

Ring test  
Acidic herbicides  
(free acids, esters and conjugates)  
in grapefruit  
P2106-RT



## Summary

The entire report is available to participants only.

Designed, realised and evaluated by

**PROOF-ACS GmbH**  
**Bremen, Germany**

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A handwritten signature in blue ink that reads "Schindler".

Dr. Birgit Schindler

The proficiency test evaluates the performances of laboratories with respect to their ability to quantify acidic herbicides in grapefruit. 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. Clopyralid and fenoxaprop were spiked as free acids, while 2,4-DB, 2,4,5-T, fluazifop, haloxyfop, and MCPA were spiked as esters and 2,4-D, 2,4-dichlorprop, and haloxyfop 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 parameter, which are spiked as free acids (clopyralid and fenoxaprop). The evaluation with respect to the esters (without hydrolysis) is provided for information only.

23 laboratories across ten countries (Austria, Belgium, France, Germany, Greece, Italy, Poland, South Africa, Spain, and Switzerland) took part in the test. 22 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  $\leq |2|$ .
- 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 $\leq  2 $	Trueness criterion: no. of participants with results within 70-120 % recovery of the spiked level
2,4-D spiked as 2,4-D glucoside	0.075*	0.0727	22	19	14
	0.13				
2,4-DB spiked as methyl ester	0.068*	0.0531	19	14	10
	0.072				
2,4-Dichlorprop spiked as dichlorprop-glucoside	0.052*	0.0472	22	19	16
	0.088				
2,4,5-T spiked as ethylhexyl ester	0.030*	0.0292	19	16	14
	0.043				
Fluazifop spiked as fluazifop-p-butyl	0.044*	0.0423	20	16	12
	0.052				
Haloxyfop spiked as haloxyfop glucoside, and haloxyfop ethoxyethyl ester	0.136*	0.116	21	20	16
	0.10 0.080				
MCPA spiked as MCPA ethylhexyl ester	0.037*	0.0325	20	15	14
	0.058				
Clopyralid (without hydrolysis)	0.029	0.0307	14	13	12
Fenoxaprop-P (without hydrolysis)	0.065	0.0589	14	13	13

\* 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 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-DB, 2,4,5-T, fluazifop, haloxyfop, and MCPA.
- False negative results were reported of 2,4-DB, 2,4,5-T, clopyralid, fenoxaprop, fluazifop, haloxyfop, and MCPA by one or more labs. False positive results were reported of 4-CPA, 2,4,5-TP, dicamba, and fluroxypyr. Four labs did not analyse the samples for 2,4,5-T, clopyralid, or 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 (91 to 106 % recovery of the spiked levels for all parameters except 2,4-DB (78 % recovery of spike)).
- Two labs quantified all parameters correctly with respect to the comparability criterion and the trueness criterion.