

# Simultaneous Supercritical Fluid Derivatization and Extraction of Pesticide and Plant Growth Regulator in Fruits and Vegetables: An Unsuccessful Project

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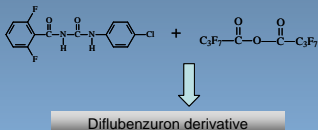
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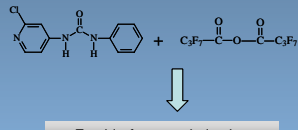
## INTRODUCTION

Simultaneous supercritical fluid derivatization and extraction has been evaluated to be applied in multiresidue analysis of pesticides and plant growth regulators in fruit and vegetables. Six relatively new crop protection products (Diflubenuron, Imidacloprid, Fludioxonil, Cyprodinil, Forchlorfenuron and Nitenpyram), with a group to be derivatised in its molecule, were selected within the framework of Project AGL2005-01418 "Simultaneous Supercritical Fluid Derivatization and Extraction of Pesticide and Plant Growth Regulator Residues in Fruits and Vegetables" supported by Spanish Ministry of Science and Innovation and the EU (FEDER)

### DIFFLUBENZURON

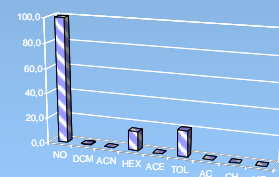


### FORCHLORFENURON



### DERIVATIZATION (VIAL)

- 10 µL pesticide standard solution
- Dryness N<sub>2</sub>
- Derivatization reagent addition 5µL HFBA 5µL Pyridine
- 2h Room temperature
- Evaporate to dryness with N<sub>2</sub>
- Adjust to 1 mL with Toluene
- Clean up with PSA
- GC/MS Determination



Diflubenuron derivative obtained in vial using different solvents (normalized signals/reference no solvent=100)  
 NO = no solvent, DCM = Dichloromethane, ACN = Acetonitrile, HEX = Hexanes, ACE = Ethyl acetate, TOL = Toluene, AC = Acetone, CH = Cyclohexane, ME = Methanol

## OBJECTIVES

- Asses different standard derivatization processes in solvents of Diflubenuron, Imidacloprid, Fludioxonil, Cyprodinil, Forchlorfenuron and Nitenpyram, all pesticides containing an amine secondary group in their molecule
- Evaluate the suitability of the SFE technique as a medium for extraction and derivatization of the studied pesticides and plant growth regulator
- Try the utility of solid phases as support of derivatization reactions in solvent and supercritical carbon dioxide media
- Develop a multiresidue methodology rapid and environmentally friendly for the analysis of non-GC amenable plant protection products in fruits and vegetables by simultaneous SFE-derivatization and GC-MS/ECD

### DERIVATIZATION ON SOLID PHASE

100 mg solid phase  
 10 µL pesticide standard solution

Derivatization reagents addition  
 5µL HFBA  
 5µL Pyridine

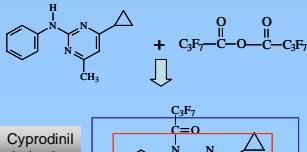
2h Room temperature

Evaporate to dryness with N<sub>2</sub>

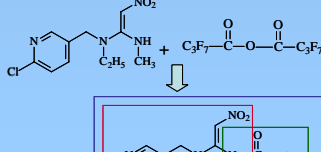
Adjust to 1 mL with Toluene

GC/MS Determination

### CYPRODINIL

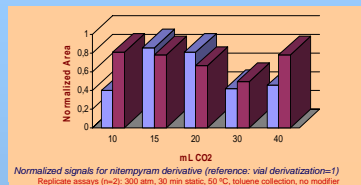
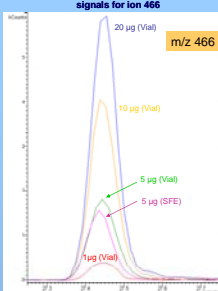


### NITENPYRAM

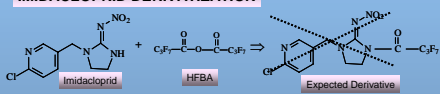


## SUPERCritical FLUID EXTRACTION/DERIVATIZATION

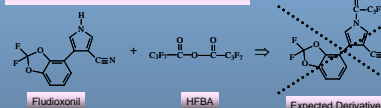
### Nitenpyram derivative GC MS signals for ion 466



### IMIDACLOPRID DERIVATIZATION

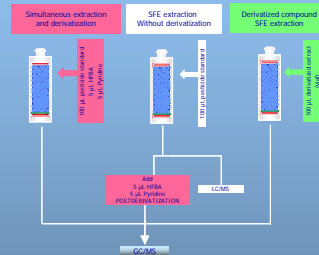


### FLUDIOXONIL DERIVATIZATION



PESTICIDE	ION (m/z)	VIAL DERIVATIZATION	NORMALIZED SIGNALS FOR SELECTED IONS (REFERENCE: VIAL DERIVATIZATION = 100)		
			SFE Derivatized Compound	Simultaneous SFE Extraction and Derivatization	Postderivatization
DIFFLUBENZURON	323	80899	96	19	107
FORCHLORFENURON	324	7937	98	0	12
CYPRODINIL	252	154167	117	45	95

Normalized signals obtained for simultaneous extraction and derivatization of Diflubenuron, Forchlorfenuron and Cyprodinil (300 atm, 50°C, no modifier, 15 mL CO<sub>2</sub>; Reference vial derivatization=100)



METHANOL VOLUME (µL)	NORMALIZED SIGNALS FOR SELECTED IONS (REFERENCE VIAL DERIVATIZATION = 100)		
	ION m/z 323	ION m/z 154	ION m/z 126
200	8	4	9
100	18	9	18
0	118	61	113

Normalized signals obtained for SFE simultaneous extraction and derivatization of Diflubenuron using a layer of 20 mg of hydromatrix placed at the top of extraction cartridge filled with glass beads and assessing different volumes of methanol as modifier

- Best results for conventional derivatization in "vial" for Diflubenuron, Fludioxonil, Forchlorfenuron and Nitenpyram were obtained by means of acylation reactions, after solvent evaporation, using HFBA and pyridine as derivatization reagent and catalyst respectively. However, the reproducibility of the derivatization process was not suitable for quantitative analysis.
- Derivatized compounds of imidacloprid and fludioxonil could not be obtained/characterized along all the study.
- Characteristic m/z ions of the GC/MS spectra (EI, 70 eV) obtained for the derivatised compounds are: 323 (100%, molecular ion) and 126 (80%) for Diflubenuron; 324 (70%, molecular ion) and 155 (100%) for Forchlorfenuron; 252 (100%, molecular ion) for Cyprodinil; and 466 (40%, molecular ion) and 210 (100%) for Nitenpyram.
- Simultaneous supercritical carbon dioxide derivatization/extraction of Diflubenuron, Fludioxonil, Forchlorfenuron and Nitenpyram was achieved on glass beads and on some drying agents, but in all cases recovery values were scarcely reproducible. Best results were obtained without using modifier, and the addition of water and other polar solvent lead to obtain null recoveries.
- Finally, spiked blank vegetable samples (tomato, zucchini and watermelon) were prepared for simultaneous SFE-derivatization by using different solid phases (hydromatrix, magnesium sulfate, celite, florisil and others) obtaining in all cases null recoveries under all the assessed SFE conditions

## ACKNOWLEDGMENTS

This study was supported by Spanish Ministry of Science and Innovation (AGL2005-01418) and EU

