New approaches in proficiency testing: Spiking of original non-homogenised food products

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Introduction

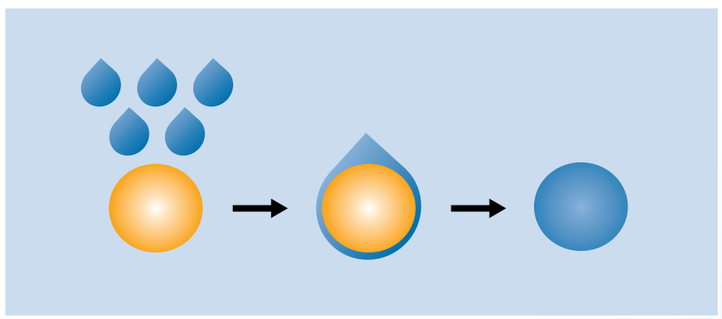
The use of homogenised food products as test materials in proficiency testing is currently standing practice. However, homogenised test material is not suitable to verify the quality of the homogenisation procedure as one of the crucial steps in sample preparation.

Slight differences in homogenisation may highly influence the reliability and robustness of analytical results in particular with respect to temperature or pH-sensitive analytes or complex matrices. Consequently, it is desirable that spiked but non-homogenised original food products are provided in proficiency testing schemes instead of homogenates [1].

Prerequisites, preparation procedures and evaluation

Two approaches can be applied to overcome the challenge of spiking original but non-homogenised food products:

A) Coating the food with the analytes



Prerequisites

- Smooth products
- No notches, crushes or incisions on the surface
- Preferably small products (plenty of single items per analytical sample)

Preparation procedure – flax seeds

- Use flax seeds, free of pesticides (<0.01 mg/kg)
- Mix the un-chopped flax seeds for 1 hour
- Avoid damage of the flax seeds
- Add the spiking solution over a period of 30 minutes under continuous stirring
- Continue stirring to ensure a homogeneous distribution of the material

Verification of the spiking procedure – Homogeneity testing
The homogeneity testing according to the Harmonised Protocol [2] confirms the homogeneous distribution of the pesticides in the test material (exemplarily shown in table 1).

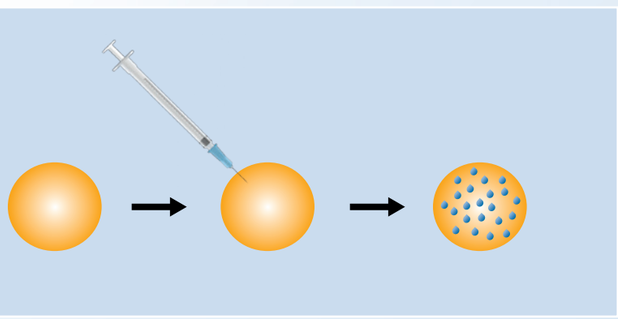
Evaluation
Each sub-sample contains the exact same amount of analytes. Consequently, the test material can be treated like homogenates during evaluation.

- Trueness – as recovery of the spiked level
- Comparability – according to the z-score model [2]

Subsample	Extr. No.	Isofenphos-methyl (mg/kg)	Pirimiphos-methyl (mg/kg)	Trifluralin (mg/kg)
1	1	0.020	0.031	0.023
	2	0.020	0.032	0.025
2	1	0.019	0.032	0.022
	2	0.020	0.034	0.025
3	1	0.019	0.032	0.021
	2	0.018	0.028	0.021
4	1	0.019	0.031	0.025
	2	0.020	0.032	0.023
5	1	0.018	0.032	0.021
	2	0.018	0.030	0.022
6	1	0.017	0.028	0.021
	2	0.019	0.031	0.022
7	1	0.018	0.031	0.021
	2	0.017	0.025	0.019
Mean [mg/kg]		**0.019**	**0.031**	**0.022**
Standard deviation [mg/kg]		0.0010	0.0024	0.0019
Coefficient of variation [%]		**5.4**	**8.0**	**8.7**

Table 1: Verification of the homogeneity of the flax seed test material

B) Injecting the analytes



Prerequisites

- Absorptive food products
- Food must be suitable to inject the spiking solution with a syringe
- Preferably small food products → homogenised as whole pieces in the lab. If the food product is too large, the laboratory might tend to cut it into pieces before homogenisation → uncontrollable loss of analytes

Preparation procedure – kumquats and Brussels sprouts

- Use e.g. Brussels sprouts or kumquats, free of pesticides (<0.01 mg/kg)
- Pick several items (e.g. 10 kumquats) per sample – one sprout or kumquat is a too small quantity of material for a reliable analysis
- Sort the items according to their individual weight to end up at a similar overall weight of each sample
- Inject a defined volume of a pesticide mixture to each single item with a syringe
- Assign a unique sample identifier to each sample
- Determine the exact overall weight of each sample (consisting of e.g. 10 items)

Verification of the spiking procedure – Reproducibility testing
Five samples, 10 kumquats or Brussels sprouts each, are randomly chosen from all prepared samples. Each sample is analysed for the spiked pesticides. The reproducibility data are exemplarily presented for imazalil in kumquats (table 2).
The individual concentration of the spiked level of each sample is calculated by the total quantity of pesticides spiked to each kumquat and the overall weight of the test sample.

Evaluation
Fruits and vegetables are natural products and consequently the overall weight of the different samples is not totally equal (see table 2). Injecting the same amount of spiking solution to each item, the spiked level varies slightly between the samples. During evaluation, the individual spiked level of each individual sample has to be considered. The spiked level is calculated of the overall amount of spiking solution injected to e.g. 10 kumquats (e.g. 10 × 50 µl = 500 µl), the concentration of the spiking solution and the overall weight of the test sample.

- Trueness – evaluation of the results of each laboratory individually with respect to the recovery of the actual amount (spiked level) of pesticides in each individual sample. The stability of analytes in the provided material must be ensured across the whole testing period.
- Comparability – percentage of recovery of the individual spiked levels.

Test sample No.	Overall weight of the test sample	Individual spiked level (mg/kg)	Extraction 1 (mg/kg)	Extraction 2 (mg/kg)	Recovery of the spiked level
1	129.75	0.035	0.038	0.037	107.1
2	131.04	0.035	0.036	0.036	102.9
3	129.34	0.036	0.035	0.037	100.0
4	129.51	0.036	0.036	0.035	98.6
5	130.96	0.035	0.033	0.033	94.3
Mean recovery of the spiked value [mg/kg]					100.6
Standard deviation [mg/kg]					4.8
Coefficient of variation [%]					4.8

Table 2: Reproducibility testing of imazalil in kumquats

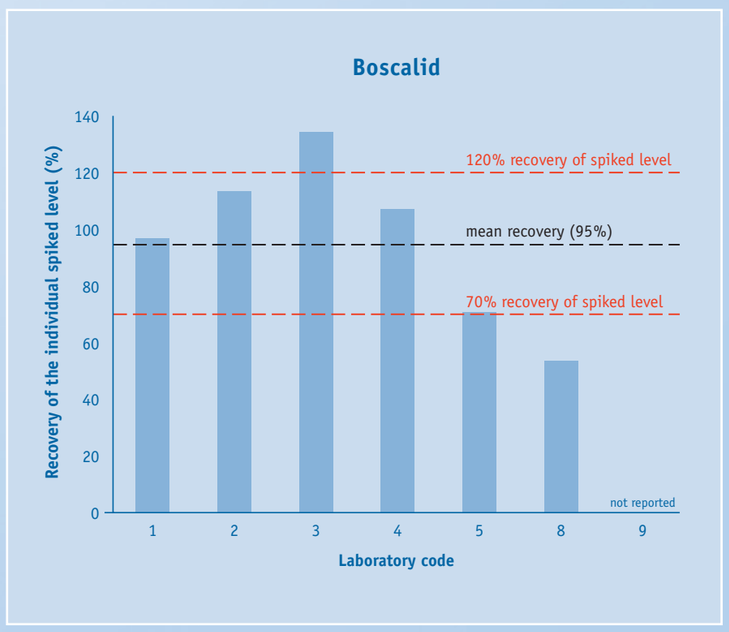


Figure 1: Evaluation of the results of boscalid in Brussels sprouts.

Fields of application

- Including all sample preparation steps in proficiency testing,
- Checking the quality of the homogenisation step,
- Identifying areas of improvement in homogenising demanding matrices like oil seeds,
- Checking the impact of sample preparation and homogenisation related to sensitive analytes (pH, temperature, particle size, …),
- Testing the laboratories' performance under routine conditions, as appearance and texture is identical to routine samples.

Conclusion

New approaches on how to spike original non-homogenised samples are presented.

The selection of appropriate raw material, and the establishment of a reliable verification of the spiking and of the stability of the spiked analytes are discussed in order to identify the new approaches in proficiency testing and their feasibility.
We conclude that non-homogenised test samples will deliver a significant improvement for the verification of comprehensive analytical performances, including the important step of sample preparation (homogenisation).

REFERENCES:
[1] M. Anastassiades, J. Hepperle, D. Roué, I. Sigalov, "Extractability of Incurred Residues using QuEChERS", 3rd Joint EURL-Workshop, Presentation, Freiburg 27–28 Sept 2011.
[2] M. Thompson, S. L. R. Ellison, and R. Wood, "The International Harmonized Protocol for the proficiency testing of analytical chemistry laboratories (IUPAC Technical Report)", Pure Appl. Chem., vol. 78, no. 1, pp. 145–196, 2006.