Centro de Investigação de Montanha CIMO — FROM NATURE TO PRODUCTS, TOWARDS SUSTAINABILITY

LSRE-LCM — SHAKING THE PRESENT SHAPING THE FUTURE

RAPID DETERMINATION OF SOME OF THE MOST USED PESTICIDES IN NORTHEAST PORTUGAL AS EMERGING CONTAMINANTS IN RIVERS BY SPME/GC-MS

A. Oliveira[1], R. Ben Hmida[1], A. Ribeiro[1,2], P. Brito[1], A. Queiroz[1,*]

[1]CIMO, Centro de Investigação de Montanha, Instituto Politécnico de Bragança
Campus de Santa Apolónia, 5300-253 Bragança, Portugal
*e-mail: amqueiroz@ipb.pt

[2] LA LSRE-LCM, Laboratory of Separation and Reaction Engineering, University of Porto
Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal

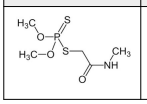
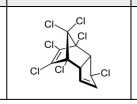
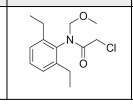
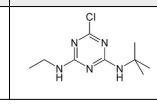
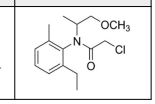
Case Study: Pesticides as Emerging Contaminants

POLLUTANTS
- Contaminants present in several environmental sources

EMERGING POLLUTANTS
- Only detected due to new developments in analytical instrumental techniques and methods
- Only considered pollutants very recently

EMERGING MICRO-POLLUTANTS: *Present in very low concentrations (µg/L, ng/L or below)*
- Persistent Organic Pollutants (POP's)
- Endocrine Disruptor Compounds (EDC's);
- Pharmaceutical and Personal Care Products (PPCP's)
- Pesticides

SOME OF THE MOST USED PESTICIDES IN NORTHEAST PORTUGAL AND TUNISIA

INSECTICIDES		HERBICIDES		
Dimethoate	Heptachlor	Alachlor	Terbuthylazine	Metolachlor
				

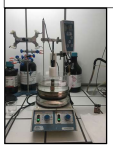
EXPERIMENTAL METHODOLOGY

1. ANALYTICAL METHOD DEVELOPMENT

1.1 GC-MS optimization

- Temperatures
- Split ratio
- FullScan/SIM

1.2 SPME optimization



- Extraction time
- pH value
- Ionic strength
- Extraction temperature

1.3 Statistical Validation

- Calibration curves/linearity
- Limit of detection
- Limit of quantification
- Repeatability
- Reproducibility (results not presented)

2. IMPLEMENTATION OF METHODOLOGY

2.1 Analysis of real samples


Sabor river


Onor river


Fervença river

Experimental Results and Discussion

1.1 GC-MS optimization

Oven temperature Program "Method 1"

Rate	Temperature (°C)	Hold Time (min)
-	50	1
25	100	-
10	300	5

Peak#	Name	Ret.Time (min)
1	Dimethoate	12.813
2	Terbuthylazine	13.587
3	Alachlor	15.786
4	Heptachlor	15.857
5	Metolachlor	16.838

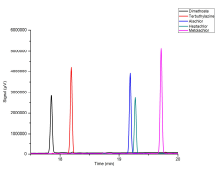
Oven temperature Program "Method 2"

Rate	Temperature (°C)	Hold Time (min)
-	80	2
15	190	4
10	290	2

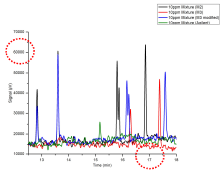
Oven temperature Program "Method 3"

Rate	Temperature (°C)	Hold Time (min)
-	120	2
15	190	4
10	227	1

Method 1 / Split 1:50 / Fullscan
1000 ppm

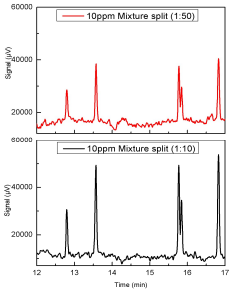


Method 2 / Split 1:50 / Fullscan
10 ppm

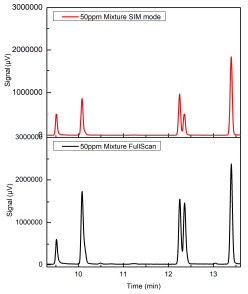


Method 3 has better signal and the shortest run time
Split 1:10 has a better signal
FullScan mode allows higher detector signal than SIM mode

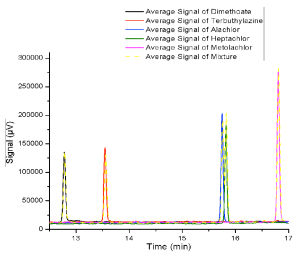
- **Split values / Splitless**

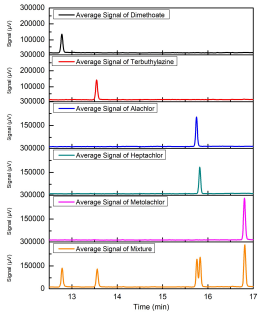


- **SIM / FullScan MS modes**



- **Identification / Repeatability using SIM mode**





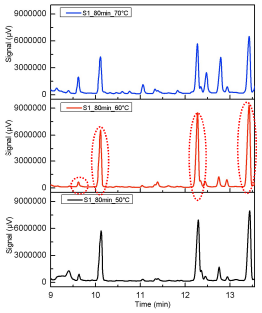
Pesticide	Retention Time (min)	Relative Standard Deviation (%)
Dimethoate	12.780	7.47
Terbuthylazine	13.546	7.06
Alachlor	15.749	5.12
Heptachlor	15.821	3.42
Metolachlor	16.806	2.46

RSD values are between 2.5 and 7.5%.

1.2 SPME optimization (PDMS/DVB fiber)

Extraction time	80 min
Extraction temperature	60°C
pH	2
NaCl	10%
Desorption time	4 min
Desorption temperature	250°C
agitation	1000 rpm

SPME optimized method
Right Figure: Example for extraction temperature selection (between 50 °C, 60 °C and 70 °C)



1.3 Statistical Validation

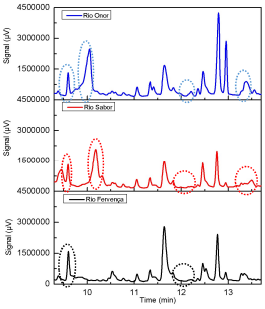
Pesticide	Linear range (ppb)	$a \pm t.S_a$	$b \pm t.S_b$	Coefficient of determination (R^2)	Limit of Detection (ppb)	Limit of Quantification (ppb)
Dimethoate	25 - 75	1458830 ± 139412	15620 ± 2639	0.991	6.1	20.2
Heptachlor	25 - 75	-543942 ± 297762	30679 ± 5637	0.990	6.6	22.0
Alachlor	10 - 60	1090704 ± 2362839	408635 ± 57562	0.994	5.3	17.6
Metolachlor	10 - 60	2659877 ± 3521017	533439 ± 85776	0.992	6.0	20.1
Terbuthylazine	10 - 60	130279 ± 1580494	342397 ± 38503	0.996	4.2	14.1

Linearity of the SPME/GC-MS method was confirmed ($R^2 \geq 0.99$)

2.1 Analysis of real samples

Concentration (ppb)	Dimethoate	Terbuthylazine	Alachlor	Heptachlor	Metolachlor
Onor river	133.7	26.6	D/NQ	22.4	D/NQ
Sabor river	58.7	44.9	D/NQ	D/NQ	D/NQ
Fervença river	201.0	ND/NQ	D/NQ	D/NQ	D/NQ

D/NQ : Detected, not quantified
ND/NQ : Not detected, not quantified
At least one pesticide was quantified in all river samples



Conclusions & Future Work

- SPME/GC-MS methodology validated.
- GC-MS optimized conditions: Temperature program 3; split 1:10; FullScan mode; Repeatability values under 7.5%.
- SPME optimized conditions: PDMS/DVB fiber; Extraction during 40 min at 60 ºC and 1000 rpm; sample with pH=2 and 10% NaCl; Desorption during 4 min at 250 ºC.
- Study of SPME using CAR-PDMS fiber.
- Study of GC-MS analysis using the SIM mode of analysis.

REFERENCES

[1] "Lista de pesticidas a pesquisar em água destinada ao consumo humano, Triénio 2019-2021", Ao abrigo do disposto no Decreto-Lei nº 306/2007, de 27 de agosto, alterado pelo Decreto-Lei nº 152/2017, de 7 de dezembro. Direção Geral de alimentação e veterinária. República Portuguesa. Lisboa 2018.

[2] *"Projet d´intensification de l´agriculture irriguée en Tunisie (PIAIT)"*. Ministère de l'Agriculture, des Ressources Hydrauliques et de la Pêche (MARHP). Direction Générale du Génie Rural et de l'Exploitation des Eaux (DGGREE). République de Tunisie. Version définitive, Mars 2018.

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