The Effect of Laboratory Lighting on the Isomerisation of Pesticides

Authors: Joanne Gilbert, Sharon Swales
Smithers, Harrogate

ABSTRACT

Concerns have been raised regarding possible differences in the effects, degradation and transformation of different isomeric forms of plant protection products. New guidance was issued by EFSA in July 2019[1] to ensure that the required information is available to complete the risk assessment of active substances of plant protection products which contain stereoisomers as components or impurities or may form transformation products which contain stereoisomers. In the course of performing environmental fate studies, it is important to know if any change in the isomeric form of an active ingredient is due to natural processes in the test system or if it has been brought about by the extraction and/or work-up of the samples in the laboratory. During an adsorption/desorption study (OECD 106) that was conducted on a pesticide active ingredient, an unknown degradate was observed which eluted very close to the parent peak on the radio-HPLC chromatogram. This poster shows how the unknown was identified as an isomer of the parent compound and that it was formed by the action of the laboratory lighting on the sample extracts during the work-up stages. [1] EFSA Journal 2019; 17(8):5804

On analyzing supernatants and soil extracts from an OECD 106 study, a peak was seen which eluted very close to the parent peak. This peak was identified by LC-MS as an isomer of the test substance. As the amount of isomer increased in samples which had been out on the laboratory bench, an experiment was performed to establish if laboratory lighting was responsible for the isomerisation.

Samples of 0.01M $CaCl_2$ solution, with and without equilibration with control soil, were treated with test substance. All samples were concentrated for HPLC analysis under nitrogen in the same way as the study samples, except that the dark samples were wrapped in foil to exclude light as much as possible.

All samples were analysed by HPLC and results are shown in Table 1.

Table 1: Percentage applied radioactivity present as parent and isomer in samples concentrated under light and dark conditions and with and without soil

Equilibrated with soil	No				Yes			
Light/Dark	Light		Dark		Light		Dark	
Test substance	96.3	96.6	97.9	97.8	95.1	91.1	98.9	99.1
Isomer*	1.1	0.8	ND	ND	3.5	6.3	ND	ND
Unknowns	2.5	2.4	2.1	2.1	0.9	2.5	1.0	0.7
Unresolved Background	0.2	0.2	ND	0.2	0.6	0.1	0.1	0.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* This peak was identified by LC-MS as an isomer of the parent test substance
ND = Not detected (or < 0.1%)

The isomer accounted for 1% applied radioactivity (AR) in the $CaCl_2$ only samples that were concentrated under normal lighting conditions. This increased to 4 to 6% AR in the presence of soil extracts (Figure 1). No isomer was seen in any of the samples which were kept in the dark (Figure 2).

Normal laboratory lighting may cause isomerisation of some plant protection products during sample work-up

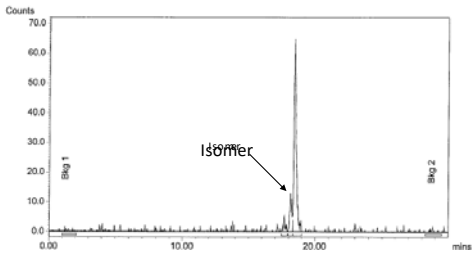


Figure 1: test substance in $CaCl_2$ solution equilibrated with soil and concentrated under normal laboratory lighting

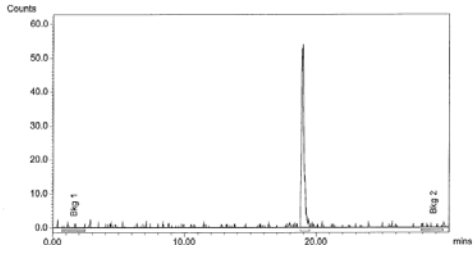


Figure 2: test substance in CaCl2 solution equilibrated with soil and concentrated under dark conditions

Conclusion:

Preparing samples for HPLC analysis under normal laboratory lighting has resulted in isomerisation of this test substance. This effect is more pronounced in the presence of soil. For this and subsequent studies, additional measures, such as using opaque and amber vessels, working under red lighting and wrapping samples with foil, were taken to exclude light during sample work-up which prevented the isomerisation of this test substance.



Contact Joanne Gilbert at infoERS@smithers.com for more information.