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### **CERTIFICATE of ATTENDANCE**

This is to certify that:

#### ANTONIA GARRIDO FRENICH

has attended the

XXI SCIENTIFIC MEETING OF THE SPANISH SOCIETY OF CHROMATOGRAPHY AND RELATED TECHNIQUES

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## NON-TARGETED APPROACHES BASED ON LIQUID CHROMATOGRAPHY COUPLED TO HIGH-RESOLUTION MASS SPECTROMETRY TO MONITOR FLUTRIAFOL DEGRADATION IN GREENHOUSE TOMATO CROPS

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Flutriafol is a systemic triazole fungicide to control diseases of many crops (fruits, vegetables, etc.). This fungicide is extremely persistent in soil ( $DT_{50} > 1100$  days), presenting high potential for mobility. Therefore, it may be found in different types of commercial products [1].

A study was developed to evaluate the natural behaviour and dissipation of flutriafol, including its potentially generated metabolites in tomato. For that, tomato samples, which were previously treated with the commercial product (IMPACT® EVO) at the manufacturer recommended dose, were monitored over a period of 53 days in greenhouse conditions. An ultra high-performance liquid chromatography coupled to Q-Orbitrap mass spectrometry (UHPLC-Q-Orbitrap-MS) was performed by applying targeted and non-targeted approaches (based on suspect screening and unknown analysis). The mobile phase consisted of a water solution with 0.1% formic acid (eluent A) and methanol (eluent B), obtaining a total running time of 14 min. Flutriafol dissipation was adequately fitted to a biphasic kinetic model (R<sup>2</sup> > 0.96 and DT<sub>50</sub> of 8.9 days). Regarding suspect screening, 3 metabolites (dimethyl sulphate, triazole alanine and triazole acetic acid) were tentatively detected from the second day after application of the plant protection product until the end of the study. A semi-quantitative estimation was performed (using the parent compound), finding the highest concentration for triazole acetic acid (at 3.6 µg kg<sup>-1</sup>) the seventh day. Unknown analysis was carried out and 3 new metabolites  $(C_{16}H_{14}F_2N_4,\ C_{19}H_{17}F_2N_5O_2\ \ and\ \ C_{22}H_{23}F_2N_3O_6)\ \ were\ \ tentatively\ \ detected\ \ during\ \ the\ \ study,$ achieving the maximum concentration the last day (at 4.4 μg kg<sup>-1</sup>) for C<sub>22</sub>H<sub>23</sub>F<sub>2</sub>N<sub>3</sub>O<sub>6</sub> metabolite. The results confirms that the proposed analytical method is reliable for flutriafol detection and its metabolites, in tomato, under greenhouse conditions. Despite the fact that flutriafol is a very persistent compound, up 6 metabolites were detected in this study.

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[1] M.E. Hergueta-Castillo, E. López-Rodríguez, R. López-Ruiz, R. Romero-González, A. Garrido Frenich, Food Chemistry, 368 (2022) 130860-130869.