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Analytical difficulties for specific pesticide-matrix combinations encountered in the European Union proficiency tests in fruits and vegetables.

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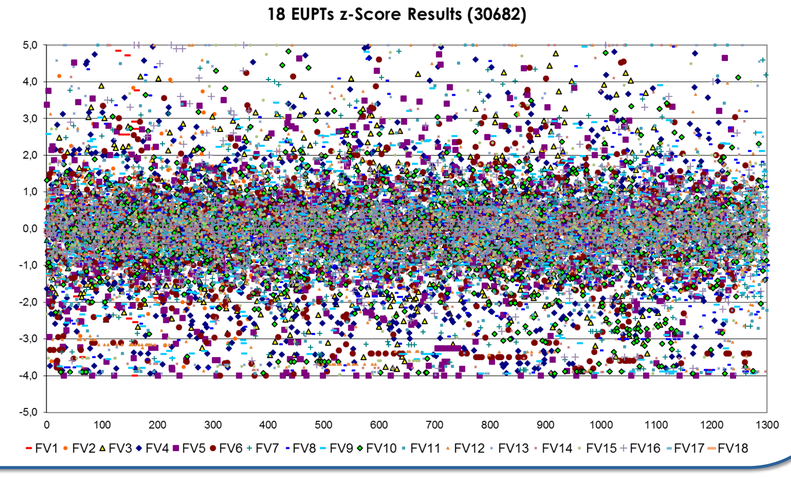
ABSTRACT

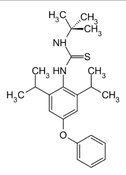
Over the last 21 years, the European Commission´s Directorate-General for Health and Food Safety (DG-SANTE) has organised the European proficiency tests for pesticide residues in fruits and vegetables (EUPT-FV) under the auspices of the European Union Reference Laboratories (EURL). Since 2004 the EURL for Pesticide Residues in Fruits and Vegetables (EURL-FV) in the University of Almería, Spain, has organised them on behalf of DG SANTE. These EUPT-FVs have been carried out on a yearly basis. All official laboratories within the European Union undertaking pesticide residue analyses within the frame of National and EU official controls are obliged to take part in them. From 2009 there are two new proficiency test schemes in fruits and vegetables: one based on screening methods and another one on difficult matrices.

The collection of information during the past years (EUPT-FV06 to EUPT-FV18) involving European official laboratories for pesticide residue control has generated an important database of more than 25 000 pesticide residue results using Multi-residue Methods (MRMs), and has led to very valuable achievements in areas such as sample preparation, data dispersion and statistical evaluation; as well as giving an overview as to the effectiveness of proficiency tests as an important tool in the development of quality control results in laboratories involved in food control. Is from this experience where specific analytical problems have been detected for certain matrix-pesticide combinations. One example is the case of diafenthiuron. That pesticide was present in the EUPT-FV-SM07 test item (broccoli), but only 9% of the laboratories were able to report it. Further investigation was carried out by the EURL-FV and the results thereof will be presented. Another example where the extraction method applied in the proficiency test for a specific compound in a certain matrix influenced the results obtained is the one of chlorothalonil in coriander (EUPT-FV-FH01). In this case, bimodality was observed: one mode with the results obtained by acidifying the sample prior to extraction or using acetone as the extraction solvent, and the other one without acidifying before the extraction using acetonitrile or ethyl acetate based extraction methods.



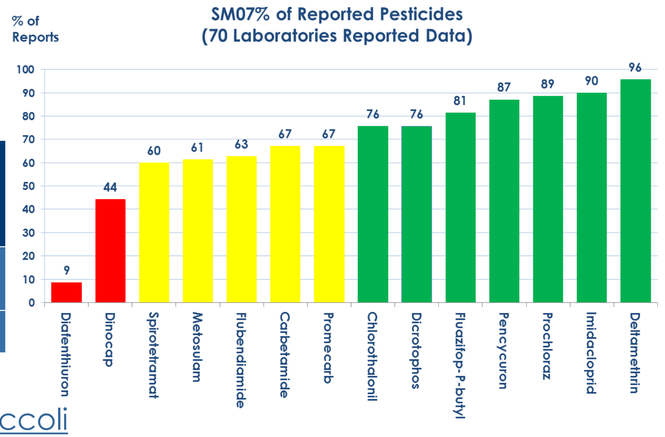
Diafenthiuron in broccoli

EUPT-FV-SM07

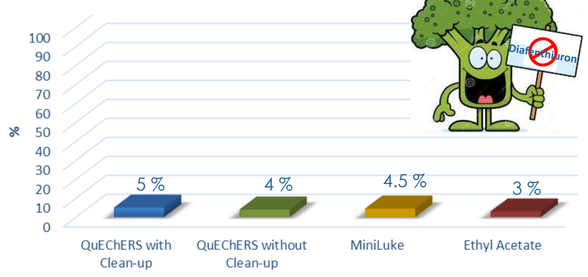


Diafenthiuron was present in EUPT-FV-SM07 test item (broccoli), but only 9% of the laboratories were able to report it.

	Carbetamide	Chlorothalonil	Deltamethrin	Diafenthiuron	Dicrotophos	Dinocap	Fluazifop-P-butyl	Flubendiamide	Imidacloprid	Metosulam	Pencycuron	Prochloraz	Promecarb	Spirotetramat
Total Number of Reported Pesticides	47	53	67	6	53	31	57	44	63	43	61	62	47	42
% of Reported Pesticides	67	76	96	9	76	44	81	63	90	61	87	89	67	60

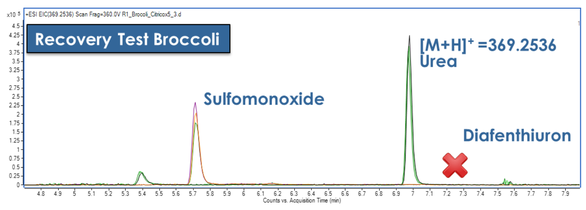


Recovery of diafenthiuron in broccoli 0.050 mg/kg



Recoveries of diafenthiuron by QuEChERS with and without clean-up and Miniluke extraction method.

Recoveries were studied using different extraction methods and in all of them the values were very low.



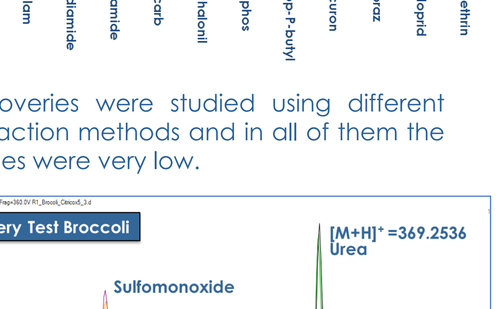
Extracted ion chromatogram of diafenthiuron and its main transformation products in broccoli

Degradation of diafenthiuron in broccoli

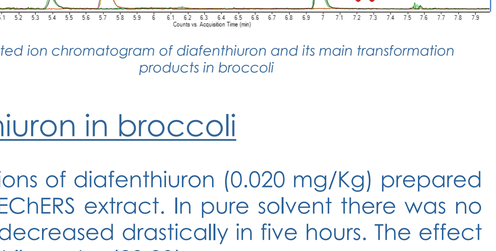
A degradation study was carried out with three standard solutions of diafenthiuron (0.020 mg/Kg) prepared in acetonitrile, in acetonitrile:water (20:80) and in broccoli QuEChERS extract. In pure solvent there was no degradation of the pesticide, but in broccoli extract the area decreased drastically in five hours. The effect was similar when the extract was diluted five times with acetonitrile:water (20:80).

The analysis of a recovery test in broccoli by LC-QTOF-MS revealed the presence of two degradation products of diafenthiuron: the urea and the sulfomonoxide forms.

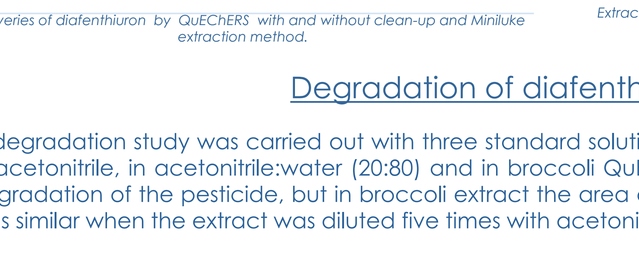
Different strategies were followed in order to achieve good recoveries of diafenthiuron in broccoli. Three antioxidant agents (ascorbic acid, citric acid and tocopherol) were evaluated. Furthermore, other studies at different pHs (3, 5 and 9) or different solvents were conducted in order to avoid the observed degradation in matrix. The results of these studies are shown in **poster PD 047** (Influence of the antioxidant tocopherol on diafenthiuron recoveries using QuEChERS protocol, Sonia Herrera, Ana Lozano, Ana Mª Aguilera del Real, Amadeo R. Fernández-Alba)



*Degradation study of diafenthiuron in acetonitrile (**blue**), in acetonitrile:water (20:80) (**purple**) and in broccoli QuEChERS extract (**green**)*

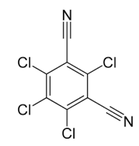


Degradation study of diafenthiuron in broccoli QuEChERS extract 5 times diluted (ACN:Water,20:80)

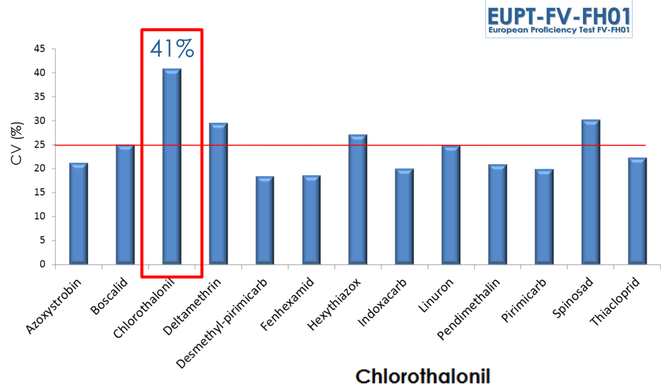


Chlorothalonil in coriander leaves

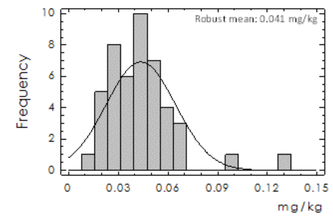
EUPT-FV-FH01



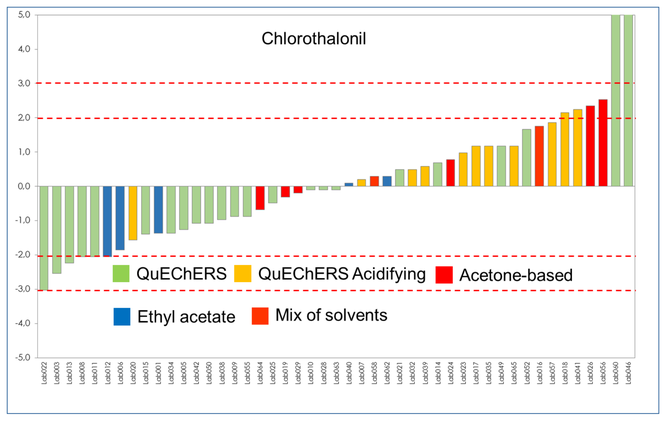
Chlorothalonil was one of the pesticides used for the treatment of coriander leaves for EUPT-FV-FH01. The dispersion of the results for that compound was above the 25% of fit for purpose relative standard deviation used for the evaluation of the results in the EUPTs



The study of the statistical distribution of chlorothalonil results revealed a case of **bimodality**.



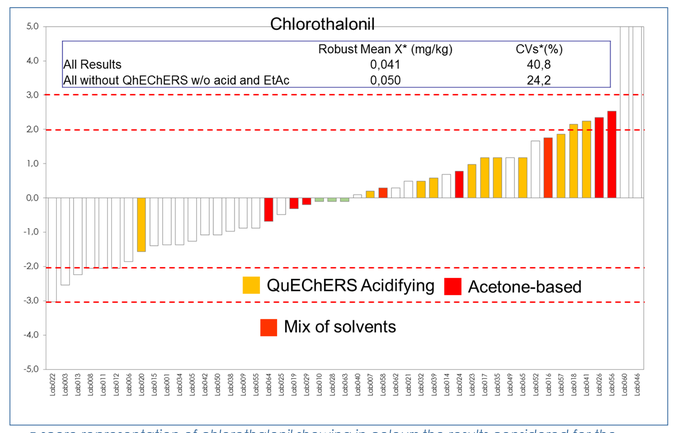
Histogram of residue data from all the laboratories corresponding to chlorothalonil



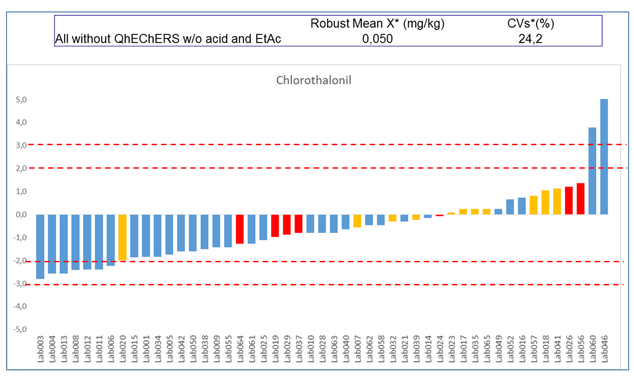
z-score representation of chlorothalonil using all the results for the estimation of the assigned value

The evaluation of the extraction method used by each participant for chlorothalonil showed that the methods based on acetonitrile without acidifying before the extraction or based on ethyl acetate presented underestimation of the concentration.

The assigned value was recalculated using only the results obtained with acetonitrile-based methods acidifying before the extraction or acetone-based methods.



z-score representation of chlorothalonil showing in colours the results considered for the recalculation of the assigned value



Final z-score representation of chlorothalonil using the recalculated assigned value

The new robust mean value for chlorothalonil was 0.050 mg/kg, with a CV(%) of 24.2%. This new assigned value was used for the recalculation of the z-scores.

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