

# Development and optimization of a new extraction of pesticides from soil using direct-immersion SPME LC-Tips followed by GC-MS/MS

R. S. Carvalho<sup>1</sup>, J. Brinco<sup>1</sup>, M. Gomes da Silva<sup>2</sup>, A. B. Ribeiro<sup>1</sup>, P. Guedes<sup>1</sup>, E. P. Mateus<sup>1</sup>

<sup>1</sup>CENSE – Center for Environmental and Sustainability Research & CHANGE - Global Change and Sustainability Institute, NOVA School of Science and Technology, NOVA University Lisbon, 2829-516 Caparica, Portugal. Email: rsi.carvalho@campus.fct.unl.pt

<sup>2</sup>LAQV/REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, NOVA University Lisbon, 2829-516, Caparica, Portugal



## Introduction

Modern agriculture requires the use of pesticides in order to ensure crop yields and prevent losses and disease. Since pesticides contaminate environmental systems, there is a need to develop them qualitatively and quantitatively. This work describes the development and optimization of a new methodology for extracting pesticides from soil, which is potentially greener and simpler than the ones currently used. It employs a new Solid Phase MicroExtraction (SPME) configuration, where the fiber is held on a micropipette tip, followed by Gas Chromatography-Tandem Mass Spectrometry (GC-MS/MS) analysis. This SPME configuration was developed specifically for DI-SPME (Direct Immersion).

## Chromatographic Conditions

Instrument: Bruker Scion 456 GC-MS/MS (TQ)

Inlet mode: PTV

Carrier Gas: Helium, 0.7mL/min

Column: ZB-5ms (20m x 0.18 mm i.d., 0,18µm df)

Column: 50° C for 3 min, then 20° C/min to 250° C, then 4° C/min to 310° C, held for 2 min

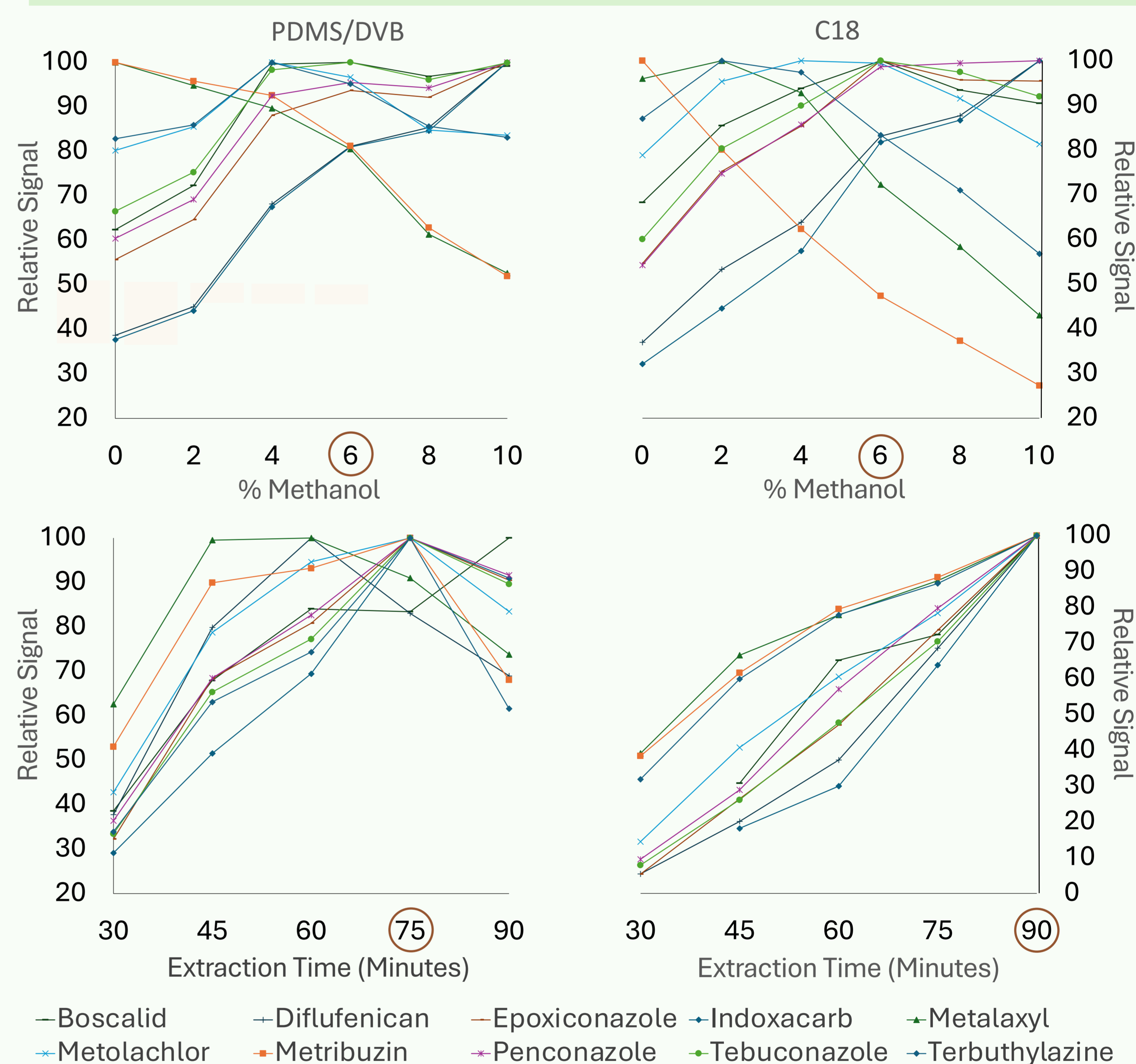
## Method Development and Optimization

### 1. Design of Experiments (DoE) - Plackett-Burman

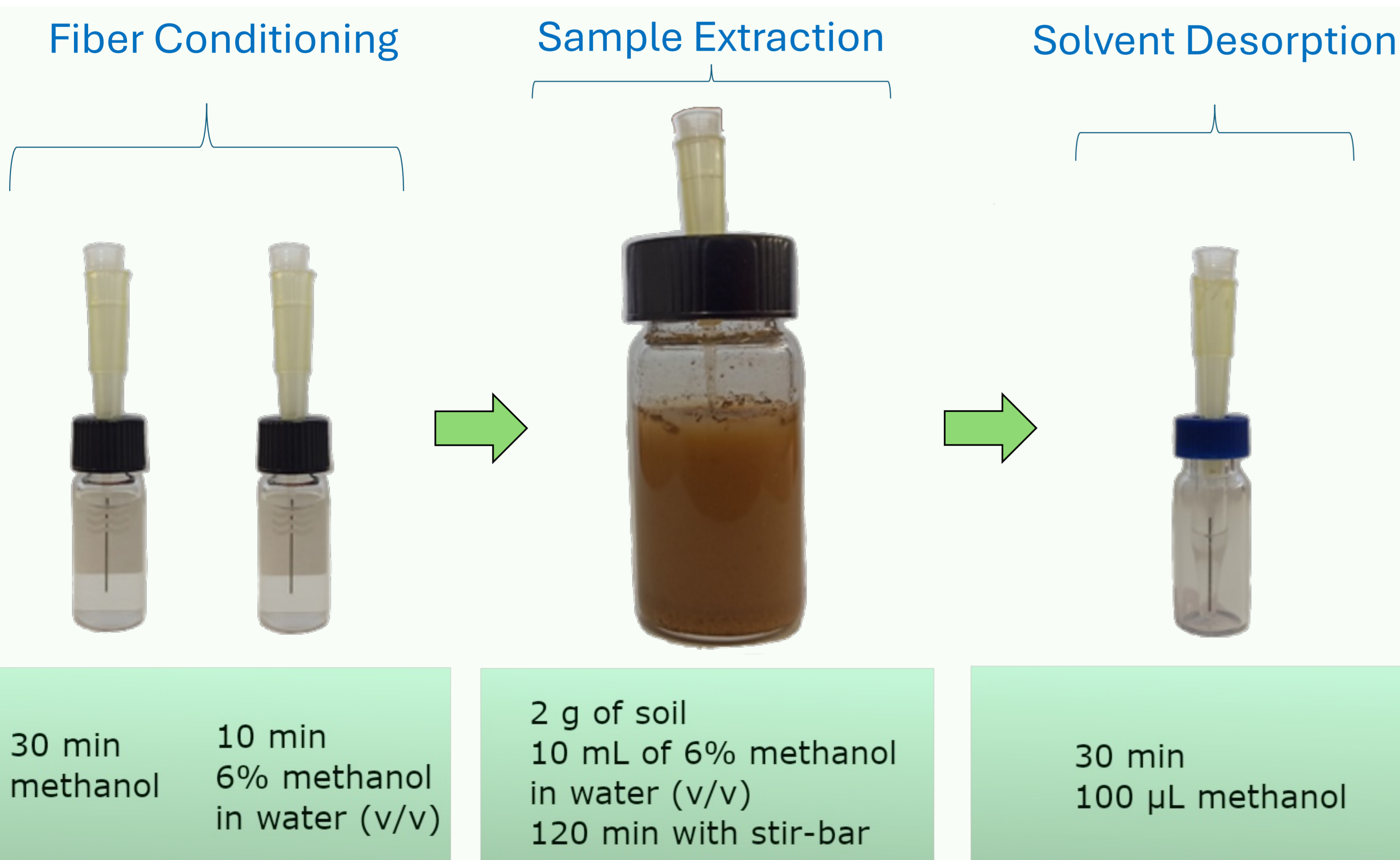
Plackett-Burman design was used to analyze **10 variables**, each at two levels, performing **12 experiments** in triplicate. **Ten pesticides** (Boscalid, Diflufenican, Epoxiconazole, Indoxacarb, Metalaxyl, Metolachlor, Metribuzin, Penconazole, Tebuconazole and Terbutylazine) and an **agricultural soil** (sandy-loam texture; 3% of organic matter) were used. The soil was spiked, giving a final concentration of **50 µg/kg for each pesticide**.

Variables Studied		Results
Use of Buffer	Yes or No	No
Concentration of Analyte Protectants [1]	250 or 500 mg L <sup>-1</sup>	500 mg L <sup>-1</sup>
Extraction Time	30 or 60 minutes	60 minutes
Fiber Coating	PDMS/DVB or C18	Analyte Dependet
Percentage of Organic Solvent	1 or 10%	Inconclusive
Retro-Extraction Time	10 or 30 minutes	30 minutes
Use of Salts	Yes or No	No
Type of Organic Solvent	MeCN or MeOH	MeOH
Use of Ultrasounds	Yes or No	No
Volume of Solvent	10 or 12 mL	10 mL

### 2. Optimizing % of Organic Solvent and Extraction Time



## Final Method



## Validation Results

Fiber Chemistry	C18	PDMS/DVB
R <sup>2</sup>	0.92 - 0.99	0.94 - 0.98
LoD	0.1 – 10 µg/kg	0.01 – 10 µg/kg
LoQ	1 – 20 µg/kg	0.1 – 20 µg/kg

## Conclusion

This work reports for the first time the use of direct-immersion SPME for the extraction of pesticides from soil. This new method generates very clean extracts and high concentration factors. It also produces little toxic waste per sample and appears to be very cost-effective. However, it suffers from poor repeatability, which must be mitigated by the use of an isotopically-labeled internal standard.

### Reference

[1] Anastassiades, M., Mastovska, K. & Lehotay, S. Evaluation of Analyte Protectants to Improve Gas Chromatographic Analysis of Pesticides. *J. Chromatogr. A* 1015, 163–184 (2003).

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