

Ring test Acidic herbicides (with hydrolysis) in broccoli P2614-RT



Summary

The entire report is available to participants only.

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

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The report is approved by

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PROOF-ACS is a DAkkS accredited proficiency testing provider according to DIN EN ISO 17043:2023 (D-EP-22211-01-00). This ring test is covered by the scope of accreditation.

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.

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The proficiency test evaluates the performances of laboratories with respect to their ability to quantify acidic herbicides in broccoli. 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 acidic herbicides. The esters are in some cases within the scope of common multi-method approaches. 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 especially of conjugates is still limited.

The test material is spiked with free acids, esters, and conjugates of acidic herbicides to include the alkaline hydrolysis in the ring test. Clopyralid and fenoxaprop are spiked as free acids, while MCPA is spiked as glucoside. 2,4-D, fluazifop, fluroxypyr, and haloxyfop are spiked as esters.

The participants are asked to report results with and without applying an alkaline hydrolysis for the acidic herbicides. The sum of the free acid, the ester and the conjugate after hydrolysis is used for evaluation of parameters, which are spiked as esters or glucosides (2,4-D, fluazifop, fluroxypyr, haloxyfop, and MCPA). The results without hydrolysis are used for evaluation of clopyralid and fenoxaprop. The evaluation with respect to the esters (without hydrolysis) is provided for information only.

Homogenates of broccoli, 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.

19 laboratories across seven countries (Germany, Greece, Italy, Netherlands, Poland, South Africa, and Spain) took part in the test. 17 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 absolute value of the z-score should be at least ≤ 2 . The comparability criterion is applied to all parameters.
- 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. The trueness criterion is applied to all parameters.

Results

Parameter	Spiked level [mg/kg]	Assigned value [mg/kg]	Total number of results	Comparability criterion: no. of participants, with $ z\text{-score} \leq 2$	Trueness criterion: no. of participants with results within 70-120 % recovery of the spiked level
2,4-D (sum) with hydrolysis	0.088*	0.0882	16	16	16
spiked: 2,4-D butyl ester	0.11				
Fluazifop (sum) with hydrolysis	0.26*	0.275	15	14	14
spiked: fluazifop-p-butyl	0.31				
Fluroxypyr (sum) with hydrolysis	0.038*	0.0423	13	13	8
spiked: fluroxypyr methylheptyl	0.055				
Haloxypop (sum) with hydrolysis	0.067*	0.0695	16	15	15
spiked: haloxypop methyl ester	0.070				
MCPA (sum) with hydrolysis	0.082*	0.0827	16	15	12
spiked: MCPA glucoside	0.13				
Clopyralid (without hydrolysis)	0.22	0.194	15	12	12
Fenoxaprop (without hydrolysis)	0.081	0.0680	9	8	6

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

To summarise,

- The results with hydrolysis are considered for evaluation of all acidic herbicides, which are spiked as esters or glucosides. The applied alkaline hydrolysis is well suitable for the cleavage of the glucosides. The analysis of the esters of the acidic herbicides is more challenging but feasible for most of the labs.
- The performance of the laboratories improved a lot compared to earlier ring tests related to acidic herbicides.
- The highest number of false negative results is observed for fenoxaprop.
- One of the labs reported a false positive result of 2,4,5-T (0.043 mg/kg).
- The most challenging ester is the most branched ester in the test, fluroxypyr methylheptyl. 5 labs overestimate the true concentration level in the test material.
- The assigned values are in good accordance with the spiked levels for all acidic herbicides (84 to 110 % recovery of the spiked level).
- 3 out of 17 labs quantified all acidic herbicides correctly with respect to the comparability criterion and the trueness criterion.