

Ring test  
Acidic herbicides  
(free acids, esters and conjugates)  
in rapeseed oil  
P2104-RT



## Summary

The entire report is available to participants only.

Designed, realised and evaluated by

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

April 2021,

A handwritten signature in blue ink that reads "Schindler". The signature is fluid and cursive, with a large initial 'S'.

Dr. Birgit Schindler

The proficiency test evaluates the performances of laboratories with respect to their ability to quantify acidic herbicides in rapeseed oil. After application of the pesticide formulations, esters and conjugates of acidic herbicides are formed on the plant in addition to the 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 is spiked with free acids, esters and conjugates of acidic herbicides. Clopyralid, dicamba, and triclopyr are spiked as free acids, while 2,4-D, fluazifop, and haloxyfop are spiked as esters and 2,4-dichlorprop and MCPA are spiked as glucosides.

The participants were asked to report results with and without applying an alkaline hydrolysis. The results after hydrolysis, which correspond to the sum of the respective free acid, the ester and the conjugate was used for evaluation of parameters, which are spiked as esters or glucosides (2,4-D, 2,4-dichlorprop, 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, dicamba, and triclopyr).

8 laboratories across five European countries (Austria, Bulgaria, Germany, Italy, Netherlands) 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  $\leq |2|$ . The comparability criterion is not applicable to clopyralid, dicamba, and triclopyr due to the limited number of reported results.
- 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 (sum) with hydrolysis                       | 0.080*               | 0.0737                 | 8                       | 7   | 6   |
| spiked as 2,4-D butyl ester                       | 0.10                 |                        |                         |   |   |
| 2,4-Dichlorprop (sum) with hydrolysis             | 0.053*               | 0.0494                 | 8                       | 8   | 8   |
| spiked as 2,4-dichlorprop glucoside               | 0.090                |                        |                         |   |   |
| Fluazifop (sum) with hydrolysis                   | 0.12*                | 0.102                  | 8                       | 5   | 4   |
| spiked as fluazifop-p-butyl                       | 0.14                 |                        |                         |   |   |
| Haloxyfop (sum) with hydrolysis                   | 0.085*               | 0.0676                 | 8                       | 7   | 5   |
| spiked as haloxyfop-p-methyl ester                | 0.088                |                        |                         |   |   |
| MCPA (sum) with hydrolysis                        | 0.061*               | 0.0593                 | 8                       | 7   | 6   |
| spiked as MCPA glucoside                          | 0.11                 |                        |                         |   |   |
| Clopyralid without hydrolysis spiked as free acid | 0.066                |                        | 5                       | Not evaluated   | 5   |
| Dicamba without hydrolysis spiked as free acid    | 0.073                |                        | 5                       | Not evaluated   | 4   |
| Triclopyr without hydrolysis spiked as free acid  | 0.040                |                        | 6                       | Not evaluated   | 5   |

\* calculated of the concentration level of the respective spiked ester or glucoside

To summarise,

- All 8 labs identified 2,4-D, 2,4-dichlorprop, haloxyfop, and MCPA correctly. One lab failed to identify fluazifop, while three labs failed to identify clopyralid, dicamba, and triclopyr correctly.
- 1 out of 8 labs quantified all parameters correctly with respect to the comparability criterion (if applicable) and with respect to the trueness criterion.
- 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 (80 to 97 % recovery of the spiked levels).
- The alkaline hydrolysis is well suitable for the cleavage of the glucoside conjugates of 2,4-dichlorprop and MCPA.
- The quantification of the esters of 2,4-D and haloxyfop after hydrolysis is well feasible for most of the labs. The correct quantification of fluazifop is more challenging. Compared to previous ring tests, the laboratories improved the conditions of the hydrolysis.