Supplementary Material

Synthesis of sol-gel poly(ethyleneglycol) coated foams for the microextraction of multiclass pesticides from apple juice samples

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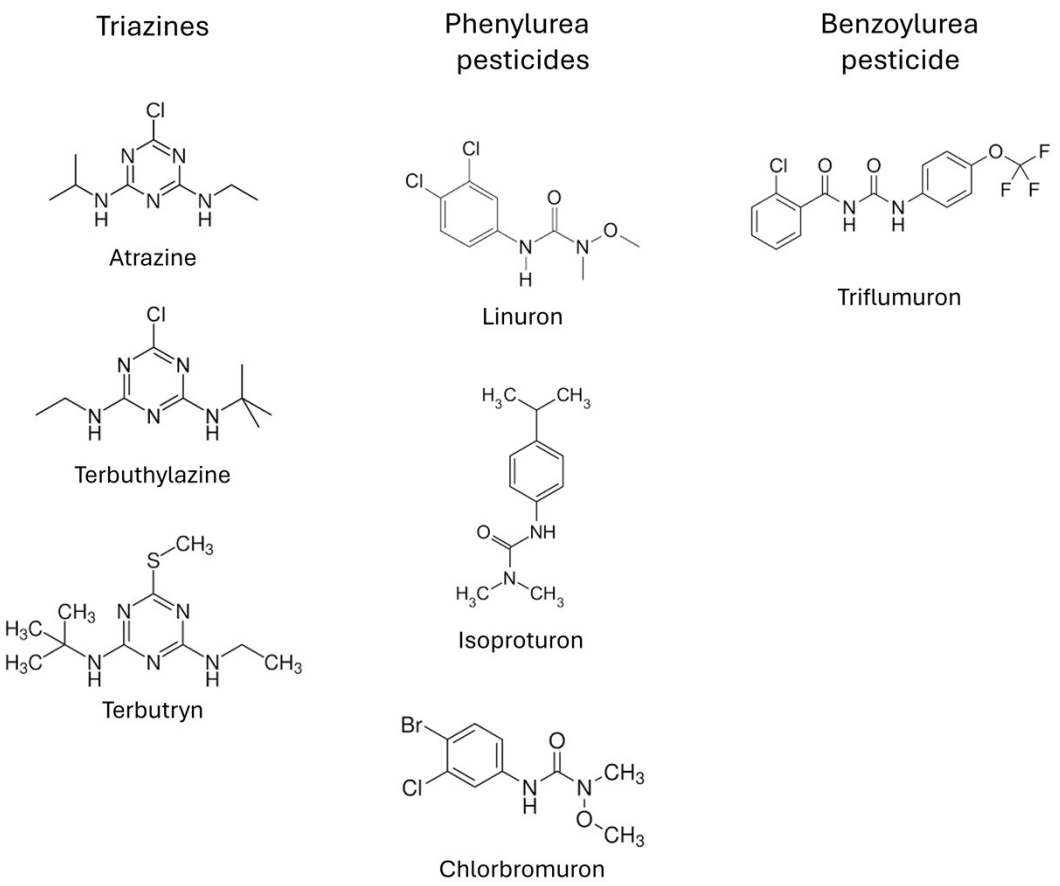

Figure S1. Chemical structures of the studied pesticides.

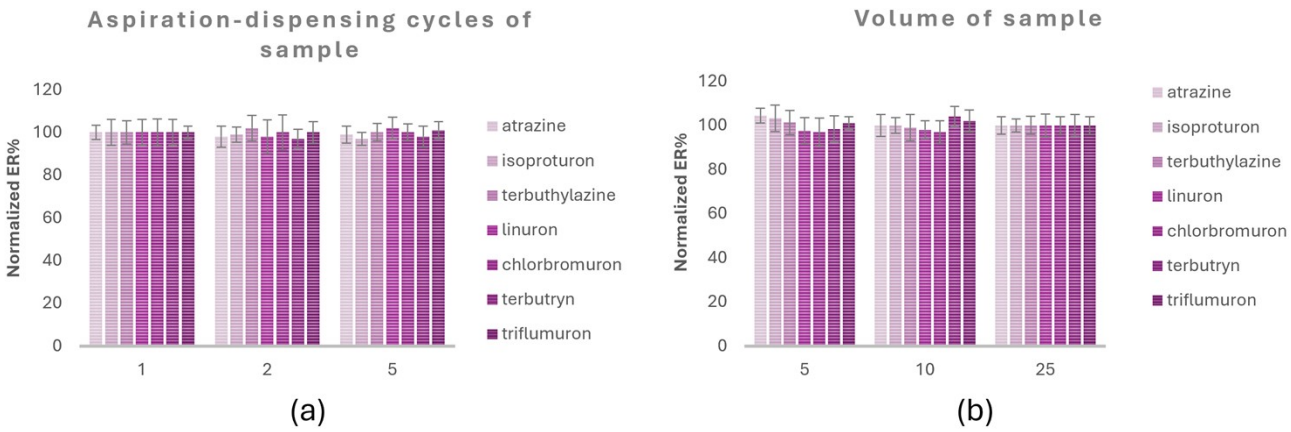

Figure S2. Normalized ER% (average of two repetitions ± standard deviation) for the investigation of the effect of (a) aspiration-dispensing cycles of the same aliquot of the sample, and (b) volume of sample on the performance of the FIS-SPE protocol

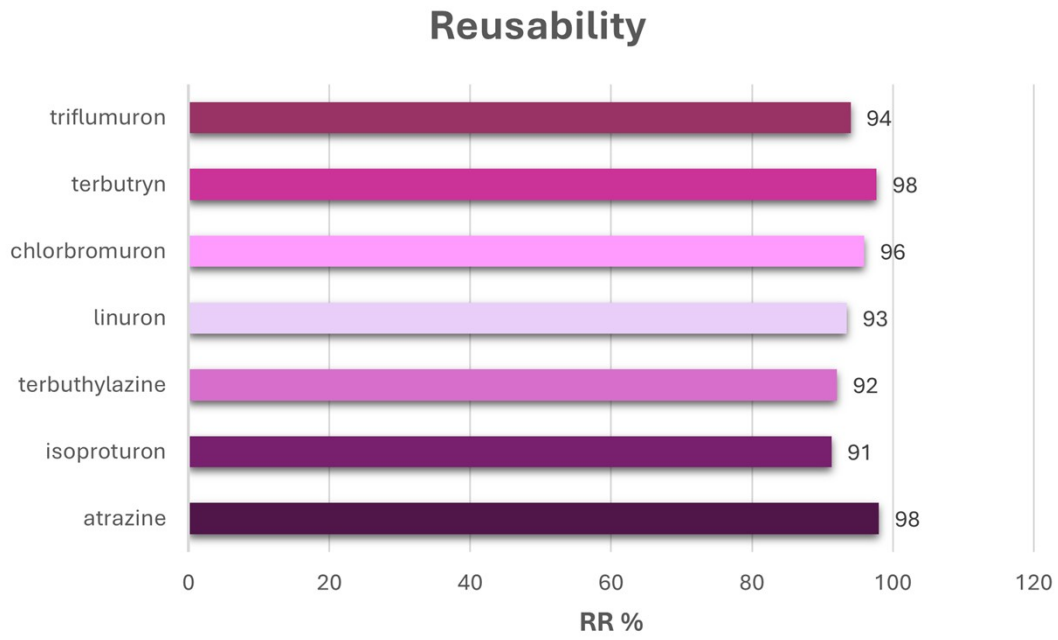

Figure S3. Evaluation of reusability of the sol-gel CW 20 M coated foam, expressed as relative recovery (RR%) after thirty-five consecutive extractions.

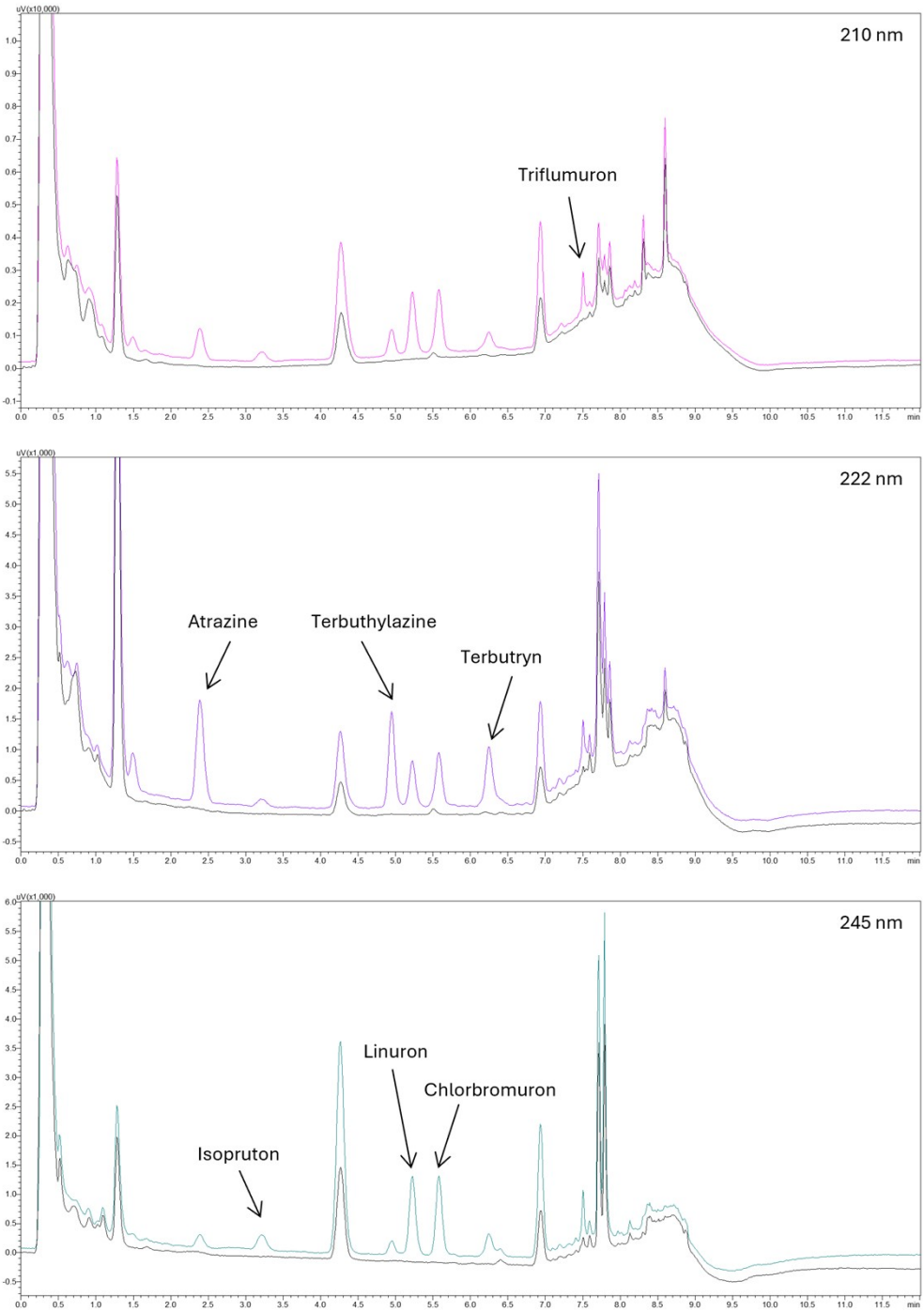

Figure S4. Chromatograms of the analysis of blank (black line) and spiked (colored line) apple juice samples (50 ng mL^{-1}) through the developed method at the optimum wavelength for each analyte.

Table S1. HPLC gradient program of the mobile phase.

Time (min)	Composition	
	A (Water)	**B (ACN)**
0.00	75	25
2.50	75	25
4.50	65	35
5.50	65	35
6.00	60	40
8.00	10	90
9.00	75	25
12.00	75	25

Table S2. Trueness and precision of the proposed FIS-SPE-HPLC-DAD method.

Analyte	Added ($ng\ mL^{-1}$)	Intra-Day (n=3)			Inter-Day (n=3 × 3)		
		Found ($ng\ mL^{-1}$)	RSD%	RR%	Found ($ng\ mL^{-1}$)	RSD%	RR%
Atrazine	25.0	27.1 ± 1.0	4	108	24.5 ± 1.1	4	98
	250.0	267 ± 17	6	107	229 ± 25	11	92
Isoproturon	25.0	21.7 ± 1.6	8	87	25.3 ± 1.9	7	101
	250.0	279 ± 29	10	112	226 ± 21	9	90
Terbuthylazine	25.0	23.3 ± 2.0	8	93	26.6 ± 1.9	7	106
	250.0	276 ± 21	8	110	230 ± 28	12	92
Linuron	25.0	28.1 ± 2.4	8	112	24.3 ± 2.8	12	97
	250.0	290 ± 26	9	116	231 ± 25	11	92
Chlorbromuron	25.0	27.4 ± 2.2	8	110	25.1 ± 2.6	11	100
	250.0	289 ± 27	9	116	238 ± 22	9	95
Terbutryn	25.0	26.8 ± 1.5	6	107	26.3 ± 3.1	12	105
	250.0	235 ± 10	4	94	256 ± 14	5	102
Triflumuron	25.0	23.1 ± 1.9	8	92	26.4 ± 2.4	9	106
	250.0	240 ± 17	7	96	251 ± 22	9	100

Table S3. Robustness evaluation of the FIS-SPE-HPLC-DAD method.

Parameter (optimum value)	Variations	Relative recovery %						
		Atrazine	**Isopruton**	**Terbuthylazine**	**Linuron**	**Chlorbromuron**	**Terbutryn**	**Triflumuron**
Vsample (25 mL)	**26 mL**	98	99	98	100	98	99	99
	24 mL	98	97	96	98	102	98	97
Veluent (500 µL)	**525 µL**	102	98	100	97	99	102	102
	475 µL	97	96	98	105	97	98	97
Foam height (1.5 cm)	**1.6 cm**	96	97	97	104	105	96	95
	1.4 cm	101	101	101	103	96	101	100

Table S4. ComplexGAPI attributes and their justification.

#	ComplexGAPI Attribute	Justification	Color
1	Collection	At-line	Yellow
2	Preservation	None	Green
3	Transport	Required	Red
4	Storage	Under normal conditions	Yellow
5	Type of method	Extraction required	Red
6	Scale of extraction	Miniaturized FIS-SPE	Yellow
7	Solvents/reagents used	Non-green solvents/reagents used	Red
8	Additional treatment	None	Green
9	Solvents/reagents amount	<10 mL	Green
10	Health hazard	Moderately toxic; NFPA: 2-3	Yellow
11	Safety hazard	Highest NFPA flammability or instability score: 2-3	Yellow
12	Energy	≤ 1.5 kWh per sample	Yellow
13	Occupational hazard	Hermetic sealing of analytical process	Green
14	Waste	>10 mL	Red
15	Waste treatment	No treatment	Red
	Yield and conditions		
I	Yield	>89%	Green
II	Temperature/time	Heating > 1 h	Red
III	Number of green economy rules met	5-6	Green

#	ComplexGAPI Attribute	Justification	Color
IV_a	Health hazard	Moderately toxic; NFPA: 2-3	Yellow
IV_b	Safety hazard	Highest NFPA flammability or instability score: 2-3	Yellow
V_a	Technical set	Common setup	Green
V_b	Energy	≤ 0.1 kWh per sample	Green
V_c	Occupational hazard	Hermetization of the analytical process	Green
VI_a	End products workup, purification	None/simple process	Green
VI_b	Purity	>98%	Green
-	**E-factor**	1	-

Table S5. BAGI attributes and their justification.

#	BAGI Attribute	Justification	Points	Color
1	Type of Analysis	Quantitative and confirmatory (HPLC-DAD)	10	Dark blue
2	Multi- or single-element analysis	Multi-element analysis for 2-15 compounds of different classes	7.5	Blue
3	Analytical technique	HPLC-DAD: Simple instrumentation available in most QC labs	7.5	Blue
4	Simultaneous sample preparation	1	2.5	White
5	Sample preparation	FIS-SPE Miniaturized sample preparation	5.0	Light blue
6	Samples per h	2-4 (12 min analysis time + 1 min sample preparation)	5.0	Light blue
7	Reagents and materials	Sol-gel foam needs to be synthesized in the lab (simple procedure, common instrumentation)	5.0	Light blue
8	Preconcentration	No preconcentration required	10	Dark blue
9	Degree of automation	Semi-automation (HPLC autosampler)	7.5	Blue
10	Amount of sample	25 mL of juice	7.5	Blue

Table S6. Determination of pesticides in fruit juice samples through the proposed method (average value ± standard deviation).

Analytes	Added (ng mL^{-1})	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
		Found (ng mL^{-1})	RR%	Found (ng mL^{-1})	RR %	Found (ng mL^{-1})	RR%	Found (ng mL^{-1})	RR%	Found (ng mL^{-1})	RR %	Found (ng mL^{-1})	RR%
Atrazine	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-
	25.0	27.4 ± 2.4	109.5	26.2 ± 1.2	104.9	24.4 ± 2.3	97.8	25.4 ± 1.0	101.6	29.2 ± 2.3	116.7	27.3 ± 0.5	109.4
Isoproturon	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-
	25.0	24.2 ± 1.2	96.6	23.0 ± 2.5	92.0	28.7 ± 2.8	114.8	21.2 ± 1.2	85.0	27.7 ± 1.2	110.9	23.8 ± 1.3	95.1
Terbuthylazine	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-
	25.0	23.7 ± 1.9	94.7	25.3 ± 1.4	101.3	22.0 ± 1.0	88.2	21.1 ± 0.3	84.8	29.1 ± 0.7	116.6	23.6 ± 0.8	94.3
Linuron	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-
	25.0	27.0 ± 2.3	108.0	29.1 ± 1.4	116.4	29.5 ± 0.5	118.0	25.9 ± 1.2	103.8	29.4 ± 1.5	117.6	25.5 ± 0.9	102.0
Chlorbromuron	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-
	25.0	26.8 ± 2.6	107.3	29.4 ± 2.9	117.6	29.4 ± 3.0	117.6	28.6 ± 1.0	114.3	28.2 ± 2.9	112.7	23.7 ± 1.4	94.7
Terbutryn	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-
	25.0	26.3 ± 1.8	105.1	29.1 ± 3.2	116.3	27.5 ± 0.9	110.2	23.5 ± 2.2	93.9	23.8 ± 0.7	95.1	23.9 ± 0.7	95.7

Analytes	Added (ng mL^{-1})	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
		Found (ng mL^{-1})	RR%	Found (ng mL^{-1})	RR %	Found (ng mL^{-1})	RR%	Found (ng mL^{-1})	RR%	Found (ng mL^{-1})	RR %	Found (ng mL^{-1})	RR%
Triflumuron	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-	< LOD	-
	25.0	22.5 ± 3.5	90.1	21.8 ± 1.0	87.4	24.0 ± 0.3	95.8	28.6 ± 1.4	114.3	21.4 ± 1.5	85.7	22.4 ± 2.0	89.8