

Ring test  
Acidic herbicides and o-phenylphenol  
(both with hydrolysis)  
in orange  
P2428-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

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The report was approved by

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Participants with any comments or concerns related to this ring test are invited to contact:

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PROOF-ACS is a DAkkS accredited proficiency testing provider according to DIN EN ISO 17043:2010 (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.

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The proficiency test evaluates the performances of laboratories with respect to their ability to quantify acidic herbicides and o-phenylphenol in orange. 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.

o-Phenylphenol was included in the scheme, as it is another pesticide, which is common in citrus matrices and is regulated with the respective conjugates according to regulation (EC) 396/2005.

The test material was spiked with free acids, esters, and conjugates of acidic herbicides to include the alkaline hydrolysis in the ring test. 4-CPA, clopyralid, fenoxaprop-P, and triclopyr were spiked as free acids, while 2,4-dichlorprop was spiked as glucoside and 2,4-D, 2,4,5-T, fluroxypyr, and MCPA were spiked as esters. o-Phenylphenol was spiked as glucoside.

The participants were asked to report results with and without applying an alkaline hydrolysis for the acidic herbicides. 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, fluroxypyr, and MCPA). The results without hydrolysis are used for evaluation of 4-CPA, clopyralid, fenoxaprop-P, and triclopyr. The evaluation with respect to the esters (without hydrolysis) is provided for information only.

With respect to o-phenylphenol, the laboratories were asked to report results with and without hydrolysis as well. The results with hydrolysis are considered for evaluation.

Orange homogenates, 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. The oranges are deep-frozen with liquid nitrogen during homogenisation and during the whole spiking process.

15 laboratories across six countries (Germany, Greece, Italy, Poland, Spain, and Vietnam) 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 z-score should be at least  $\leq |2|$ . The comparability criterion is not applicable to o-phenylphenol.
- 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 spiked as 2,4-D butyl ester	0.17*	0.152	14	14	14
	0.21				
2,4-Dichlorprop (sum) with hydrolysis spiked as 2,4-dichlorprop-glucoside	0.13*	0.126	14	13	11
	0.22				
2,4,5-T (sum) with hydrolysis spiked as 2,4,5-T ethylhexyl ester	0.035*	0.0300	13	12	11
	0.050				
Fluroxypyr (sum) with hydrolysis spiked as fluroxypyr methylheptyl ester	0.030*	0.0253	13	12	9
	0.043				
MCPA (sum) with hydrolysis spiked as 2-ethylhexyl ester	0.042*	0.0367	14	13	11
	0.066				
o-Phenylphenol spiked as o-phenylphenol glucosid	0.41*	-	11	-	2
	0.80				
4-CPA (free acid, without hydrolysis)	0.066	0.0597	13	11	10
Clopyralid (free acid, without hydrolysis)	0.088	0.0808	13	13	11
Fenoxaprop-P (free acid, without hydrolysis)	0.077	0.0795	13	11	9
Triclopyr (free acid, without hydrolysis)	0.084	0.0777	14	14	12

\* 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 and esters of the acidic herbicides for most of the labs.
- The results without hydrolysis are considered for evaluation of 4-CPA, clopyralid, fenoxaprop-P, 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 (84 to 103 % recovery of the spiked level).
- A lab reported a false positive result related to 2,4-DB.
- Three labs reported false negative results related to 4-CPA, 2,4,5-T, and o-phenylphenol respectively.
- Four labs quantified all acidic herbicides correctly with respect to the comparability criterion and the trueness criterion.
- The overall performance with respect to the quantification of o-phenylphenol is not satisfying. An alkaline hydrolysis was applied by most of the laboratories. The applied alkaline hydrolysis is not suitable for the cleavage of the glucoside. The labs should check, improve, and validate the conditions of hydrolysis of o-phenylphenol.
- Only two labs provided satisfying results with respect to o-phenylphenol. The successful laboratories applied an acidic hydrolysis.