

SUPPLEMENTARY MATERIALS

Development and Validation of a Gas Chromatography-Mass Spectrometry Method for Determining Acaricides in Bee Pollen

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Table S1. Evaluation of the extraction efficiency (recovery percentages) and the matrix effect when employing 10 mL of different solvent mixtures with spiked blank bee pollen samples at medium level (100 µg kg⁻¹) (mean ± %RSD; three replicates that were injected in triplicate).

Acaricide	ACN/AcOH (99:1 ; v/v)		ACN/TEA (98:2 ; v/v)		ACN/Hx (50:50 ; v/v)		AcOEt/Cx (20:80 ; v/v)		AcOEt/Cx (50:50 ; v/v)	
	EE	ME	EE	ME	EE	ME	EE	ME	EE	ME
Atrazine	10	16	111	48	98	1	80	-2	85	-2
Chlorpyrifos		-	51	-21	35	-32	-	-	-	-
Chlorfenvinphos	11	3	56	-2	64	-11	99	-10	108	-8
α-Endosulfan	7	-4	53	-29	33	-28	89	-30	90	-15
Bromopropylate	15	5	54	50	35	31	85	15	104	7
Coumaphos	12	15	86	77	44	83	92	20	98	10
τ-Fluvalinate	15	1	38	43	45	-13	101	14	109	16

ACN, acetonitrile; AcOEt, ethyl acetate; AcOH, acetic acid; Cx, cyclohexane; EE, extraction efficiency; Hx, hexane; ME, matrix effect; TEA, triethylamine.

Table S2. Summary of precision studies (minimum and maximum %RSD values) for the determination of acaricides in spiked blank bee pollen samples.

	Spiking Level	Multifloral Bee Pollen	
		Min.	Max.
Intraday precision	Low	2	5
	Medium	4	8
	High	3	7
Interday precision	Low	4	7
	Medium	4	7
	High	2	5

Low level, LOQ, (see Table 3); **Medium level**, 100 $\mu\text{g kg}^{-1}$; **High level**, 700 $\mu\text{g kg}^{-1}$.

Table S3. Chemical structure of the studied acaricides.

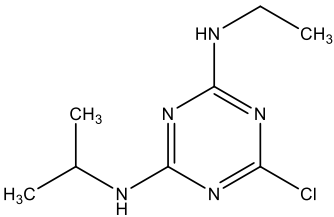
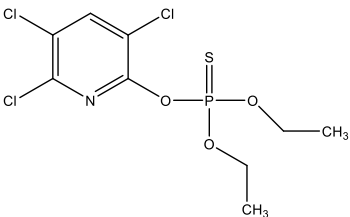
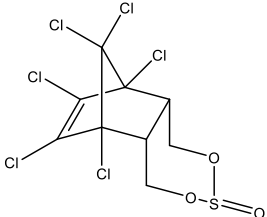
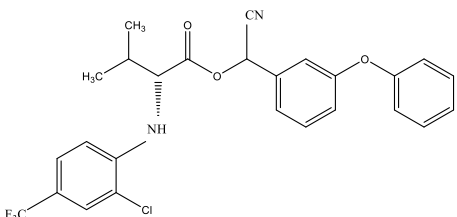
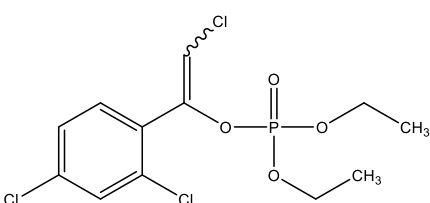
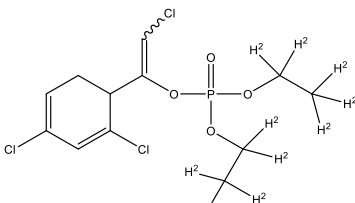
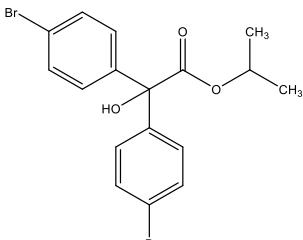
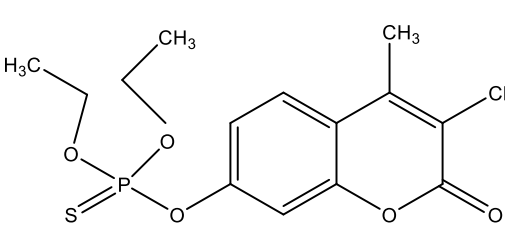
Atrazine	Chlorpyrifos
CAS number: 1912-24-9	CAS number: 2921-88-2
	
α -Endosulfan	τ -Fluvalinate
CAS number: 959-98-8	CAS number: 102851-06-9
	
Chlorfenvinphos	Chlorfenvinphos-d ₁₀
CAS number: 470-90-6	CAS number: 1346606-54-9
	
Bromopropylate	Coumaphos
CAS number: 18181-80-1	CAS number: 56-72-4
	

Figure S1. MS spectra of chlorfenvinphos in standard in (A) solvent and (B) in matrix at the same concentration (0.5 mg L⁻¹). The GC-MS conditions are summarized in subsection 3.4 and **Table 1**.

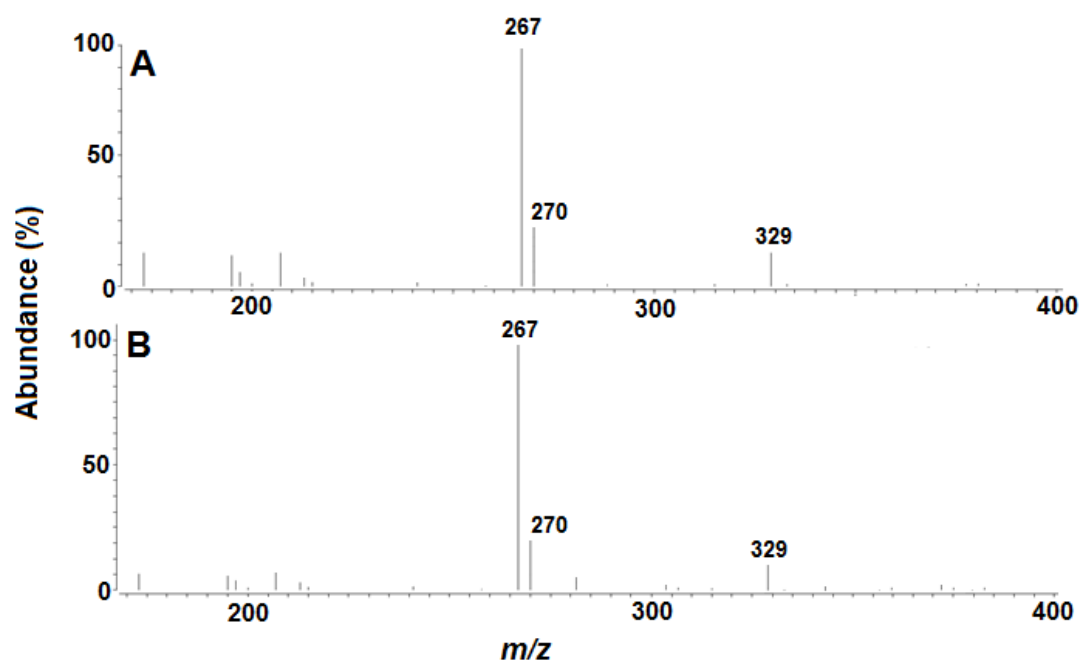


Figure S2. Representative GC-MS chromatogram (SIM mode using the quantification/target ions; see **Table 1**) obtained from multifloral bee pollen sample (E3; 97 $\mu\text{g kg}^{-1}$) with endogenous τ -fluvalinate content over LOQ. GC-MS conditions are summarized in Subsection 3.4 and **Table 1**.

