

Ring test
Acidic herbicides (with hydrolysis)
in cabbage
P2311-RT



Summary

The entire report is available to participants only.

The ring test was designed, realised, evaluated, and authorised on behalf of PROOF-ACS GmbH by

Dr. Birgit Schindler
Managing Director PROOF-ACS GmbH
Project coordinator

The report was approved by

Dr. Birgit Schindler

Participants with any comments or concerns related to this ring test are invited to contact:

PROOF-ACS GmbH
Gottlieb-Daimler-Str. 1
28237 Bremen
Phone: +49 421 388 928 50
E-mail: proof@proof-acs.de
www.proof-acs.de

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PROOF-ACS GmbH does not have any analytical laboratory facilities of its own. Homogeneity testing and stability testing are subcontracted to laboratories, accredited according to DIN EN ISO 17025. The subcontracted laboratory may also participate in the ring tests. If so, the laboratory is treated in the same way as other participants and the same rules of confidentiality apply.

The proficiency test evaluates the performances of laboratories with respect to their ability to quantify acidic herbicides in cabbage. 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.

The test material was spiked with free acids, esters, and conjugates of acidic herbicides to include the alkaline hydrolysis in the ring test, t. Clopyralid and triclopyr were spiked as free acid, while MCPA was spiked as glucoside and 2,4-D, 2,4-DB, 2,4-dichlorprop, 2,4,5-T, fluazifop, and haloxyfop were spiked as esters.

The participants were asked to report results with and without applying 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 (2,4-D, 2,4-DB, 2,4-dichlorprop, fluazifop, haloxyfop, and MCPA). The results without hydrolysis are used for evaluation of clopyralid and triclopyr. The evaluation with respect to the esters (without hydrolysis) is provided for information only.

Cabbage homogenates, spiked and unspiked, are provided as test material and blank material. The test material is spiked with a mix-solution of all parameters in acetone. The cabbage is deep-frozen with liquid nitrogen during homogenisation and during the whole spiking process.

21 laboratories across seven countries (France, Germany, Greece, Italy, Netherlands, Poland, and Spain) took part in the test. 19 labs reported results and are considered for evaluation.

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 (sum) with hydrolysis spiked as 2,4-D ethylhexyl	0.086*	0.0829	19	18	17
	0.13				
2,4-DB (sum) with hydrolysis spiked as 2,4-DB ethylhexyl	0.043*	0.0295	17	16	7
	0.062				
2,4-Dichlorprop (sum) with hydrolysis spiked as 2,4-dichlorprop-butotyl	0.047*	0.0477	19	19	15
	0.067				
2,4,5-T (sum) with hydrolysis spiked as 2,4,5-T ethylhexyl ester	0.032*	0.0274	18	15	14
	0.046				
Fluazifop (sum) with hydrolysis spiked as fluazifop-P butyl ester	0.030*	0.0283	19	19	18
	0.035				
Haloxyfop (sum) with hydrolysis spiked as haloxyfop p-methyl ester	0.085*	0.0811	19	19	17
	0.088				
MCPA (sum) with hydrolysis spiked as glucoside	0.10*	0.0917	19	19	18
	0.18				
Clopyralid (free acid, without hydrolysis)	0.035	0.0341	17	15	14
Triclopyr (free acid, without hydrolysis)	0.059	0.0563	18	17	17

* Calculated of the concentration level of the respective spiked ester or glucoside.

To summarise,

- The alkaline hydrolysis is well suitable for the cleavage of the glucoside conjugate of MCPA.
- The analysis of the respective esters is more challenging. However, hydrolysis step, as applied by the labs, is well suitable for most of the spiked esters.
- The ethylhexyl ester of 2,4-DB is the most challenging parameter in the test.
- A lab reported a false positive result related to fluroxypyr.
- Another lab reported a false negative result related to 2,4-DB and clopyralid.
- The results without hydrolysis are considered for evaluation with respect to clopyralid and triclopyr. Most of the labs are able to provide reliable results related to the two parameters.
- The overall performance of the labs is good. The assigned values are in good accordance with the spiked levels (85 to 102 % recovery of the spiked levels for all parameters except 2,4-DB).
- Four labs quantified all acidic herbicides correctly with respect to the comparability criterion and the trueness criterion.