

Ring test
Acidic herbicides (with hydrolysis)
in strawberries
P2511-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

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The report was approved by

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PROOF-ACS is a DAkkS accredited proficiency testing provider according to DIN EN ISO 17043:2010 (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 strawberries. 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, 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 especially of 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. Clopyralid, dicamba, and triclopyr were spiked as free acids, while MCPB was spiked as glucoside. 2,4-D, 2,4-DB, 2,4-dichlorprop, fluroxypyr, and haloxyfop were spiked as esters.

The participants were 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 was used for evaluation of parameters, which are spiked as esters or glucosides (2,4-D, 2,4-DB, 2,4-dichlorprop, fluroxypyr, haloxyfop, and MCPB). The results without hydrolysis are used for evaluation of clopyralid, dicamba, and triclopyr. The evaluation with respect to the esters (without hydrolysis) is provided for information only.

A strawberry homogenate, spiked and unspiked, is provided as test material and blank material. The test material is spiked with a mix-solution of all parameters in acetone.

10 laboratories across six countries (Bulgaria, Germany, Greece, Italy, Spain, and Vietnam) took part in the test. All 10 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 not applicable to 2,4-DB. The cleavage of the ester of 2,4-DB is challenging, and thus the results of half of the labs are too low. These labs are not “fit for purpose”.
- 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 spiked as 2,4-D-2-ethylhexyl ester	0.12*	0.122	10	9	9
	0.18				
2,4-DB (sum) with hydrolysis spiked as 2,4-DB-2-ethylhexyl ester	0.054*	0.0349**	9	Not applicable	5
	0.078				
2,4-Dichlorprop (sum) with hydrolysis spiked as 2,4-dichlorprop-2-ethylhexyl ester	0.088*	0.0945	10	10	9
	0.13				
Fluroxypyr (sum) with hydrolysis spiked as fluroxypyr-1-methylheptyl ester	0.046*	0.0529	9	9	5
	0.066				
Haloxypop (sum) with hydrolysis spiked as haloxypop-2-ethoxyethyl ester	0.040*	0.0431	10	10	7
	0.048				
MCPB (sum) with hydrolysis spiked as MCPB glucoside	0.076*	0.0795	9	8	7
	0.13				
Clopyralid (free acid, without hydrolysis)	0.24	0.224	10	8	7
Dicamba (free acid, without hydrolysis)	0.058	0.0574	9	7	7
Triclopyr (free acid, without hydrolysis)	0.027	0.0269	10	8	7

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

** The assigned value is provided for information only.

To summarise,

- The performance of the laboratories improved a lot compared to earlier ring tests related to acidic herbicides.
- 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 still challenging for some of the labs.
- The most challenging ester is 2,4-DB ethylhexyl. Low recoveries were reported by half of the labs, probably due to incomplete cleavage of the ester. The comparability criterion is thus not applicable for evaluation of 2,4-DB (sum).
- The results without hydrolysis are considered for evaluation of clopyralid, dicamba, and triclopyr. Most of the labs can provide reliable results related to the parameters.
- The assigned values are in good accordance with the spiked levels for all acidic herbicides (93 to 115 % recovery of the spiked level), except 2,4-DB (65 % recovery of the spiked level).
- None of the labs reported false positive results.
- Three labs reported false negative results related to 2,4-DB, fluroxypyr, and MCPB respectively.
- None of the labs quantified all acidic herbicides correctly with respect to the comparability criterion and the trueness criterion.