

PESTICIDE RESIDUE RESEARCH GROUP

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Influence of the antioxidant tocopherol on diafenthiuron recoveries using QuEChERS protocol

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INTRODUCTION

In general, the implementation of a multiresidue method in the laboratory assumes that a group of pesticides can present some difficulties for the adequate extraction level as consequence of specific interaction with the matrix or degradation processes. In the EUPT-SM07, where the broccoli was selected as matrix, diafenthiuron was only reported by 9% of the laboratories due to the degradation of this compound through the analytical process. The current study seeks to explain and overcome the detection problems for diafenthiuron in the scope of QuEChERS multiresidue method. Three antioxidant agents such as ascorbic acid, citric acid and tocopherol were evaluated in QuEChERS protocol to intend to increase of diafenthiuron recovery in different matrices. In addition, the stabilization of the compound after recoveries was also evaluated.

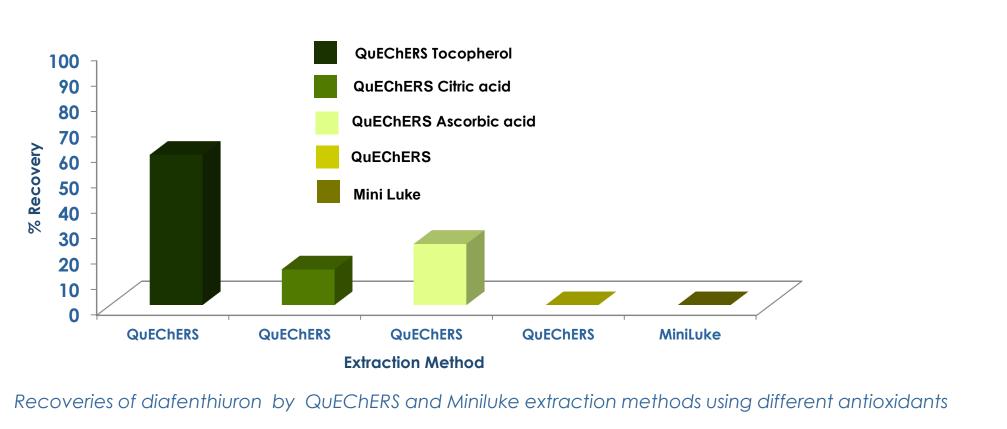
Furthermore, other studies at different pHs (3, 5 and 9) or different solvents were conducted in order to avoid the observed degradation in matrix.

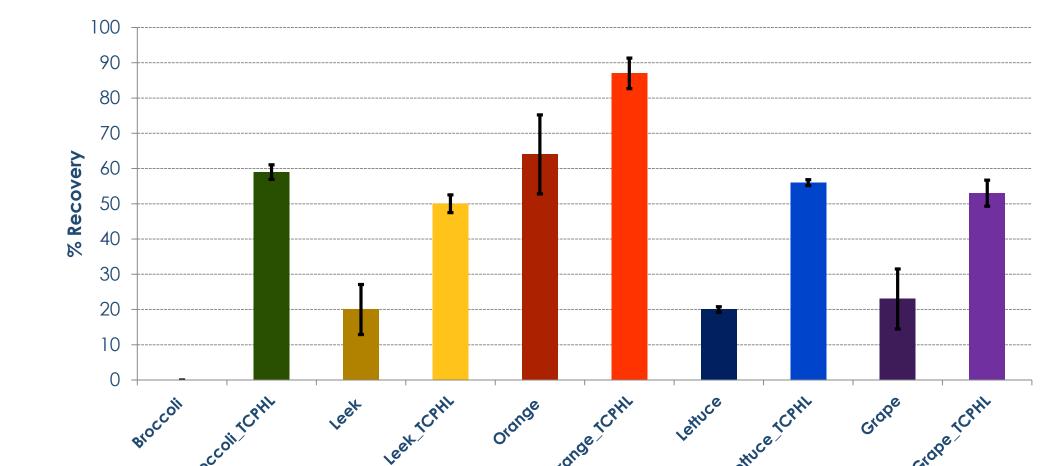
EXPERIMENTAL Chromatography LC-QTOF-MS/MS LC-QqQ-MS Sample handling Agilent 1290 UHPLC system MS parameters MS parameters Column: C8 Agilent. 50mm x 2.1 mm (1.8 µm) Blank matrix > Full-scan ESI (+) mode > ESI mode: positive Mobile phase: Nebulizer: 30 psi Dynamic MRM Agilent 6550 QToF-MS/MS A: Water (0.1 % formic acid) 0.4% Tocopherol in ➤ Gas Temp: 160 °C EtAc > Rt window: 0.8 min B: AcN (5% water, 0.1% formic acid) and MiliQ > Sheath Gas: 350 °C Nebulizer: 45 psi Spiking at appropriate level Cap. Voltage: 4000 V. Gradient ➤ Gas Temp: 120 °C > Frag. Voltage: 360 V > Sheath Gas: 375 °C **Phase** Agilent 6490 QqQ-MS ➤ High Resolution 4 GHz **QuEChERS** protocol Cap. Voltage: 4000 V. Mobil Auto MS/MS Settings -AcN > Frag. Voltage: 380 V $-H_2O$ ➤ Mass range: 50 – 500 m/z Diluted 5 times with AcN > Acquisition rate: 2 spectra/sec 12 10

min

RESULTS





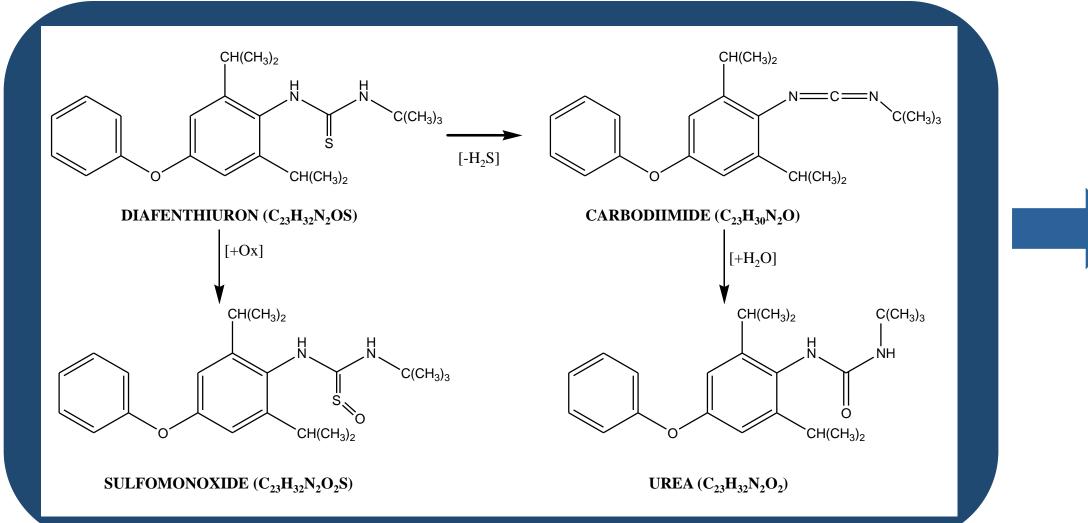


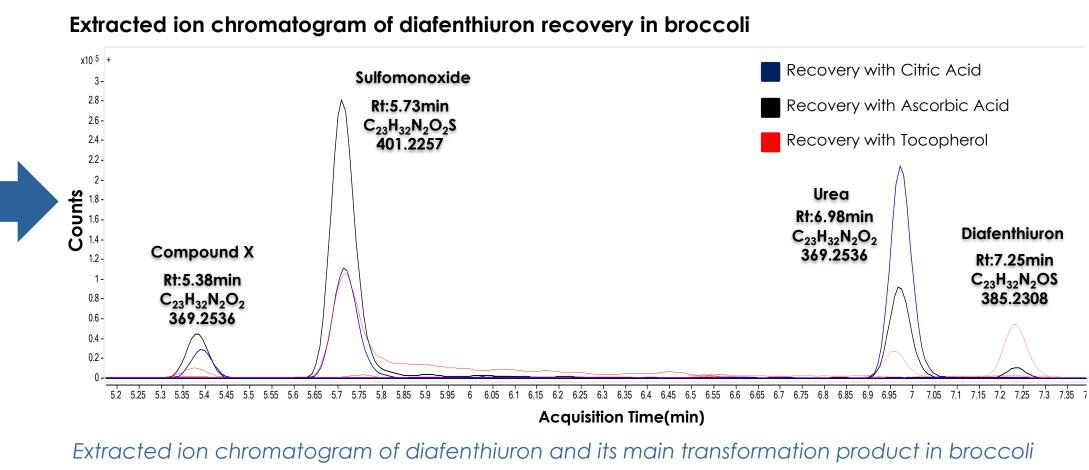
Recovery of diafenthiuron in different matrices

Recoveries of diafenthiuron and RSD(%) with/without TCPHL (Tocopherol) in different matrices

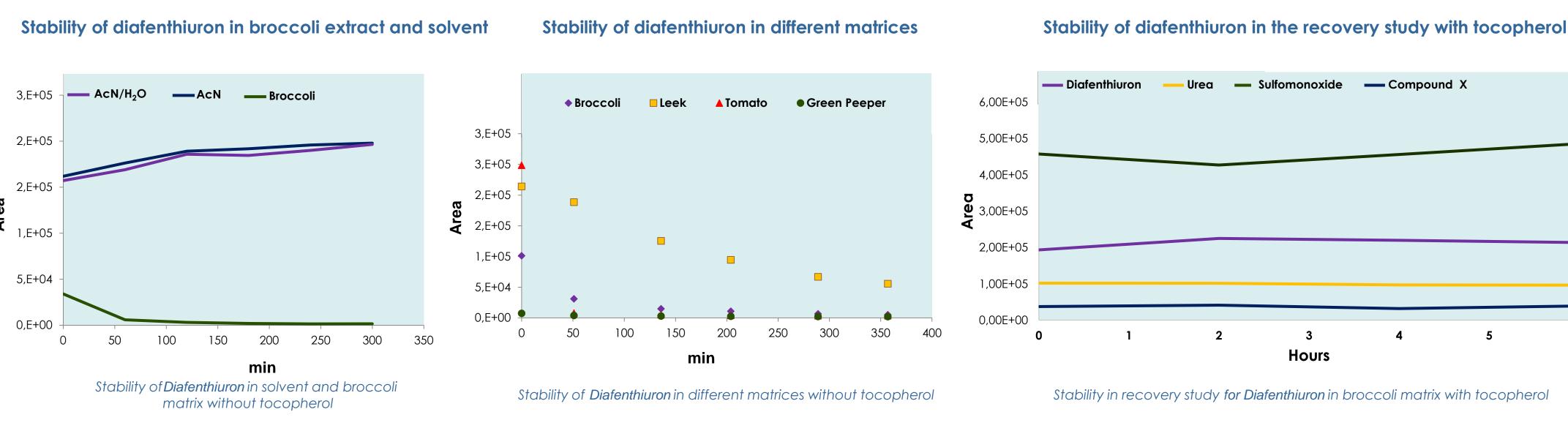
<u>Degradation of diafenthiuron in broccoli</u>

Collision Energy: 0, 10, 20 V

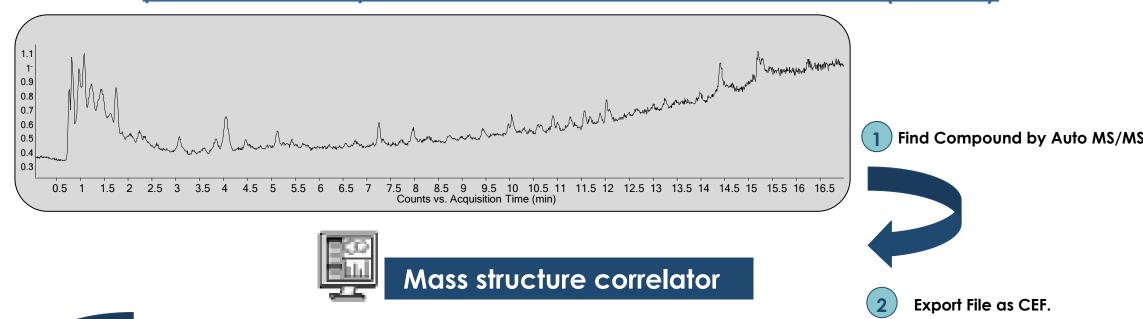


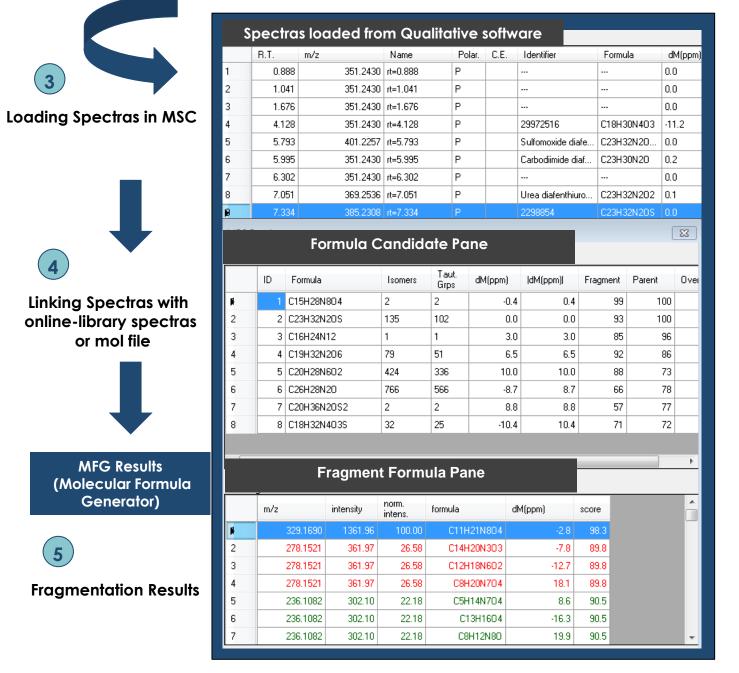


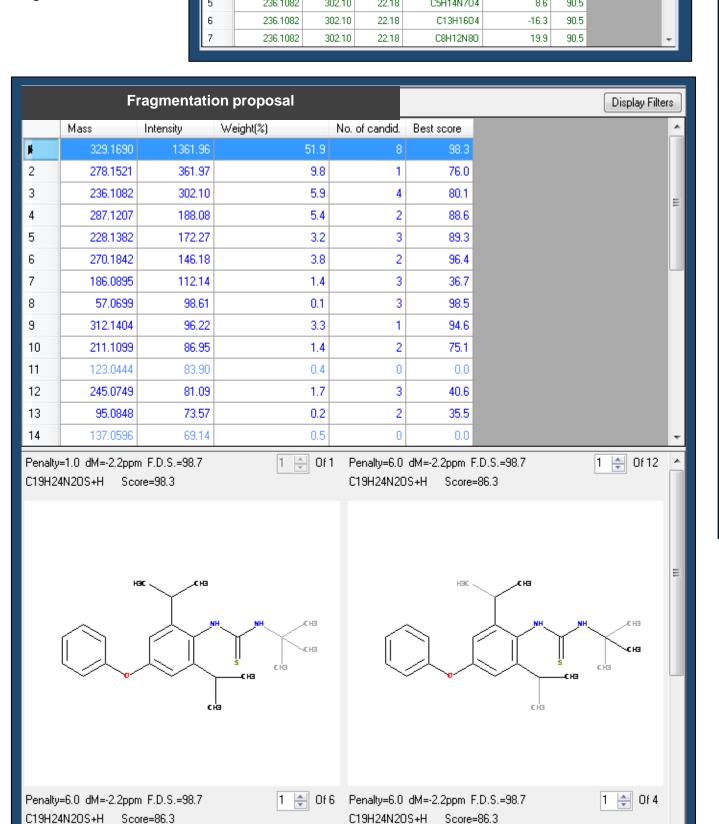
Stability of diafenthiuron

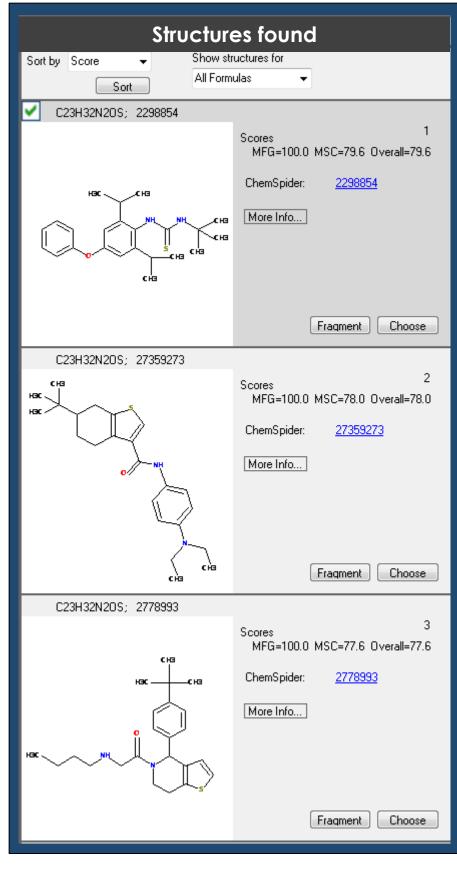


Identification of diafenthiuron and its main transformation products by Mass Structure Correlator (MSC)

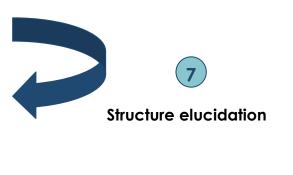








Structures found in on-line library



CONCLUSIONS

- 1. The addition of 0.4% tocopherol allowed obtaining recoveries around 60% with good reproducibility in broccoli matrix.
- 2. The recoveries in the rest of matrices were also increased. RSDs (%) lower than the RSDs in recoveries without tocopherol were achieved.
- 3. The corresponding urea and sulfomonoxide of diafenthiuron were detected in the samples after recoveries. However its carbodiimide was not detected in any evaluated sample.
- 4. After several pHs studies, improvement in stability was not seen at the pHs evaluated therefore, the degradation of diafenthiuron is not related with pH.