

Ring test
Acidic herbicides
(free acids, esters and conjugates)
in soybean flour
P2006-RT



Summary

The entire report is made available to participants only.

Designed, realised and evaluated by

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The proficiency test evaluates the performances of laboratories with respect to their ability to quantify acidic herbicides in soybean flour. After application of the pesticide formulations, esters and conjugates of acidic herbicides are formed on the plant in addition to the applied free acids. Thus, the respective esters and conjugates are included in the residue definitions of many acidic herbicides. The esters are in some cases within the scope of common multi-method approaches, and the sum of the free acids, the esters and conjugates are quantified applying an alkaline hydrolysis during sample preparation. The quantification of the esters and conjugates is inevitable, since in many cases the total quantity of the acidic herbicides is significantly higher with alkaline hydrolysis compared to the analysis without hydrolysis.

Even though esters and conjugates are of high importance, they are usually not included in common competence schemes. The availability of analytical standards of esters and conjugates is limited.

In order to include the alkaline hydrolysis in the ring test, the test material was spiked with free acids, esters and conjugates. The participants were asked to report results with and without application of an alkaline hydrolysis. The sum of free acid, ester and conjugate after hydrolysis was used for evaluation of parameters, which are spiked as esters or glucosides.

11 laboratories across four countries (Austria, Germany, Italy, and Switzerland) took part in the test. All 11 labs reported results and are considered for evaluation.

Soybean flour is provided as test material and blank material. The test material is spiked with glucosides of 2,4-D, 2,4-dichlorprop, and haloxyfop, esters of 2,4-DB, 2,4,5-T, clopyralid, dicamba, fluazifop, and MCPA and the free acids fluroxypyr and MCPA.

The performance of laboratories in the test is evaluated according to

- the identification of the spiked acidic herbicides. Parameters, which are not reported and not marked as not analysed are considered false negative.
- the comparability of the results. The evaluation of the comparability is based on the z-score model. The z-score should be at least $\leq |2|$.
- the trueness of the results. The trueness is expressed as the coverage of the spiked level in %. The coverage should be at least between 70 and 120 % of the spiked level.

Results

Parameter	Spiked level [mg/kg]	Assigned value [mg/kg]	Total number of results	Comparability criterion: no. of participants, with z-score \leq 2	Trueness criterion: no. of participants with results within 70-120 % recovery of the spiked level
2,4-D-Glucosid	0.099				
2,4-D sum	0.057*	0.0537	11	11	10
2,4-DB 2-ethylhexyl ester	0.117				
2,4-DB sum	0.081*	Not evaluated			
2,4-Dichlorprop glucoside	0.068				
2,4-Dichlorprop sum	0.040*	0.0336	10	9	8
2,4,5-T 2-ethylhexyl ester	0.054				
2,4,5-T sum	0.038*	0.0281	8	5	3
Clopyralid methyl ester	0.072				
Clopyralid sum	0.067*	0.0557	7	6**	5**
Dicamba methyl ester	0.081				
Dicamba sum	0.076*	Not evaluated			
Fluazifop-p-butyl	0.050				
Fluazifop sum	0.043*	0.0419	9	8	7
Fluroxypyr (free acid)	0.023	0.0270	8	5	4
Haloxyfop glucoside	0.12				
Haloxyfop sum	0.083*	0.0783	11	9	9
MCPA free acid	0.045	0.0421	11	11	10
MCPA 2-ethylhexyl ester	0.072				
MCPA (sum)	0.091*	0.0763	11	10	5

* calculated of the concentration level of the respective spiked ester or glucoside

** The evaluation is provided for information only.

The results related to clopyralid and dicamba are presented for information only and are not considered for evaluation. The esters are not included in the residue definitions of clopyralid and dicamba according to regulation (EC) 396/2005. 2,4-DB was not considered for evaluation. Recoveries of 2,4-DB were low during homogeneity testing as well as related to the reported results.

The results related to fluroxypyr and the free acid of MCPA are evaluated based on the results without hydrolysis.

To summarise,

- The alkaline hydrolysis is well suitable for the cleavage of the glucoside conjugates.
- The analysis of esters is challenging. Conditions of the hydrolysis need to be optimised to ensure a full cleavage of the esters. Inadequate conditions during hydrolysis result in an underestimation of the spiked levels of the esters by some of the labs or even in false negative results.
- 7 out of 11 labs identified all acidic herbicides correctly. Three labs failed to identify 2,4,5-T, three labs failed to identify fluroxypyr, one lab failed to identify 2,4-dichlorprop, and one lab failed to identify fluazifop.
- The overall performance of the labs with respect to the spiked glucosides and the free acids was good. The assigned values are in good accordance with the spiked levels (84 to 117 % recovery of the spiked levels).
- However, the assigned values related to the esters are still within an acceptable range of the spiked level (74 to 97 % recovery of the spiked levels).