	-	-	0.05	79-227	-50	-10
AMPA	Product ion	110	62.9641 78.9591	0.100	50-115	-30	-33
AMPA- <sup>13</sup> C, <sup>15</sup> N	Product ion	112	78.9591	0.05	50-115	-30	-37
Cyanuric acid	Product ion	128	41.9985	0.05	30-130	-50	-24
	Product ion		85.0044	0.05	30-130	-50	-12
Cyanuric acid <sup>3</sup> C <sub>3</sub>	Product ion	131	43.0019	0.05	30-140	-20	-21
Ethephon	Product ion	143	106.9904	0.05	50-150	-20	-9
	Product ion		78.9591	0.1	50-150	-20	-24

Ethephon -D <sub>4</sub>	Product ion	147	111.0155	0.05	50-150	-50	-9
Fosetyl-Al	Product ion	109	80.9747	0.05	40-115	-40	-14
	Product ion		62.9641	0.05	40-115	-40	-10
Fosetyl-Al-D <sub>15</sub>	Product ion	114	81.9810	0.05	40-120	-35	-16
Glufosinate	Product ion	180	136.0544	0.05	40-185	-50	-22
Glyphosate	Product ion	168	62.9641	0.05	40-175	-45	-15
	Product ion		149.9962	0.05	40-175	-45	-24
Glyphosate - <sup>13</sup> C, <sup>15</sup> N	Product ion	170	62.9641	0.1	40-180	-20	-28
HEPA	Product ion	125	78.9591	0.05	40-130	-50	-26
	Product ion		62.9641	0.05	40-130	-50	-74
HEPA-D <sub>4</sub>	Product ion	129	78.9591	0.05	40-135	-25	-34
Maleic hydrazide	Product ion	111	82.0054 83.0143	0.1	70-115	-70	-20
Maleic hydrazide -D <sub>2</sub>	Product ion	113	41.9985	0.05	35-115	-70	-55
MPP	Product ion	151	62.9641	0.05	50-160	-30	-15
	Product ion		133.0060	0.05	50-160	-30	-48
MPP-D <sub>3</sub>	Product ion	154	62.9641	0.05	40-160	-50	-50
NAG	Product ion	222	62.9641	0.05	50-230	-50	-27
	Product ion		136.0533	0.05	50-230	-50	-65
NAG D <sub>3</sub>	Product ion	225	62.9641	0.05	40-230	-55	-70
N-Acetyl Glyphosate	Product ion	210	149.9962	0.05	130-220	-50	-20
N-Acetyl Glyphosate	Product ion		62.9641	0.05	50-220	-50	-40
N-Acetyl Glyphosate <sup>13</sup> C <sub>2</sub> , <sup>15</sup> N	Product ion	213	62.9641	0.05	50-220	-74	-20
Glufosinate-D <sub>3</sub>	Product ion	183	98.0091	0.05	40-190	-50	-20

Table S3: Exact masses of precursor ions (\*) extract by TOF MS experiment and exact masses of product ion used for quantification (1) and qualification (2).

Molecule	Exact mass	Chicken Egg	Bovine fat	Cow milk
AMPA	110.0012*		2	2
	62.9641	1	1	1
	78.9591	2		

AMPA- <sup>13</sup> C, <sup>15</sup> N	78.9591	1	1	1
Cyanuric acid	128.0102*	1	2	2
	41.9985	2	1	1
Cyanuric acid <sup>3</sup> C <sub>3</sub>	142.9670*	1		
	43.0019		1	1
Ethephon	106.9904	1	1	1
	78.9591	2	2	2
Ethephon -D <sub>4</sub>	111.0155	1	1	1
Fosetyl-Al	80.9747	1	1	1
	62.9641	2	2	2
Fosetyl-Al-D <sub>15</sub>	81.9810	1	1	1
Glufosinate	180.0431*	1	1	1
	136.0544	2	2	2
Glufosinate-D <sub>3</sub>	183.0619*	1	1	1
Glyphosate	168.0067*	2		2
	62.9641	1	1	1
	149.9962		2	
Glyphosate - <sup>13</sup> C, <sup>15</sup> N	62.9641	1	1	1
HEPA	78.9591	1	1	1
	62.9641	2	2	2
HEPA-D <sub>4</sub>	78.9591	1	1	1
Maleic hydrazide	82.0054	1	1	1
	83.0143	2	2	2
Maleic hydrazide - D <sub>2</sub>	41.9985		1	
MPP	151.0166*		2	2
	62.9641	1	1	1
	133.006	2		
MPP-D <sub>3</sub>	62.9641	1	1	1
NAG	222.0537*	2	1	2
	62.9641	1	2	1
NAG D <sub>3</sub>	225.0725*		1	
	62.9641	1		1
N-Acetyl Glyphosate	149.9962	1	1	1
	62.9641	2	2	2
N-Acetyl Glyphosate <sup>13</sup> C <sub>2</sub> , <sup>15</sup> N	62.9641	1	1	1

Table S4: Relative expanded measurement uncertainty (U') data

	U' (expanded MU) (%)		
	Chicken Egg	Bovine fat	Cow milk
Glufosinate	45	41	27
MPP	48	37	24
NAG	48	46	18
Glyphosate	39	33	15

Table S5. AMPA - Verification of linearity using the method specified in C17 of the document SANTE/2019/12682

AMPA								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0	0.1692		0	0.5768		0	-0.0545	
1	0.9195	-8.0548	2.5	2.3709	-5.1630	2.5	2.2426	-10.2962
2.5	2.6109	4.4378	5	4.8476	-3.0481	5	5.1948	3.8964
5	5.0212	0.4230	10	9.3038	-6.9618	10	10.2892	2.8921
10	9.6115	-3.8850	20	20.4526	2.2630	20	19.8278	-0.8608
20	20.1678	0.8389	40	39.9482	-0.1294			
Average calibration curve equation			Average calibration curve equation			Average calibration curve equation		
y=0.0644x-0.0106			y=0.1291x-0.0730			y=0.0534x-0.003		
R <sup>2</sup> 0.999			R <sup>2</sup> 0.999			R <sup>2</sup> 0.999		

Table S6. Cyanuric acid - Verification of linearity using the method specified in C17 of the document SANTE/2019/12682

Cyanuric acid								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0	0,4270		0	0,5726		0	0.8706	
2.5	2,3898	-4,4080	1	1,1105	11,0518	2.5	2.6658	6.6333
5	4,8371	-3,2573	2.5	2,2065	-11,7391	5	4.5959	-8.0827
10	9,6243	-3,7574	5	4,5790	-8,4206	10	9.3713	-6.2866
20	20,2218	1,1090	10	9,8555	-1,4455	20	19.6757	-1.6217
			20	20,1759	0,8796	40	40.3207	0.8017
Average calibration curve equation			Average calibration curve equation			Average calibration curve equation		
y=0.1880x-0.0780			y=0.1006x-0.0562			y=0.0362x-0.0309		
R <sup>2</sup> 0.998			R <sup>2</sup> 0.997			R <sup>2</sup> 0.999		

Table S7. Ethephon - Verification of linearity using the method specified in C17 of the document  
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Ethephon								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0	0.9190		0	0.9055		0	1.2316	
2.5	2.4385	-2.4596	2.5	2.3970	-4.1210	2.5	2.6437	5.7499
5	4.4706	-10.5878	5	4.9913	-0.1731	5	4.6601	-6.7985
10	9.2505	-7.4949	10	9.6274	-3.7263	10	8.8513	-11.4871
20	20.4214	2.1069	20	19.0621	-4.6894	20	19.7439	-1.2805
			40	40.5167	1.2918	40	40.3694	0.9234
Average calibration curve equation			Average calibration curve equation			Average calibration curve equation		
y=0.1014x-0.088			y=0.0915x-0.080			y=0.0591x-0.0709		
R <sup>2</sup>			R <sup>2</sup>			R <sup>2</sup>		
0.992			0.99812773			0.997		

Table S8. Fosetyl - Verification of linearity using the method specified in C17 of the document  
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Fosetyl aluminum								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0	0.5726		0	0.4677		0	0.5811	
1	1.1105	11.0518	1	1.0740	7.4016	1	1.1398	13.9799
2.5	2.2065	-11.7391	2.5	2.3942	-4.2292	2.5	2.2071	-11.7170
5	4.5790	-8.4206	5	5.0604	1.2085	5	4.6793	-6.4145
10	9.8555	-1.4455	10	9.8363	-1.6369	10	9.6398	-3.6019
20	20.1759	0.8796	20	19.3024	-3.4880	20	20.2529	1.2646
			40	40.3647	0.9120			
Average calibration curve equation			Average calibration curve equation			Average calibration curve equation		
y=0.1006x-0.0562			y=0.1047x-0.0482			y=0.0930x-0.0527		
R <sup>2</sup>			R <sup>2</sup>			R <sup>2</sup>		
0.998			0.999			0.997		

Table S9. Glyphosate - Verification of linearity using the method specified in C17 of the document  
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Glyphosate								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0.0	0.4916		0.0	1.3805		0.0	0.2862	
1.0	1.1987	<b>19.87</b>	2.5	2.5444	<b>1.77</b>	1.0	1.0656	<b>6.56</b>
2.5	2.2873	<b>-8.51</b>	5.0	5.0145	<b>0.29</b>	2.5	2.4401	<b>-2.40</b>
5.0	4.8392	<b>-3.22</b>	10.0	8.7942	<b>-12.06</b>	5.0	4.9095	<b>-1.81</b>
10.0	9.3426	<b>-6.57</b>	20.0	19.1608	<b>-4.20</b>	10.0	9.5762	<b>-4.24</b>
20.0	20.3405	<b>1.70</b>	40.0	40.6057	<b>1.51</b>	20.0	20.2224	<b>1.11</b>
Average calibration curve equation $y=0.045x-0.021$			Average calibration curve equation $y=0.073x-0.098$			Average calibration curve equation $y=0.040x-0.011$		
R <sup>2</sup> 0.997			R <sup>2</sup> 0.996			R <sup>2</sup> 0.999		

Table S10. HEPA - Verification of linearity using the method specified in C17 of the document  
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HEPA								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0	0.6594		0	0.3822		0	0.5357	
2.5	2.4322	-2.7122	1	0.9779	-2.2096	2.5	2.7624	10.4951
5	4.7111	-5.7778	2.5	2.4350	-2.6018	5	5.1146	2.2927
10	9.3416	-6.5844	5	4.6862	-6.2769	10	8.5668	-14.3316
20	20.3558	1.7789	10	9.8899	-1.1006	20	20.5204	2.6022
			20	20.1288	0.6441			
Average calibration curve equation $y=0.061x-0.0384$			Average calibration curve equation $y=0.0925x-0.0348$			Average calibration curve equation $y=0.0634x-0.0291$		
R <sup>2</sup> 0.996			R <sup>2</sup> 0.999			R <sup>2</sup> 0.989		

Table S11. Maleic hydrazide - Verification of linearity using the method specified in C17 of the document SANTE/2019/12682

Maleic hydrazide								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0		0.4032	0	0.6449		0	0.2188	
1	13.9050	1.1390	1	1.1666	16.6563	1	1.1140	11.3969
2.5	19.7763	2.9944	2.5	2.0322	-18.7106	2.5	2.6104	4.4167
5	0.1733	5.0087	5	4.4651	-10.6977	5	4.5853	-8.2933
10	-16.1358	8.3864	10	10.1114	1.1144	10	9.8057	-1.9428
20	2.8411	20.5682	20	20.0798	0.3989	20	20.1658	0.8290
Average calibration curve equation $y=499.6199x-165.7237$			Average calibration curve equation $y=0.0490x-0.0255$			Average calibration curve equation $y=474.6082x-100.6250$		
R <sup>2</sup>	0.988		R <sup>2</sup>	0.997		R <sup>2</sup>	0.999	

Table S12. N acetyl glyphosate - Verification of linearity using the method specified in C17 of the document SANTE/2019/12682

N acetyl glyphosate								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0		0.1045	0	0.1785		0	0.2677	
1	3.6591	1.0366	1	1.0670	6.6995	1	1.1515	15.1493
2.5	-0.4756	2.4881	2.5	2.4561	-1.7541	2.5	2.5692	2.7661
5	0.3555	5.0178	5	4.6291	-7.4179	5	4.7786	-4.4286
10	-2.7397	9.7260	10	10.1693	1.6926	10	9.4423	-5.5770
20	0.6350	20.1270				20	20.2908	1.4539
Average calibration curve equation $y=0.0527x-0.005$			Average calibration curve equation $y=0.062x-0.0103$			Average calibration curve equation $y=0.0493x-0.0126$		
R <sup>2</sup>	0.999		R <sup>2</sup>	0.997		R <sup>2</sup>	0.998	

Table S13. Glufosinate ammonium - Verification of linearity using the method specified in C17 of the document SANTE/2019/12682

Glufosinate ammonium								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0.0	0.2789		0.0	0.0784		0.0	0.2600	
0.5	0.5436	8.72	0.5	0.4863	-2.74	0.5	0.5369	7.38
1.0	0.8843	-11.57	1.0	0.9934	-0.66	1.0	0.9481	-5.19
2.0	1.6551	-17.24	2.0	1.8113	-9.43	2.0	1.7405	-12.97
4.0	4.1382	3.45	4.0	4.1830	4.57	4.0	3.9289	-1.78
			8.0	7.9476	-0.66	8.0	8.0857	1.07
Average calibration curve equation			Average calibration curve equation			Average calibration curve equation		
y=0.758x-0.190			y=0.824x-0.061			y=0.923x-0.233		
R <sup>2</sup>			R <sup>2</sup>			R <sup>2</sup>		
0.977			0.998			0.997		

Table S14. MPP - Verification of linearity using the method specified in C17 of the document SANTE/2019/12682

MPP								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0.0	0.1534		0.0	0.3048		0.0	0.0725	
0.5	0.4784	-4.31	0.5	0.5309	6.18	0.2	0.2362	18.11
1.0	0.9571	-4.29	1.0	0.8794	-12.06	0.5	0.5219	4.37
2.0	1.8269	-8.66	2.0	1.8916	-5.42	1.0	0.9482	-5.18
4.0	4.0843	2.11	4.0	3.7558	-6.10	2.0	1.8453	-7.73
			8.0	8.1375	1.72	4.0	4.0759	1.90
Average calibration curve equation			Average calibration curve equation			Average calibration curve equation		
y=0.218x-0.032			y=0.392x-0.116			y=0.189x-0.013		
R <sup>2</sup>			R <sup>2</sup>			R <sup>2</sup>		
0.994			0.996			0.997		



Table S15. NAG - Verification of linearity using the method specified in C17 of the document  
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NAG								
Eggs			Bovine fat			Milk		
X	BCC	Δ%	X	BCC	Δ%	X	BCC	Δ%
0.0	0.0601		0.0	-0,1423		0.0	0.0079	
0.5	0.4777	-4.46	0.5	0,4544	-9,1216	0.2	0.2292	14.59
1.0	0.9874	-1.26	1.0	1,0474	4,7398	0.5	0.5029	0.59
2.0	1.9421	-2.90	2.0	2,1074	5,3717	1.0	0.9102	-8.98
4.0	4.0327	0.82	4.0	4,1432	3,5794	2.0	2.0652	3.26
			8.0	7,8899	-1,3764	4.0	3.9847	-0.38
Average calibration curve equation $y=0.283x-0.017$			Average calibration curve equation $y=0.828x-0.124$			Average calibration curve equation $y=0.248x-0.002$		
R <sup>2</sup> 0.999			R <sup>2</sup> 0,998			R <sup>2</sup> 0.999		