Proficiency-testing scheme for pesticides in vegetables

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INTRODUCTION

Created in 1970, BIPEA offers more than 80 Proficiency Testing Schemes in many areas, as **pesticides in vegetables**.
In December 2016, a test was conducted on a vegetable organic matrix – carrot – spiked with 34 pesticides residues, at levels ranging from 20 to 200 µg/kg.
The production of the samples was performed using a specific equipment to ensure homogeneity between all the samples, and the immediate freezing of the samples after their production ensured their stability.
42 participating laboratories were required to return their results on a dedicated website after a period of one month, and a statistical treatment of the data was performed by BIPEA according to **ISO 13528** (1). Assigned (consensus) values were calculated from the participants' results and the performances of the laboratories could then be evaluated individually and collectively according to **ISO 17043** (2).
This test allowed laboratories to draw up a general inventory of their analytical skills, and was a very useful tool to **detect bias** or non-compliant results; these proficiency tests act usually as **warning signals** for the implementation of **corrective and/or curative actions** in the laboratory.

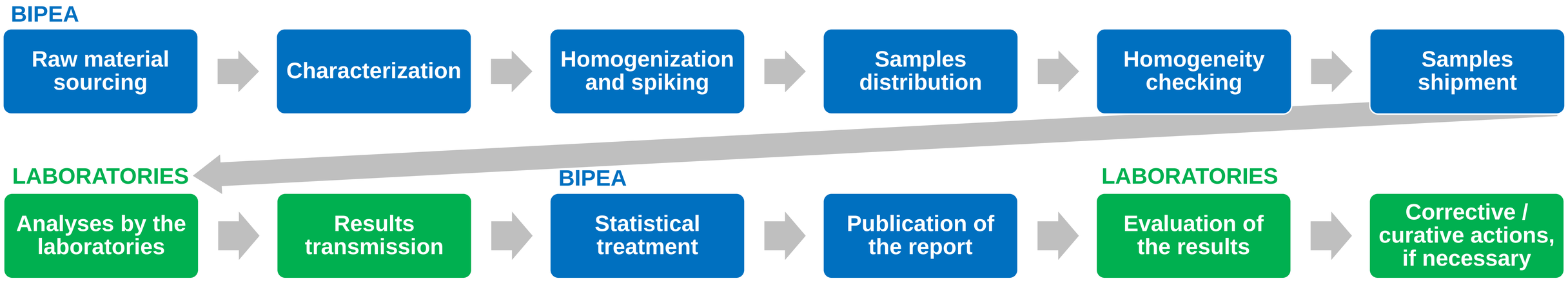

Figure 1 - Organisation of the PTS by BIPEA

SAMPLES PRODUCTION

The raw material was an organic product, first analyzed to detect the possible presence of pesticides before the production. The whole batch of carrot was ground to obtain a pasta and then spiked with a pesticides mix of all the molecules, to target final levels from **20 to 200 µg/kg**. After mixing, the product was sampled using an automatic piston system, which distributes the products in successive layers into flasks positioned on a conveyor belt, involving thus the quasi simultaneous filling of the samples and allowing to ensure the homogeneity between the samples.

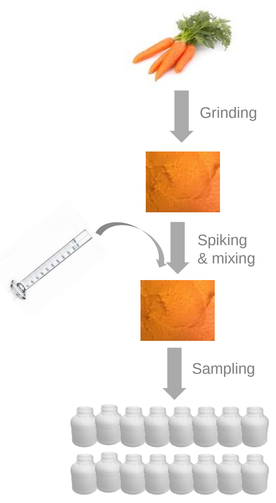

Fig. 2 – Samples production

HOMOGENEITY and STABILITY CHECK

After the production and before the shipment, BIPEA proceeded to **homogeneity** checking. Ten samples were selected from the production following a regular step and were analysed in duplo in random order (fig. 3).
The results were studied through several statistical tests:

- Fisher test (variance analysis): observed F value < critical F value;
- Test of significant inhomogeneity: between sample variance < critical c value;
- Study of the ratio of between samples standard deviation/standard deviation for proficiency assessment: s_s/SDPA < 30%.

The **stability** of the samples was verified for each molecule both through the study of the z-scores as a function of the date of analysis and the follow-up of the robust standard deviation, compared to other tests with similar products (fig.4).

STATISTICAL TREATMENT

A statistical treatment was conducted according to **ISO 13528 standard**. An assigned value (X) was estimated for each parameter according to the following rule: X = robust mean of the results included in the interval [90% SV+40%SV; 90%SV-40%SV] with SV=spiking value.
The proficiency of each laboratory was evaluated thanks to a tolerance value (TV): if X≤100, TV=50%X; if X>100, TV=40%X+10.
The results (x) could be evaluated and classified through z-scores:

$$z = \frac{x - X}{\frac{TV}{2}}$$

- $z \leq |2|$: satisfactory
- $|2| < z \leq |3|$: questionable
- $z > |3|$: unsatisfactory.

RESULTS and DISCUSSION

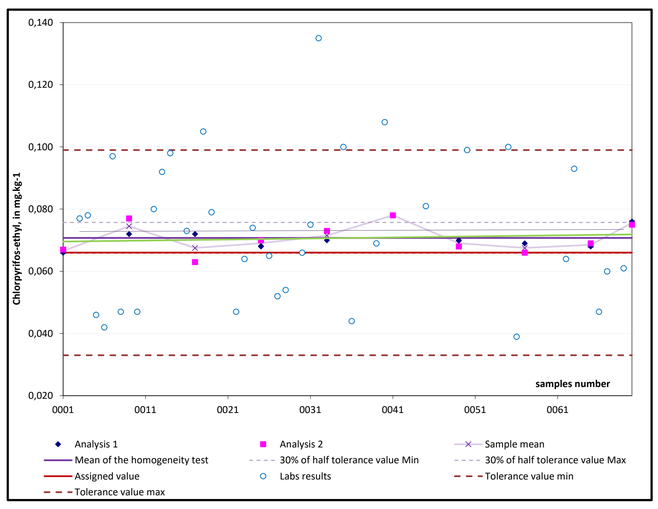

Fig. 3 – Homogeneity check as a function of the sample number

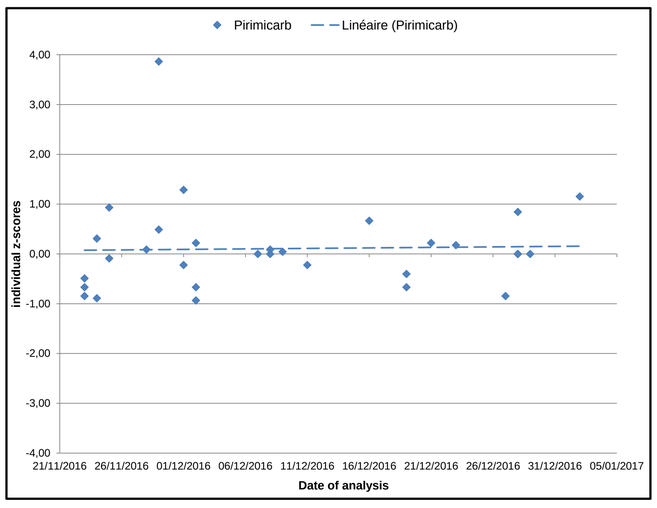

Fig. 4 – Stability check: z-scores as a function of the date of analysis

Table 1 – Overview by laboratory

lab. Number	Number of results given	Out of tolerance results (underestimated)	Out of tolerance results (overestimated)	Total out of tolerance results	% out of tolerance results
1050	5	0	0	0	0%
1109	6	0	0	0	0%
1194	14	5	1	6	43%
1247	27	0	2	2	7%
1756	32	0	0	0	0%
1802	27	1	1	2	7%
1818	22	0	0	0	0%
1831	15	0	2	2	13%
1892	30	0	1	1	3%
1893	32	2	2	4	13%
2045	29	1	3	4	14%
2076	4	0	0	0	0%
2087	26	0	4	4	15%
2244	9	0	0	0	0%
2792	24	1	1	2	8%
2862	27	0	0	0	0%
3076	32	0	2	2	6%
3397	28	0	2	2	7%
3625	17	0	0	0	0%
3667	31	0	0	0	0%
3760	4	0	0	0	0%
3843	27	0	1	1	4%
3867	26	0	1	1	4%
4043	28	1	1	2	7%
4127	20	0	0	0	0%
4376	31	0	2	2	6%
4422	27	0	3	3	11%
4958	22	1	1	2	9%
5045	3	0	0	0	0%
5137	30	1	0	1	3%
5181	31	1	0	1	3%
5403	29	3	0	3	10%
5443	4	0	1	1	25%
5484	23	0	0	0	0%
5695	23	1	1	2	9%
5749	27	1	1	2	7%
6852	3	0	1	1	33%

Five laboratories did not send back any results.
Assigned values, spiking values and percentages of out of tolerances results are given in fig.5. The highest rate of out of tolerance results was obtained for Fosetyl-Aluminium and maleic hydrazin (molecules with low participation, mono-residue technique). Otherwise, the results were good for most of the laboratories and for most of the analytical parameters, as the ratio of out of tolerance results was most of the time less or equal to 15%.
For this test, the recovery rates are satisfactory (fig.5).
The dispersion of the results (fig.6) observed through z-scores distribution, is also satisfactory (only few z-scores are superior to $|3|$). This shows a good consistency of the results from one laboratory to another, whatever the technique.
The percentage of out of tolerance results, compared to the number of results sent back by each laboratory is given in table 1. Most of the laboratories are below 10% of out of tolerance results, which shows that the laboratories are experienced and familiar with those analyses (fig.7).

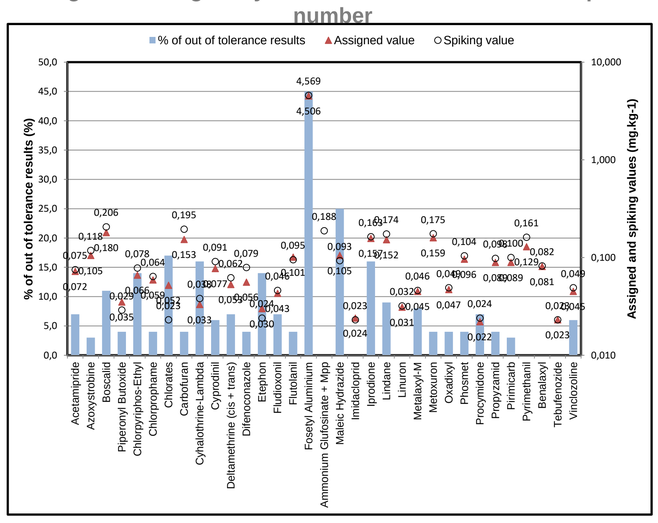

Fig. 5 - Percentage of out of tolerance results, assigned and spiking values per molecule

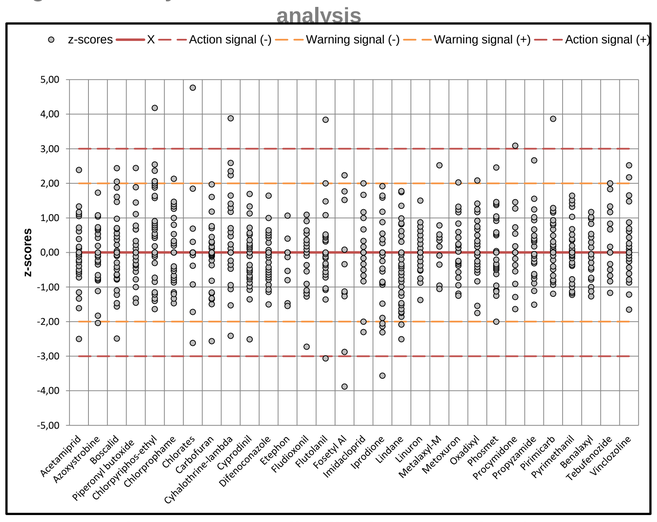

Fig. 6 - z-scores distribution per molecule

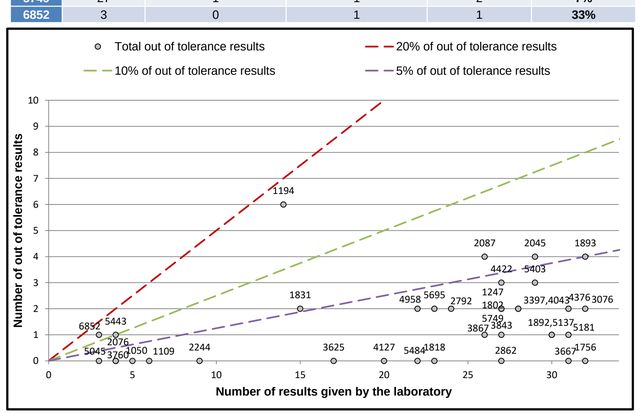

Fig. 7 – Overview by laboratory

CONCLUSION

The results obtained for this interlaboratory test were good for most of the molecules and for the major part of the laboratories. The recovery rates were satisfactory. This test is part of an annual proficiency testing program, allowing a real long-term follow-up of the laboratories' results for the different analytical parameters. The interlaboratory comparisons are a good tool of quality management and can be used to follow the performances of the laboratories, highlighting drifts or recurring analytical difficulties, which are a first step before the implementation of corrective/curative action.

REFERENCES

(1) **ISO 13528** - Statistical methods for use in proficiency testing by interlaboratory comparisons
(2) **ISO 17043** - Conformity assessment - General requirements for proficiency testing.