Facing analytical quality.

Ring test
Acidic herbicides in courgette (free acids, esters and conjugates)

P2007-RT

Summary

The entire report is available to participants only.

Designed, realised and evaluated by

PROOF-ACS GmbH
Bremen, Germany

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Dr. Birgit Schindler

The proficiency test evaluates the performances of laboratories with respect to their ability to quantify acidic herbicides in courgette. 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. 2,4-DB, 2,4-dichlorprop, dicamba, and fenoxaprop were spiked as free acids, while 2,4-D, 2,4,5-T, fluazifop and fluroxypyr were spiked as esters and 2,4-dichlorprop, 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-dichlorprop, 2,4,5-T, fluazifop, fluroxypyr, haloxyfop, MCPA). The results related to the free acids without hydrolysis are used for evaluation of parameter, which are spiked as free acids (2,4-DB, dicamba, fenoxaprop).

17 laboratories across five countries (Germany, Greece, Italy, Spain, and Vietnam) took part in the test. All 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 (sum) with hydrolysis	0.057*	0.0617	17	16	12
spiked as 2,4-D butyl ester	0.071				
2,4-Dichlorprop (sum) with hydrolysis	0.054	0.0585	17	17	13
spiked as 2,4-dichlorprop, and 2,4-dichlorprop glucoside	0.027 0.045				
2,4,5-T (sum) with hydrolysis	0.051*	0.0487	17	16	12
spiked as 2,4,5-T ethylhexyl ester	0.074				
Fluazifop (sum) with hydrolysis	0.043*	0.0492	17	16	10
spiked as fluazifop-p-butyl	0.050				
Fluroxypyr (sum) with hydrolysis	0.031*	0.0337	17	15	14
spiked as fluroxypyr 1-methyl-heptyl ester	0.045				
Haloxyfop (sum) with hydrolysis	0.039*	0.0380	17	17	15
spiked as haloxyfop glucoside	0.056				
MCPA (sum) with hydrolysis	0.066*	0.0672	17	16	14
spiked as MCPA glucoside	0.12				
2,4-DB without hydrolysis spiked as free acid	0.028	0.0303	16	14	11
Dicamba without hydrolysis spiked as free acid	0.098	0.0936	13	10	10
Fenoxaprop without hydrolysis spiked as free acid	0.12	0.141	12	10	9

* 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 conjugates.
- The analysis of esters is challenging. Compared to previous ring tests, the laboratories improved the conditions of the hydrolysis. The applied hydrolysis step of most of the labs is well suitable for the quantification of esters of 2,4-D, 2,4,5-T, fluazifop, and fluroxypyr.
- All 17 labs identified 2,4-D, 2,4,5-T, 2,4-dichlorprop, fluazifop, fluroxypyr, haloxyfop, and MCPA correctly. Two labs failed to identify 2,4-DB, while dicamba was not analysed by three labs and two labs failed to identify it correctly. Fenoxaprop was not analysed by four labs, while two more labs failed to identify fenoxaprop.
- 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 (96 to 118 % recovery of the spiked levels).