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Ring test
Acidic herbicides (with hydrolysis) in fennel seeds
P2512-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

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

The report is approved by

Dr. Birgit Schindler
cn=Dr. Birgit Schindler,
o=PROOF-ACS GmbH,
ou=Managing Director,
email=proof@proof-acs.de, c=DE
2026.01.12 15:50:41 +01'00'

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

DAkkS Deutsche Akkreditierungsstelle D-EP-22211-01-00

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.

The proficiency test evaluates the performances of laboratories with respect to their ability to quantify acidic herbicides in fennel seeds. 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 is spiked with free acids, esters, and conjugates of acidic herbicides to include the alkaline hydrolysis in the ring test. 4-CPA, dicamba, fenoprop (2,4,5-TP), fenoxaprop, and triclopyr are spiked as free acids, while dichlorprop is spiked as glucoside. 2,4-D, 2,4-DB, 2,4,5-T, fluazifop, fluroxypyr, and MCPA 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, 2,4-DB, 2,4,5-T, dichlorprop, fluazifop, fluroxypyr, and MCPA). The results without hydrolysis are used for evaluation of 4-CPA, dicamba, fenoprop, fenoxaprop, and triclopyr. The evaluation with respect to the esters (without hydrolysis) is provided for information only.

Milled and homogenised fennel seeds, 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.

16 laboratories across four countries (France, Germany, Italy, and Netherlands) took part in the test. 14 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 *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-score| ≤ 2	**Trueness criterion:** no. of participants with results within 70-120 % recovery of the spiked level
2,4-D (sum) with hydrolysis	0.044*	0.0415	13	12	12
spiked as 2,4-D ethylhexyl	0.066				
2,4-DB (sum) with hydrolysis	0.026*	-	5	not applicable	4
spiked as 2,4-DB ethylhexyl	0.038				
2,4,5-T (sum) with hydrolysis	0.076*	0.0700	13	13	10
spiked as 2,4,5-T ethylhexyl	0.11				
2,4-Dichlorprop (sum) with hydrolysis	0.14*	0.145	13	12	11
spiked as dichlorprop glucoside	0.24				
Fluazifop (sum) with hydrolysis	0.053*	0.0541	13	13	12
spiked as fluazifop methyl	0.055				
Fluroxypyr (sum) with hydrolysis	0.059*	0.0540	13	12	10
spiked as fluroxypyr methylheptyl	0.085				
MCPA (sum) with hydrolysis	0.090*	0.0784	13	13	11
spiked as MCPA ethylhexyl	0.14				
4-CPA without hydrolysis	0.033	0.0323	12	12	12
Dicamba without hydrolysis	0.099	0.0984	9	9	9
Fenoprop without hydrolysis	0.063	0.0664	11	11	10
Fenoxaprop without hydrolysis	0.038	0.0392	11	10	9
Triclopyr without hydrolysis	0.077	0.0801	13	13	11

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

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. Recoveries are low for most of the labs, probably due to incomplete cleavage of the ester. Only 4 labs reported reliable results. The comparability criterion is thus not applicable for evaluation of 2,4-DB (sum). A high number of labs reported false negative results of 2,4-DB.
- The results without hydrolysis are considered for evaluation of 4-CPA, dicamba, fenoprop, fenoxaprop, 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 (87 to 105 % recovery of the spiked level).
- None of the labs reported false positive results.
- Labs reported false negative results related to 2,4-DB, fenoprop, and dicamba.
- 4 out of 14 labs quantified all acidic herbicides correctly with respect to the comparability criterion and the trueness criterion.