Facing analytical quality.

proof acs

Ring test
Acidic herbicides
(free acids, esters and conjugates)
in lime
P2208-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
16 September 2022

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

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 exactly 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 lime. 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 of acidic herbicides. Dicamba was spiked as free acid, while 2,4-D, 2,4-DB, 2,4-dichlorprop, 2,4,5-T, and fluazifop were spiked as esters and haloxyfop, and MCPA were spiked as glucosides.

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, 2,4,5-T, fluazifop, haloxyfop, and MCPA). The results related to the free acids without hydrolysis are used for evaluation of dicamba. The evaluation with respect to the esters (without hydrolysis) is provided for information only.

30 laboratories across ten countries (Austria, Belgium, Germany, Greece, Italy, Netherlands, Serbia, South Africa, Spain, and Vietnam) took part in the test. All 30 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 ≤ |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 ≤ |2|	**Trueness criterion:** no. of participants with results within 70-120 % recovery of the spiked level
2,4-D	0.096*	0.0910	29	26	26
spiked as 2,4-D butyl ester	0.12				
2,4-DB**	0.045*	-	10	-	-
spiked as 2,4-DB ethylhexyl ester	0.065				
2,4-Dichlorprop	0.067*	-	22	-	8
spiked as dichlorprop methylheptyl ester	0.099				
2,4,5-T	0.050*	0.0485	23	23	23
spiked as i-octyl ester	0.072				
Dicamba (without hydrolysis)	0.062	0.0609	16	15	13
Fluazifop	0.033*	0.0330	29	27	24
spiked as fluazifop methyl ester	0.034				
Haloxyfop	0.030*	0.0301	29	28	23
spiked as haloxyfop glucoside	0.043				
MCPA	0.077*	0.0845	30	28	19
spiked as MCPA glucoside	0.14				

* Calculated of the concentration level of the respective spiked ester or glucoside.
** The results related to 2,4-DB are not considered for evaluation.

To summarise,

- The alkaline hydrolysis is well suitable for the cleavage of the glucoside conjugates.
- The analysis of esters is more challenging. Compared to previous ring tests, the laboratories improved the conditions of the hydrolysis. If applied correctly, the hydrolysis step of most of the labs is well suitable for the quantification of esters of 2,4-D, 2,4,5-T, and fluazifop.
- The hydrolysis of more complex esters, like spiked for 2,4-DB and 2,4-dichlorprop is more challenging.
- Quite a number of false negative results were reported of 2,4-D, 2,4-dichlorprop, 2,4,5-T, and dicamba. False positive results were reported of 4-CPA, 2,4,5-TP, clopyralid, fluroxypyr, and triclopyr.
- The overall performance of the labs with respect to the spiked glucosides, esters and the free acids was good. The assigned values are in good accordance with the spiked levels (95 to 110 % recovery of the spiked levels for all parameters except 2,4-DB and 2,4-dichlorprop). The overall performance with respect to 2,4-DB and 2,4-dichlorprop is bad.
- Two labs quantified all parameters correctly with respect to the comparability criterion and the trueness criterion.