Química Analítica

Una herramienta para censar nuestro entorno

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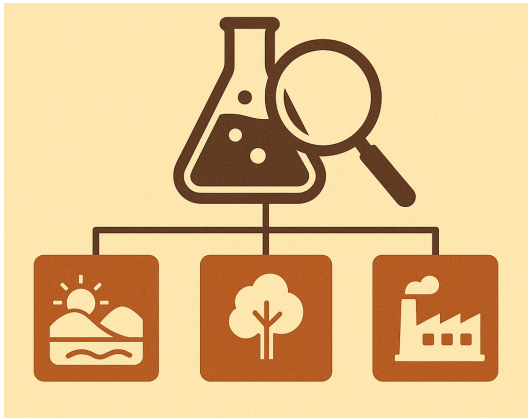
Laboratorio Química Analítica de Contaminantes Orgánicos y Elementos Traza

XVII Jornadas Científicas

Instituto de Salud Pública
Ministerio de Salud

Herramientas para censar nuestro entorno



Química analítica

Evaluación del impacto ambiental

Laboratorio Química Analítica de Contaminantes Orgánicos y Elementos Traza

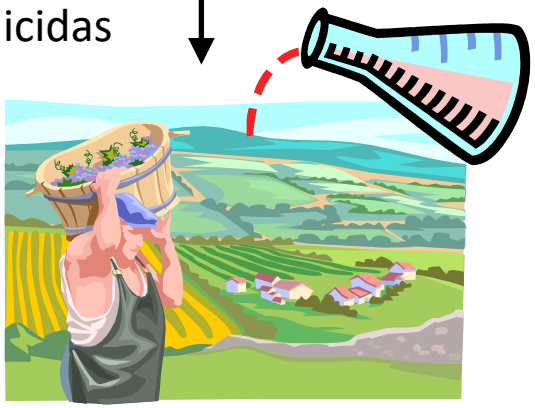
LÍNEA DE INVESTIGACIÓN DE NUESTRO GRUPO DE INVESTIGACIÓN:

Se estudia la **presencia y comportamiento de compuestos orgánicos en el medioambiente y alimentos**. En este sentido, considera el **desarrollo de metodologías analíticas basadas en métodos cromatográficos de alta resolución, métodos espectroscópicos asociados a calibración multivariada, métodos electroquímicos y técnicas de extracción instrumentales** para la determinación de distintos compuestos de origen natural o antropogénico en matrices ambientales y alimentos diversos. **Se emplea la quimiometría como herramienta eficiente para el diseño de experimentos, calibración multivariada y manejo e interpretación de la información analítica generada**. En términos generales busca **conocer el posible impacto de actividades antropogénicas sobre el medioambiente y la producción de alimentos.**

Plaguicidas en el medioambiente (suelos)

Industrialización agricultura

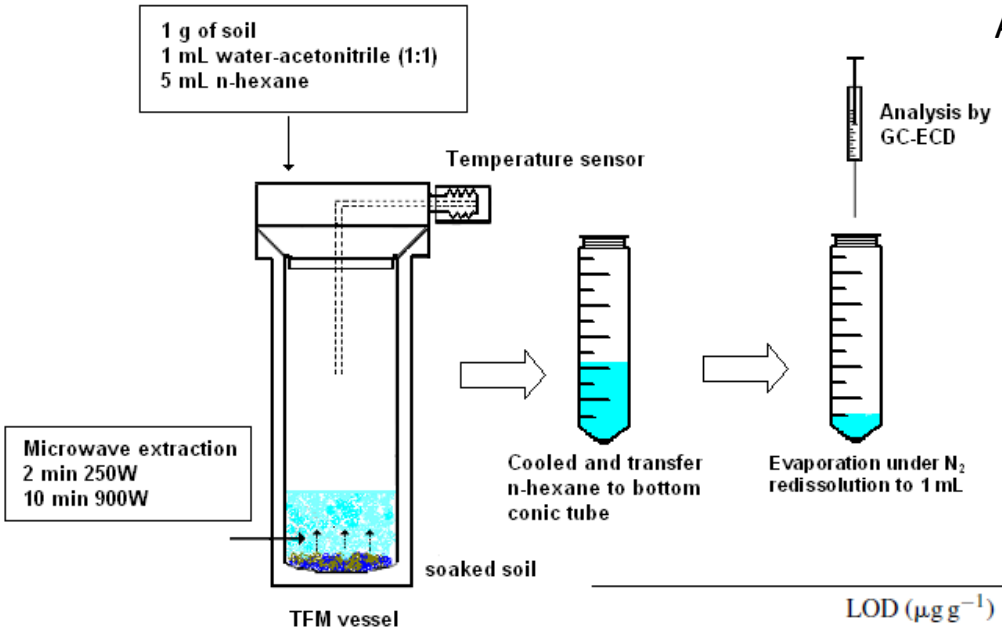
Aumento uso plaguicidas



Plaguicidas en suelos

Microwave-assisted extraction through an aqueous medium and **simultaneous cleanup by partition on hexane** for determining **pesticides in agricultural soils** by gas chromatography: A critical study

Analytica Chimica Acta 578 (2006) 122–130



	LOD ($\mu g\, g^{-1}$)	% Recovery in soil		
		TEM	VLC	QTA
Trifluralin	0.006	69 ± 5	80 ± 3 (74 ± 3)	68 ± 3 (42 ± 2)
Triallate	0.018	–	82 ± 4 (79 ± 4)	80 ± 4 (52 ± 3)
Acetochlor	0.036	–	100 ± 3 (84 ± 5)	89 ± 3 (54 ± 3)
Alachlor	0.030	–	101 ± 6 (79 ± 4)	91 ± 3 (51 ± 2)
Metolachlor	0.036	90 ± 6	104 ± 3 (83 ± 4)	99 ± 3 (57 ± 3)
Chlorpyriphos	0.010	80 ± 6	100 ± 3 (90 ± 5)	89 ± 6 (38 ± 2)
Triadimefon	0.018	78 ± 7	92 ± 5 (114 ± 6)	93 ± 3 (87 ± 8)
Endosulphan I	0.008	–	78 ± 6 (70 ± 4)	78 ± 3 (44 ± 2)
Endrin	0.009	–	78 ± 5 (77 ± 5)	79 ± 4 (47 ± 3)
Endosulphan II	0.008	–	72 ± 7 (71 ± 3)	76 ± 4 (45 ± 3)
Methoxychlor	0.010	–	73 ± 5 (64 ± 3)	72 ± 6 (97 ± 5)
Tetradifon	0.004	–	76 ± 5 (75 ± 4)	80 ± 1 (36 ± 2)

Recoveries for ultrasonic method shown in parentheses.

Parameters affecting **microwave-assisted extraction** of **organophosphorus pesticides from agricultural soil**.

Journal of Chromatography A, 1169 (2007) 40–46

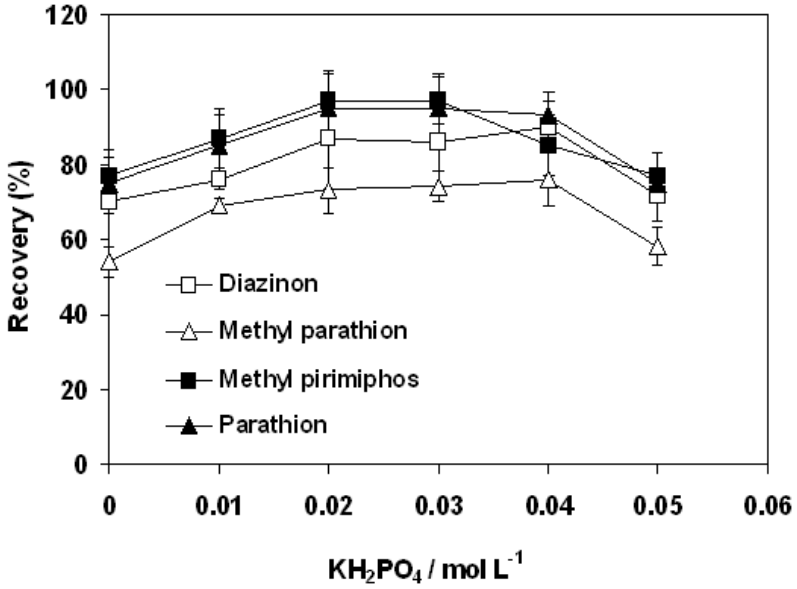
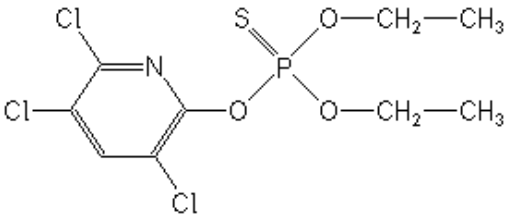


Table 3
Analytical features of the MAEP–GC–FPD method obtained under optimized conditions (LOD and LOQ 3 and 10 times the standard error of the signal obtained for six QTA soil extracts)

Compound	Analytical sensitivity ($\mu g\ g^{-1}$)[a]	LOD ($\mu g\ g^{-1}$)	LOQ ($\mu g\ g^{-1}$)	Precision (RSD)
Ethoprophos	0.002	0.006	0.019	4.8
Diazinon	0.001	0.004	0.012	3.4
Methyl parathion	0.004	0.012	0.035	7.5
Methyl pirimiphos	0.002	0.006	0.018	5.1
Fenitrothion	0.003	0.008	0.025	5.9
Parathion	0.002	0.006	0.019	3.8

Contaminantes orgánicos en alimentos

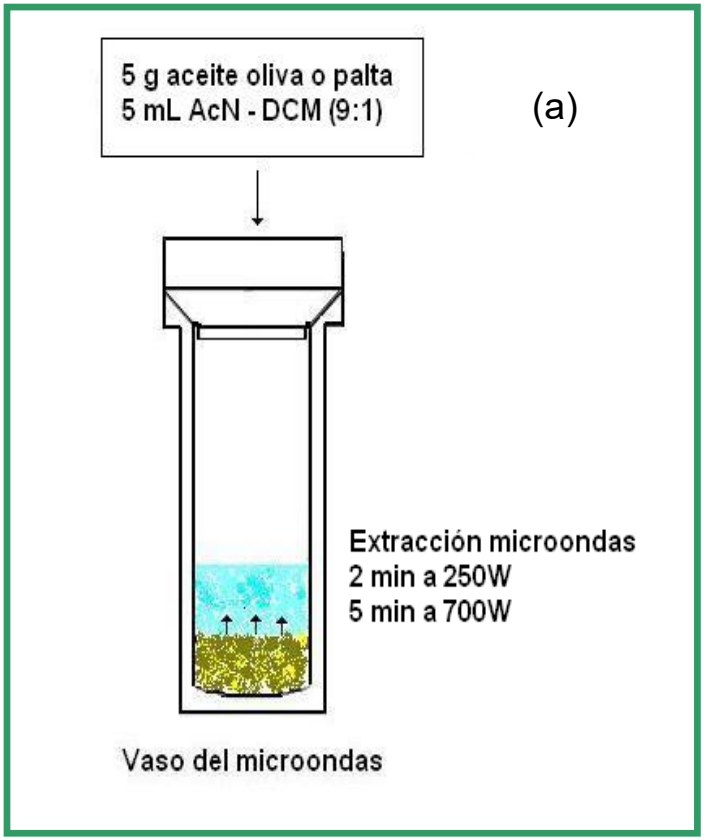
Mosca del olivo (*Dacus oleae*)

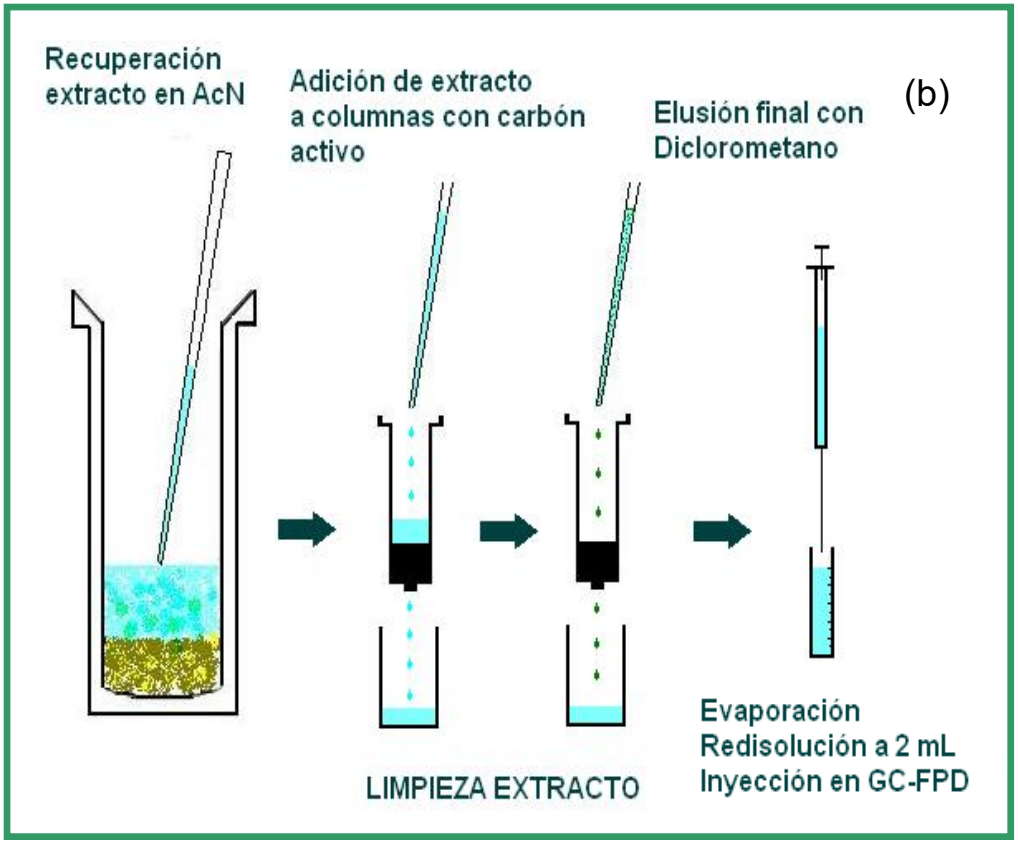


Plaguicidas organofosforados

Suitability of **microwave-assisted extraction (MAE)** coupled with solid-phase extraction (SPE) for **organophosphorus pesticide determination in olive oil**.

Journal of Chromatography A, 1207 (2008) 38–45





(a) MAE (L – L)

(b) Limpieza con SPE

Determinación con GC-FPD

Microwave-assisted extraction at atmospheric pressure coupled to different clean-up methods for the determination of **organophosphorus pesticides in olive and avocado oil**

Journal of Chromatography A, 1216 (2009) 8859–8866

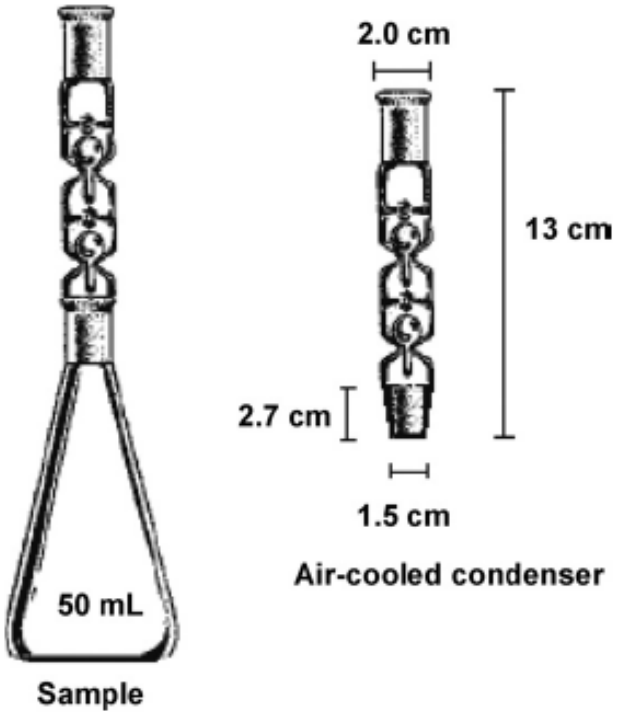
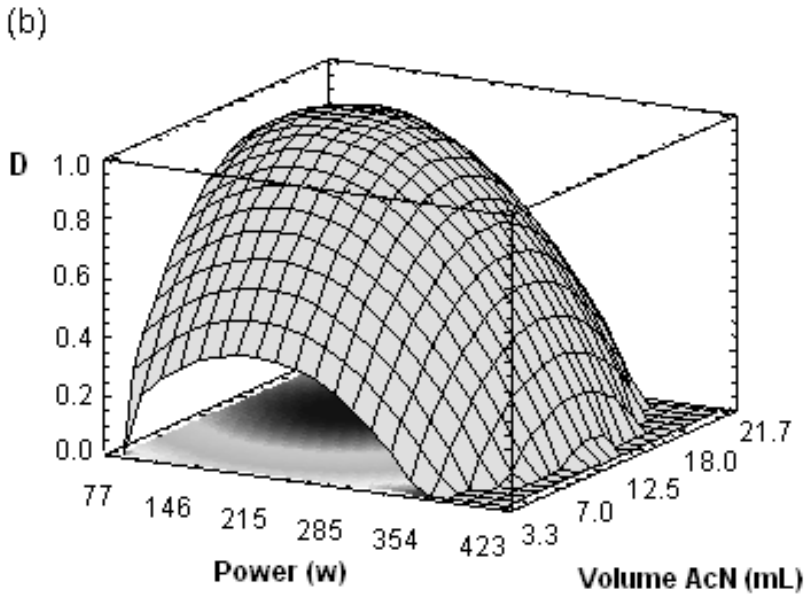


Fig. 1. Scheme of the glass system employed for atmospheric pressure microwave-assisted extraction.



Microwave-assisted extraction at atmospheric pressure coupled to different clean-up methods for the determination of **organophosphorus pesticides in olive and avocado oil**

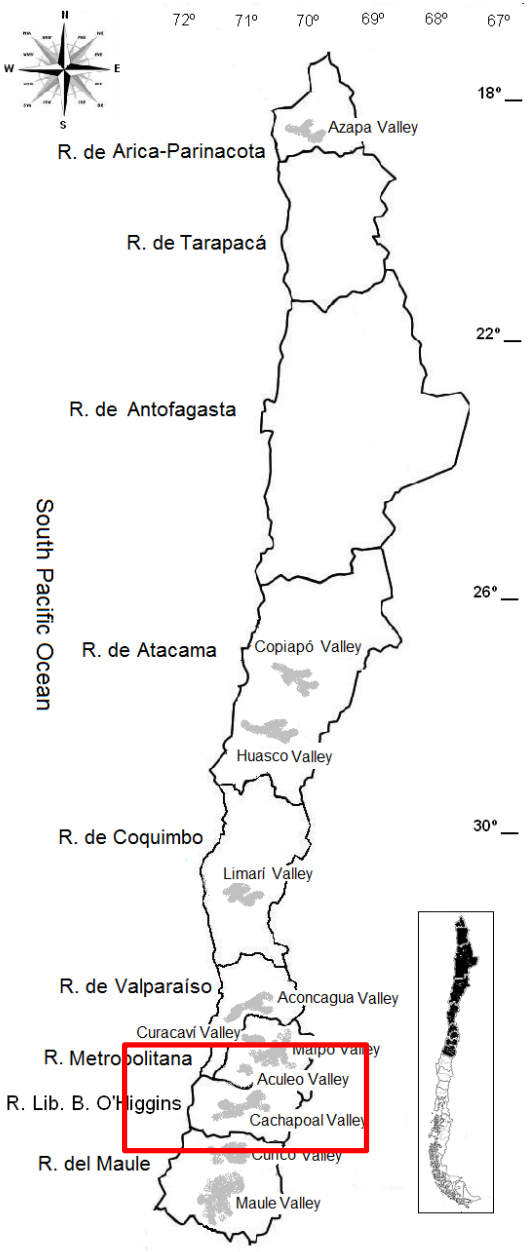
Journal of Chromatography A, 1216 (2009) 8859–8866

Table 8
Pesticide residues (μg g^{-1}) detected in virgin olive oil (VOO) and virgin avocado oil (VAO) samples produced in different regions of Chile, and MRLs according to European Legislation [9,10].

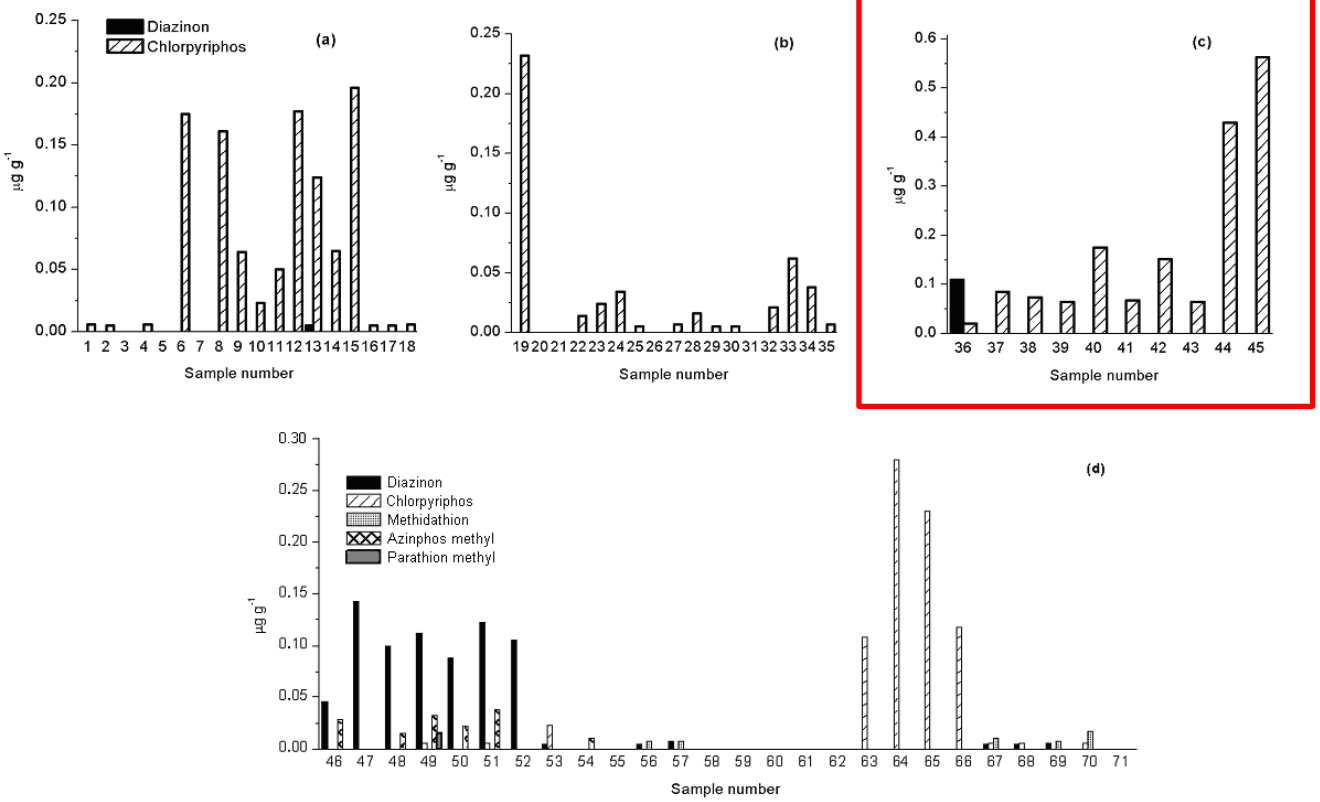
Oil sample	Valley and region ( ) of origin	Diazinon	Parathion methyl	Clorpyriphos	Methidathion	Azinphos methyl
VOO1	Copiapó (III)					
VOO2	Limarí (IV)	0.005		0.124		
VOO3	Aconcagua(V)			0.232		
VOO4	Aculeo (RM)			0.038		
VOO5	Aculeo			0.062	<0.007	
VOO6	Maipo (RM)			0.024		
VOO7	Maipo			0.016		
VOO8	Curacaví (RM)			0.007		
VOO9	Cachapoal (VI)			0.085		
VOO10	Cachapoal			0.074		
VOO11	Cachapoal			0.065		
VOO12	Curicó (VII)	0.100				0.015
VOO13	Maule (VII)	<0.004[a]			0.007	
VOO14	Curicó	0.112	<0.015	<0.005		0.032
VOO15	Curicó	0.088				0.022
VOO16	Maule					
VOO17	Maule					
VOO18	Maule			0.108		
VOO19	Maule	<0.004			0.010	
VOO20	Maule	0.004		<0.005	0.007	
VAO1	Aconcagua					
VAO2	Maipo			<0.005		
VAO3	Maipo					
VAO4	Aconcagua					
MRL (μg g^{-1}) in VOO		nr	nr	nr	2	nr
MRL (μg g^{-1}) in olives		0.010	0.020	0.050	1	0.050

nr: Non-reported.

Survey of organophosphorus pesticide residues in virgin olive oils produced in Chile

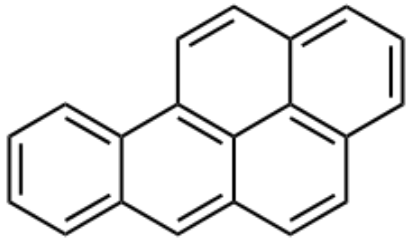


Food Additives and Contaminants: Part B
Vol. 3, No. 2, June 2010, 101–107



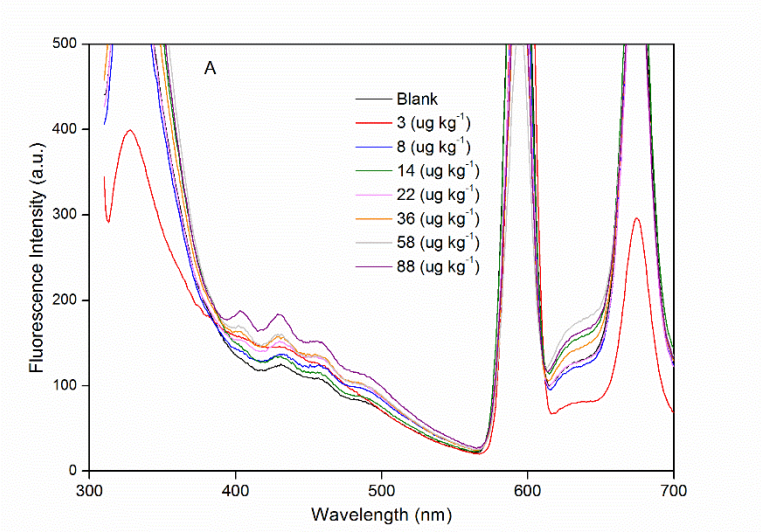
OPPs levels in 71 analyzed olive oil samples according to region of origin: (a) Arica-Parinacota, Atacama and Coquimbo; (b) Valparaíso and Metropolitana, (c) O'Higgins and (d) Maule.

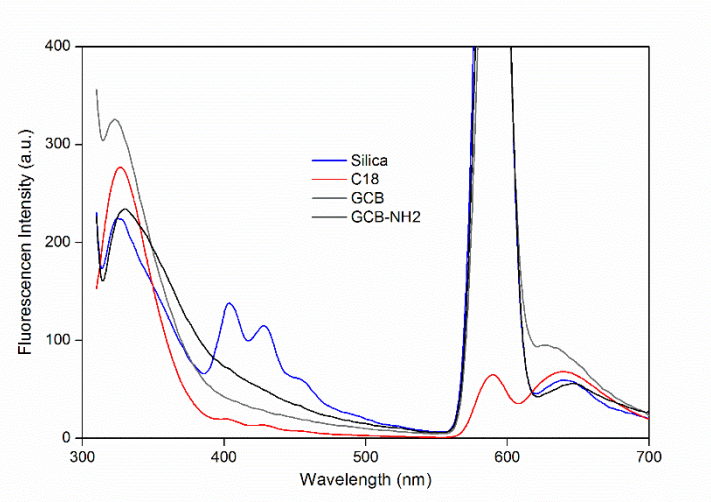

AROMÁTICOS POLICÍCLICOS EN ALIMENTOS
• Procesos de cocción a alta temperatura
• Ahumado de alimentos
• Aceites vegetales
• Contaminación ambiental

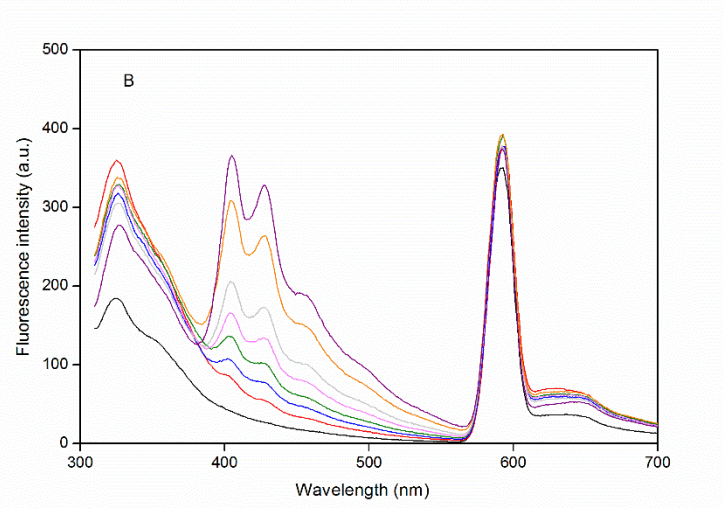


Screening of edible oils for polycyclic aromatic hydrocarbons using **microwave-assisted liquid–liquid and solid phase extraction coupled to one- to three-way fluorescence spectroscopy analysis**

Talanta 100 (2012) 439–446

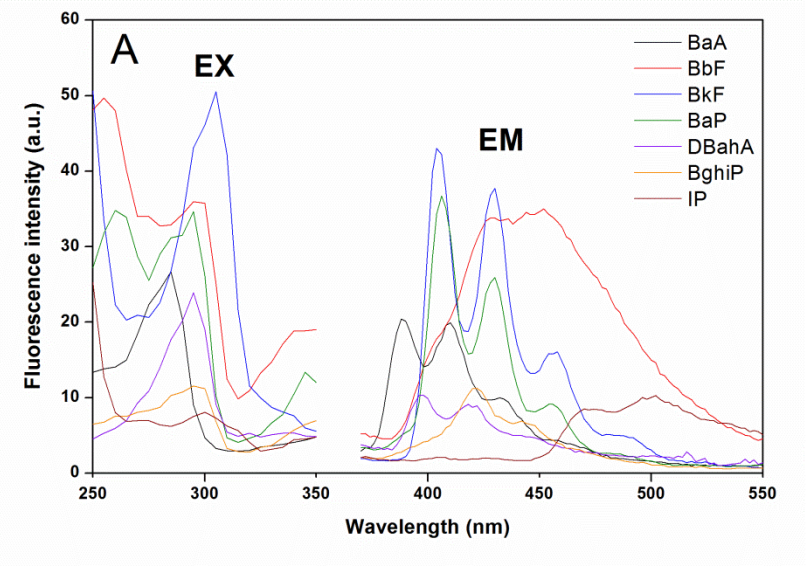


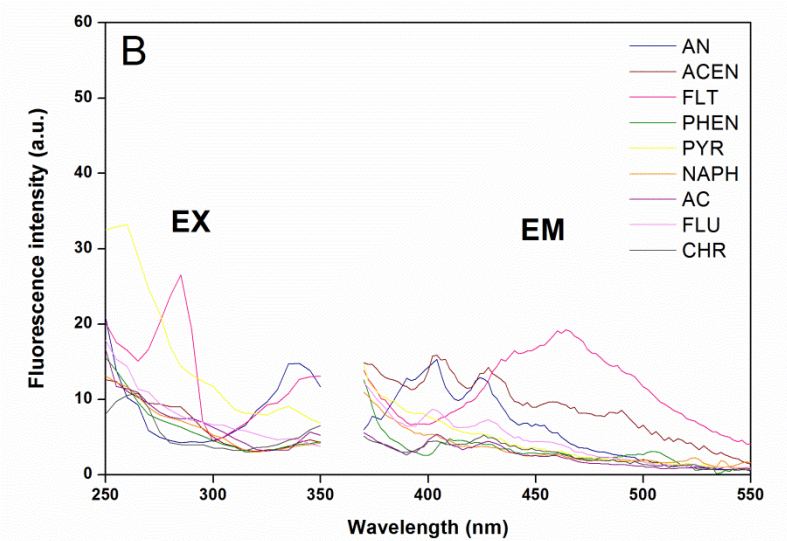


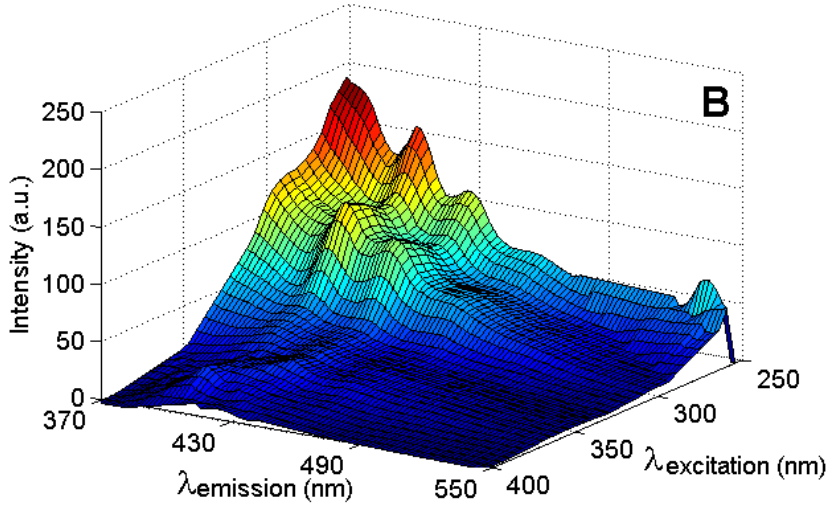


Feasibility of the determination of **polycyclic aromatic hydrocarbons in edible oils** via unfolded **partial least-squares/residual bilinearization and parallel factor analysis of fluorescence** excitation emission matrices.

Talanta 103 (2013) 361–370







U-PLS, PARAFAC →

Identificación

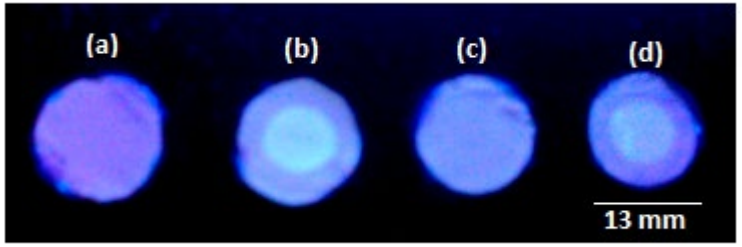
Cuantificación

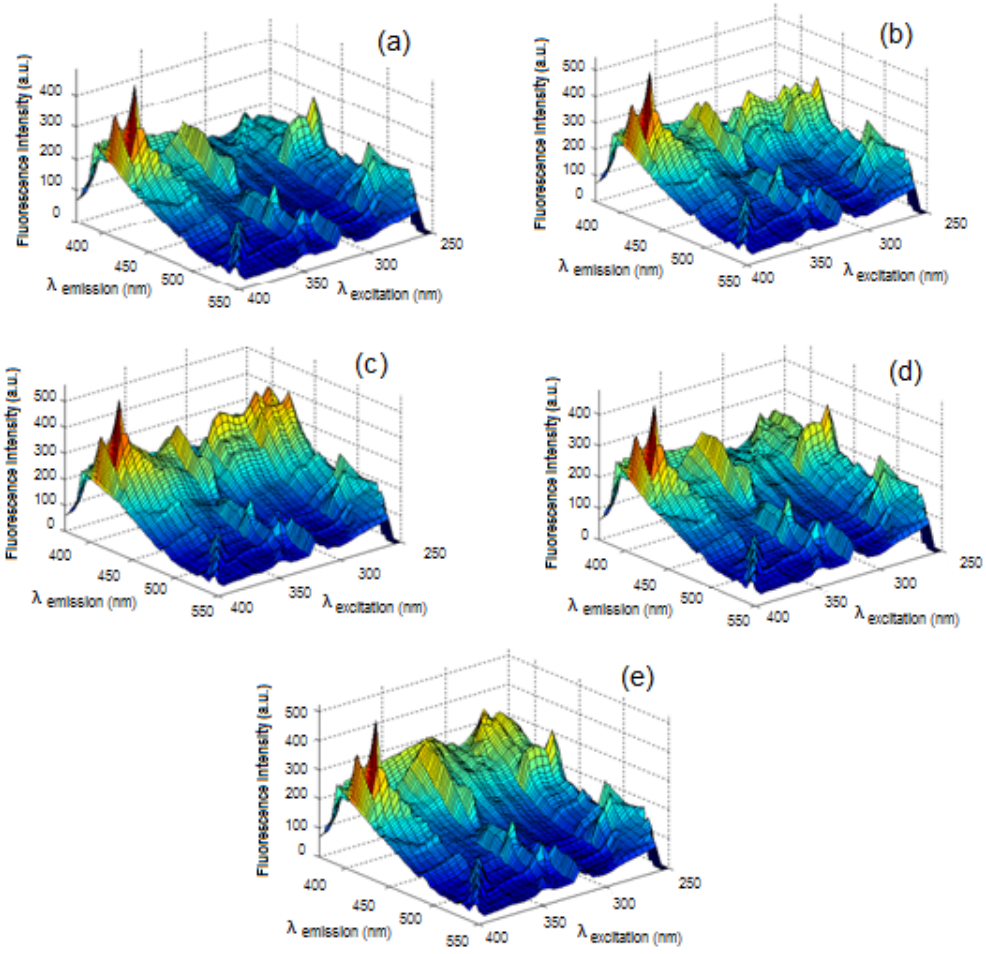
Determination of **heavy polycyclic aromatic hydrocarbons** of concern in **edible oils** via excitation–emission **fluorescence spectroscopy on nylon membranes** coupled to unfolded partial least-squares/residual bilinearization

Anal Bioanal Chem (2013) 405:7497–7507

Adsorción HAPs sobre membrana nylon

Fotografía de membranas de nylon irradiadas con lámpara UV a 254 nm





		Análisis por MAE-SPE / U-PLS/RBL (µg kg^{-1})						
Tipo aceite	Muestra	BaA	BbF	BkF	BaP	DBahA	BghiP	IP
Oliva virgen (abril 2012)	1	-[a]	-	**0,09**	-	-	-	-
	2	-	-	**0,18**	-	-	-	-
	3	-	-	**0,24**	-	-	-	-
	4	-	-	-	-	-	-	-
	5	-	-	-	-	-	-	-
	6	-	-	-	-	-	-	-
	7	-	-	-	-	-	-	-
	8	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-
	10	-	-	-	-	-	-	-
	11	-	-	-	-	-	-	-
	12	-	-	-	-	-	-	-
	13	-	-	-	-	-	-	-
	14	-	-	-	-	-	-	-
Oliva común (abril 2012)	15	-	-	**0,48**	-	**0,66**	-	-
Girasol (abril 2012)	16	-	-	-	-	-	-	-
	17	-	-	-	-	-	-	-
	18	-	-	-	-	-	-	-
	19	-	-	-	-	-	-	-
	20	-	-	-	-	-	-	-
Girasol frito (abril 2012)	21	-	-	-	-	-	-	-
Oliva virgen (noviembre 2012)	1	-	-	-	-	-	-	-
	2	-	-	-	-	-	-	-
	3	-	-	-	-		-	-
	4	-	-	-	-	**0,35**	-	-
	5	-	-	-	-	-	-	-
	6	-	-	-	-	-	-	-
	7	-	-	-	-	-	-	-
	8	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-
	10	**0,63**	-	-	**0,43**	**0,40**	-	-
Oliva virgen (octubre 2013)	1	-	-	-	-	-	-	-
	2	-	-	-	-	-	-	-
	3	-	-	-	-	-	-	-
	4	-	-	-	-	-	-	-
	5	-	-	-	-	-	-	-
	6	-	-	-	-	-	-	-
	7	-	-	-	-	-	-	-
	8	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-
	10	-	-	-	-	-	-	-
	11	**1,62**	-	-	-	-	**1,88**	-

Plaguicidas en abejas (sensores ambientales)

Caracterización de mieles

Determination of **imidacloprid in water samples** via **photochemically induced fluorescence and second-order multivariate calibration**

Talanta134 (2015) 8–15

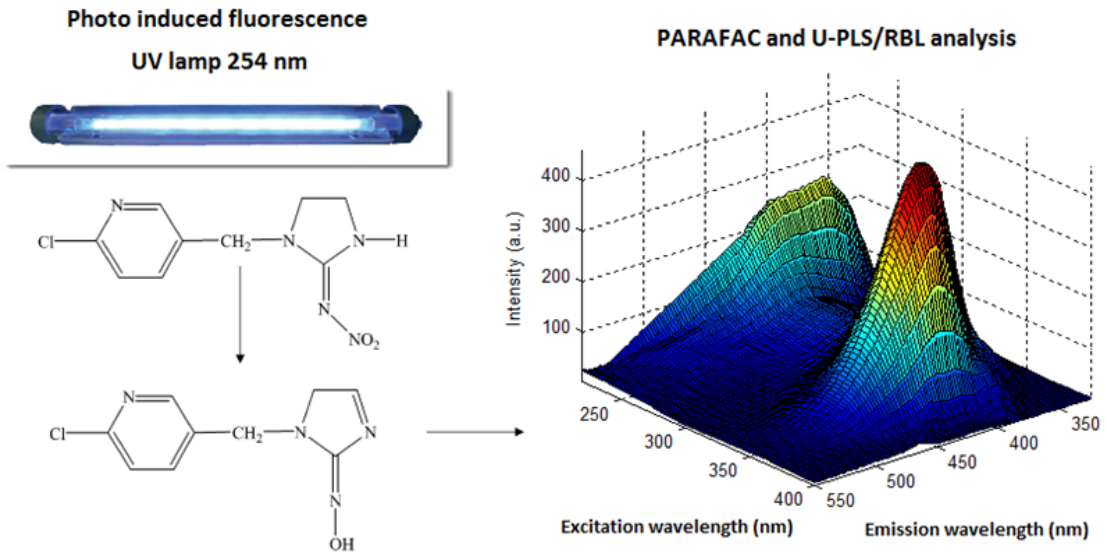


Table 3
Predictions of imidacloprid and mean LODs in irrigation ditch sample spiked with additional foreign pesticides determined by SPE-C18-PIF-EEMs with PARAFAC and U-PLS/RBL.

Sample	Foreign pesticide added (ng mL^{-1})				Predicted values of imidacloprid [a]	
	Carbofuran	Carbaryl	Fenvalerate	Atrazine	PARAFAC	U-PLS/RBL
1	10	10	50	50	8.0	7.8
2	50	10	10	50	10.6	11.0
3	10	50	50	10	8.8	10.0
4	50	50	10	10	7.2	7.2
LOD (ng mL^{-1}) [b]	–	–	–	–	0.72	1.0

[a] Imidacloprid spiked at 0.01 μg mL^{-1}.
[b] LOD calculated considering the 50-fold pre-concentration factor.

Photochemically induced fluorescence coupled to **second-order multivariate calibration** as analytical tool **for determining imidacloprid in honeybees**.

Chemometrics and Intelligent Laboratory Systems 160 (2017) 1–7

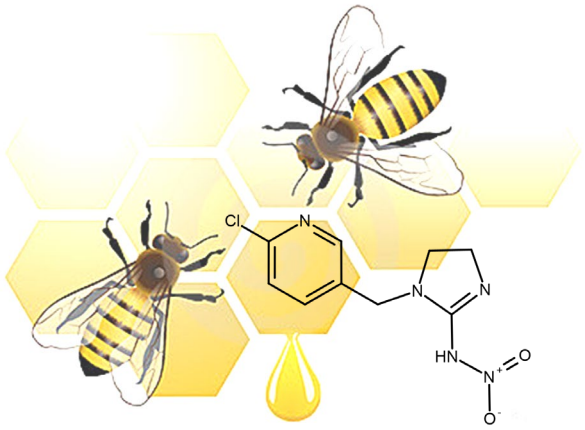
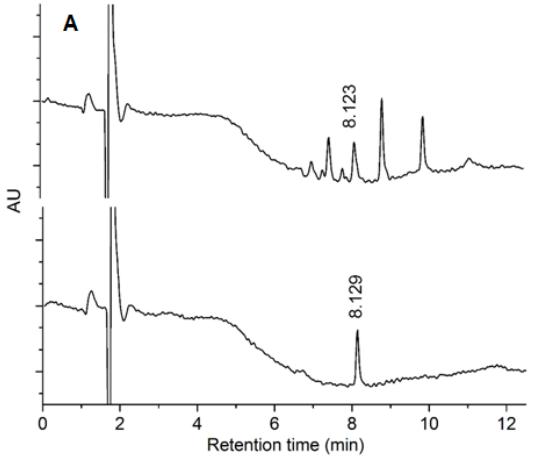


Figura 1. Fotografía que muestra la mezcla de abejas + fase C18 empacada sobre la columna de carbón grafito antes de la elusión con solvente.



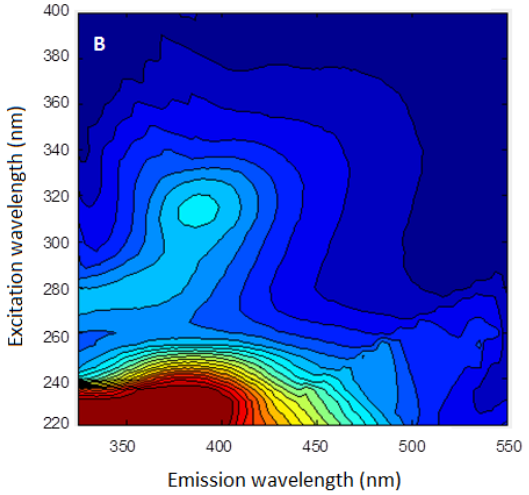
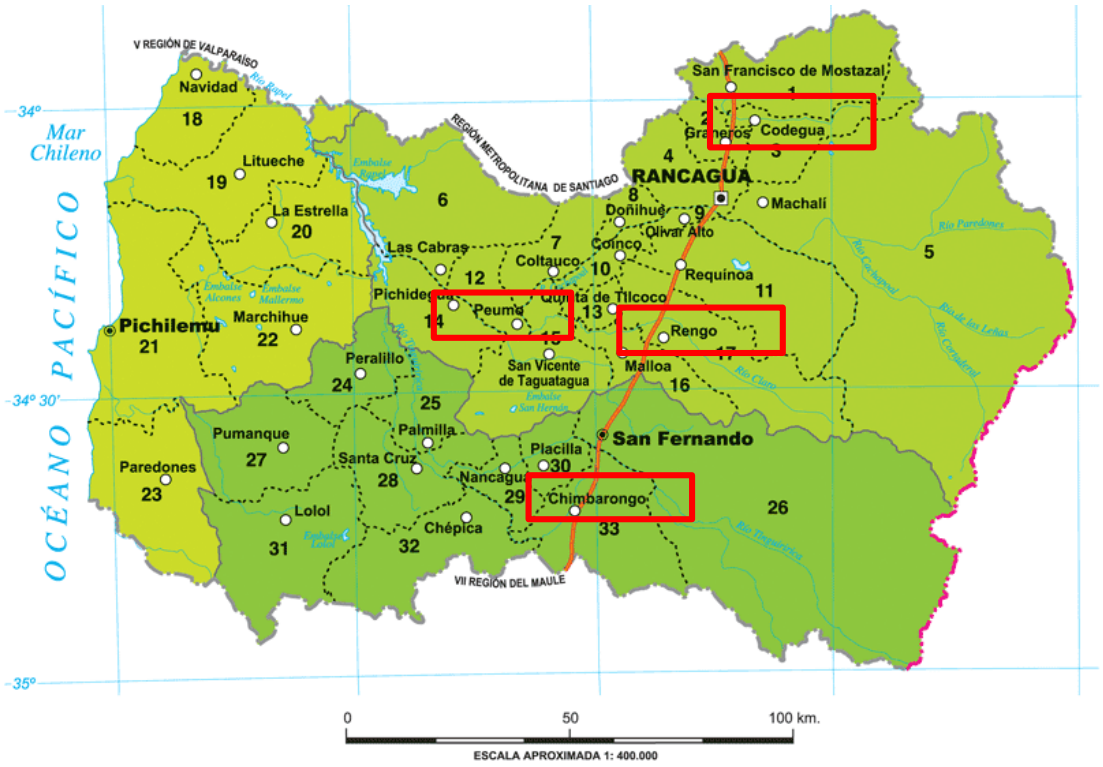


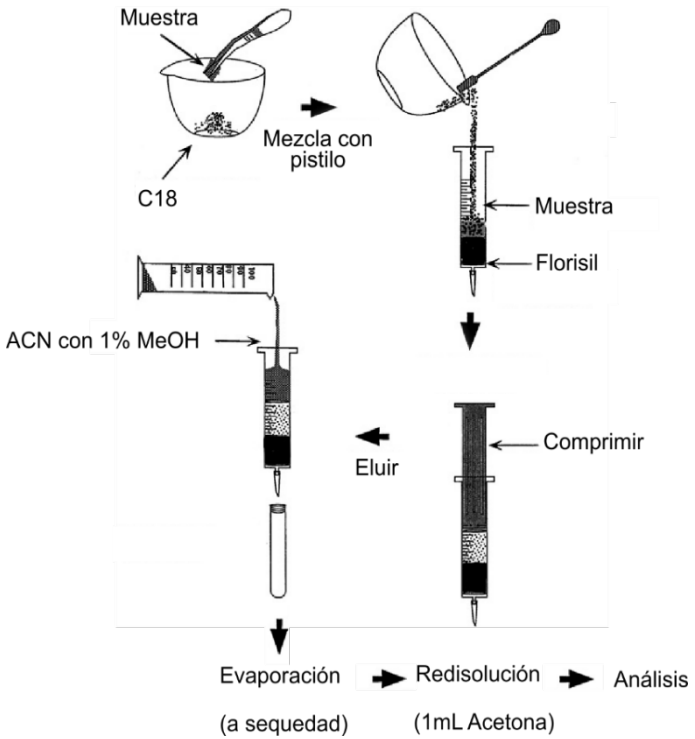
Figura 2. Cromatograma en HPLC-DAD obtenido para una muestra de abeja y un estándar de imidacloprid a 0.1 ug/ml (A); gráficos de contorno de PIF-EEM para la misma muestra (B).

Análisis de muestras de abejas de campo de la región de O'Higgins en Chile central



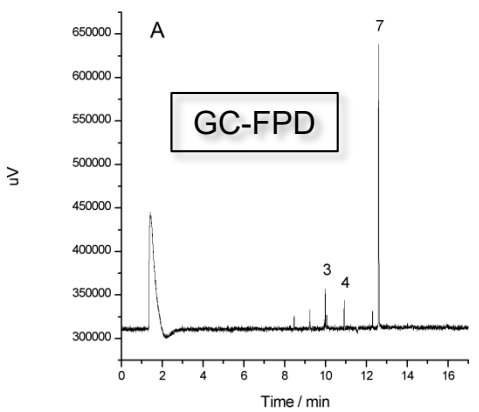
Muestra	Sector	UPLS/RBL	HPLC-DAD
1	**Rengo**	Nd	Nd
2	**Rengo**	Nd	Nd
3	**Rengo**	Nd	Nd
4	**Chimbarongo**	Nd	Nd
5	**Chimbarongo**	Nd	Nd
6	**Codegua**	Nd	Nd
7	**Codegua**	Nd	Nd
8	**Peumo**	Nd	Nd
9	**Peumo**	Nd	Nd

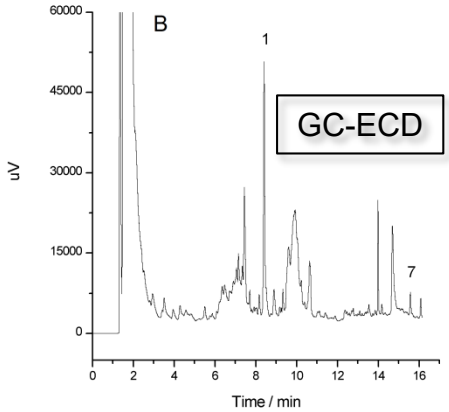
Matrix solid-phase dispersion associated to gas chromatography for the assessment in **honey bee** of a group of **pesticides of concern in the apicultural field**

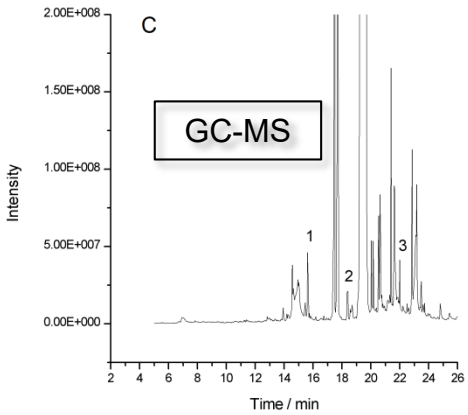


Journal of Chromatography A, 1567 (2018) 47–54

Detection	Pesticide
GC-μECD	Thiamethoxam
	Fipronil
	Acetamiprid
	Acrinathrin
GC-FPD	Methamidophos
	Dimethoate
	Diazinon
	Chlorpyriphos
	Methidathion
	Profenophos
	Azinphos methyl
	Coumaphos







Evaluación de **plaguicidas** en abejas recolectadas en la quinta y sexta región del país

Plaguicidas al nivel de traza encontrados en abejas de la quinta y sexta región.

A. Balsebre et al. / J. Chromatogr. A 1567 (2018) 47–54

Table 6
Pesticide residues detected in honeybee from Valparaíso (V) and O'Higgins (VI) regions of Chile.

		Positive samples and concentration range () / μg g^{-1}							
Region / zone	Samples	Thiamethoxam	Fipronil	Acetamiprid	Acrinathrin	Methamidophos	Diazinon	Chlorpyriphos	Coumaphos
V/Casablanca	9	-[a]	2 (<0.020)	1 (0.057)	4 (<0.020–0.026)	–	–	–	–
V/Catemu-Panquehue	9	–	–	2 (<0.047–0.100)	5 (<0.020)	–	1 (<0.015)	–	–
V/ConCon-Quintero	9	–	1 (<0.020)	1 (<0.047)	5 (<0.020)	1 (<0.007)	–	1 (<0.017)	–
V/Quillota	9	–	–	–	1 (<0.020)	3 (<0.007)	–	–	–
VI/Chimbarongo	8	1 (<0.010)[b]	–	–	5 (<0.020)	–	4 (<0.015)	7 (<0.017–0.067)	–
VI/Codegua	4	–	–	–	1 (<0.020)	–	–	4 (<0.017)	–
VI/Peumo	8	–	–	–	–	–	2 (<0.015)	4 (<0.017)	–
VI/Rengo	12	–	–	–	1 (<0.020)	–	–	7 (<0.017)	1 (<0.030)
Overall	68	1 (<0.010)	3 (<0.020)	4 (<0.047–0.100)	22 (<0.020–0.026)	4 (<0.007)	7 (<0.015)	23 (<0.017–0.067)	1 (<0.030)

[a] Residue was lower than the LOD.
[b] Lower that the mLOQ.

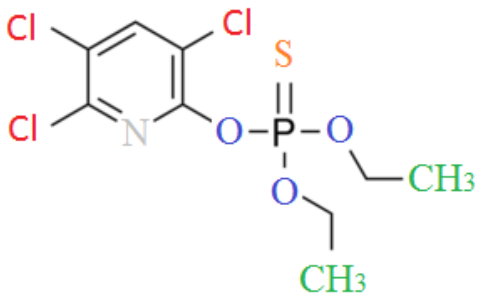


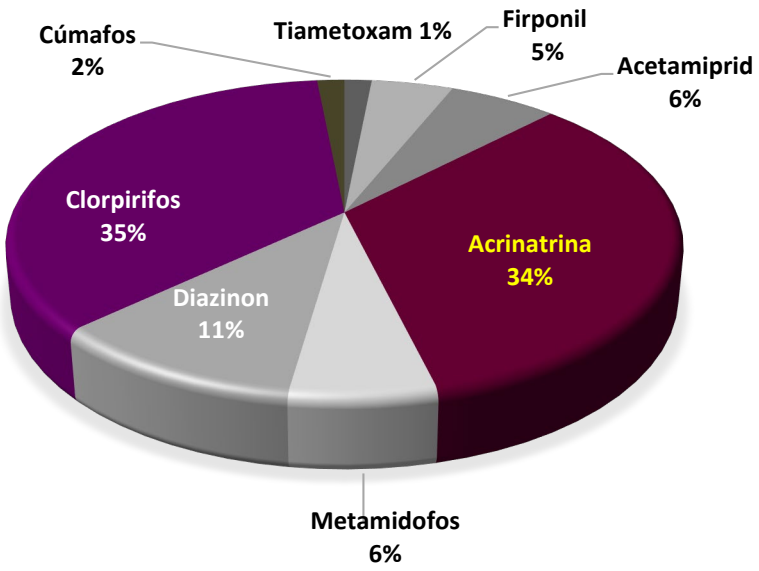
Table 7
Comparison with results obtained on the determination of the target pesticides in bees in other countries.

Country [Ref]	Samples	Positive samples and concentration range () / µg g^{-1}					
		Thiamethoxam	Fipronil	Dimethoate	Diazinon	Chlorpyriphos	Coumaphos
Chile [This work]	68[a]	1 (<0.010)	3 (<0.020)	–	7 (<0.015)	23 (<0.017–0.067)	1 (<0.030)
Uruguay [6]	31[b]	–	2 (0.150–0.170)	–	–	–	–
France [23]	307[a]	–	7 (<0.0003–0.0007)	–	–	–	14 (<0.037–25)
Egypt [24]	16[a]	–	–	–	9 (0.0002–0.0005)	1 (0.032)	–
Poland [27]	73[b]	2 (0.044–0.275)	3 (0.034–0.271)	30 (0.0014–1.6)	–	38 (0.002–3.3)	–
Poland [28]	25[b]	–	10 (0.010–0.064)	9 (0.238–4.9)	–	5 (0.010–0.056)	–
Poland [30]	33[b]	–	3 (0.008–0.017)	3 (0.258–7.3)	–	9 (0.010–576)	–
Greece [34]	27[b]	–	1 (0.082)	–	–	–	2 (0.013–0.020)
France [35]	145[a]	–	–	–	1 (<0.027)	4 (0.003–0.180)	28 (0.004–0.047)

[a] Workers bees.
[b] Poisoned dead bees.

Abejas obreras forrajeras

Abejas envenenadas muertas



Principales plaguicidas encontrados en muestras de la V y VI región en porcentaje respecto al total encontrado.

Venta de plaguicidas por región (SAG)

Compuesto activo	Ventas V región (kg)	Ventas VI región (kg)
Clorpirifos	93.850	309.658
Diazinon	4.685	66.606
Clorotalonil	16.474	46.930
Metamidofos	34.760	36.509
Acetamiprida	2.917	8.626
Tiametoxam	3.080	3.472
Acrinatrina	901	1.688
Fipronil	5	1
Coumafos	-	-

La miel ha sido consumida desde la antigüedad y desde entonces se reconocen sus propiedades benéficas para la salud

Entre las propiedades de la miel se cuentan sus aspectos nutritivos, antibacterianos, anticancerígenos y regenerador de tejidos.

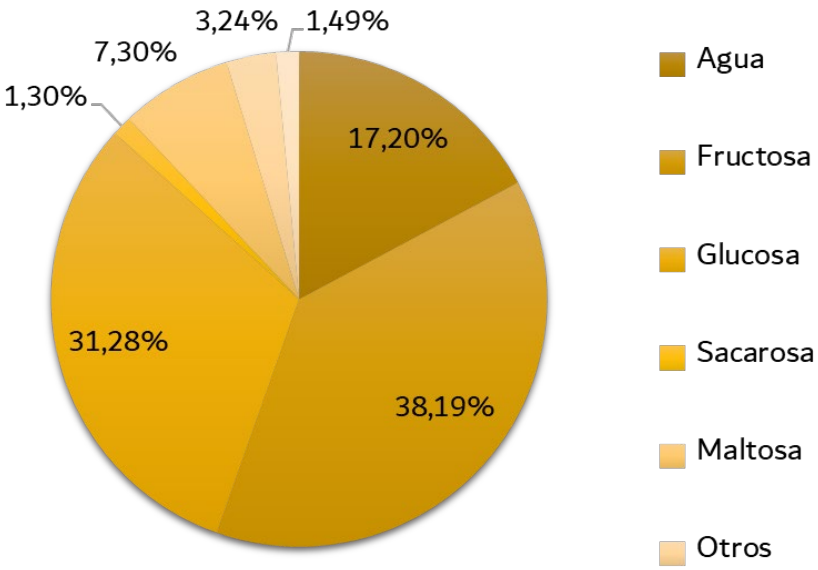
¿Qué le otorga estas propiedades?

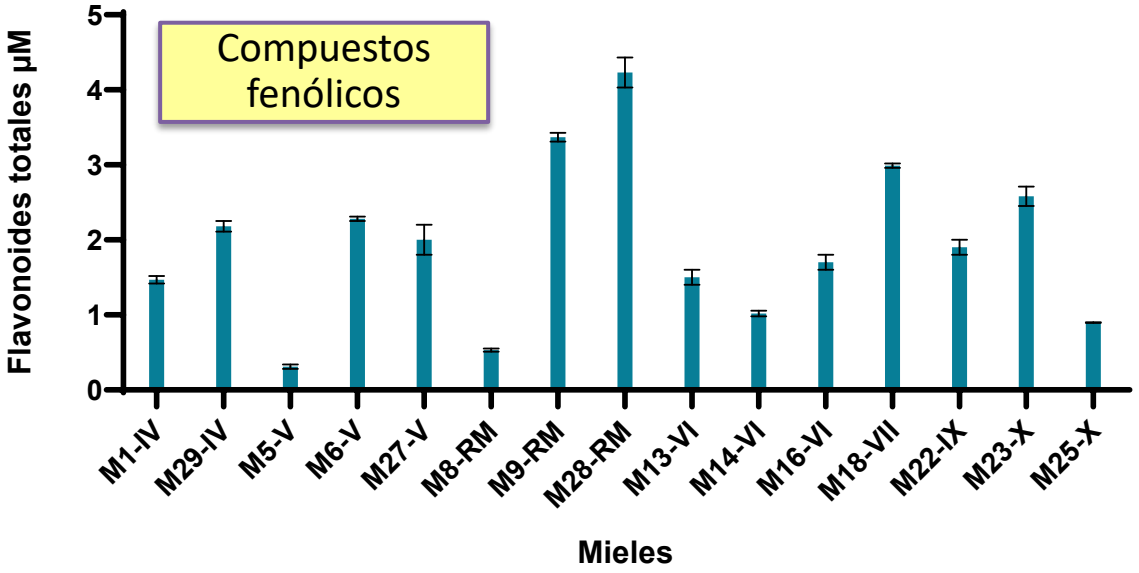
Componente animal

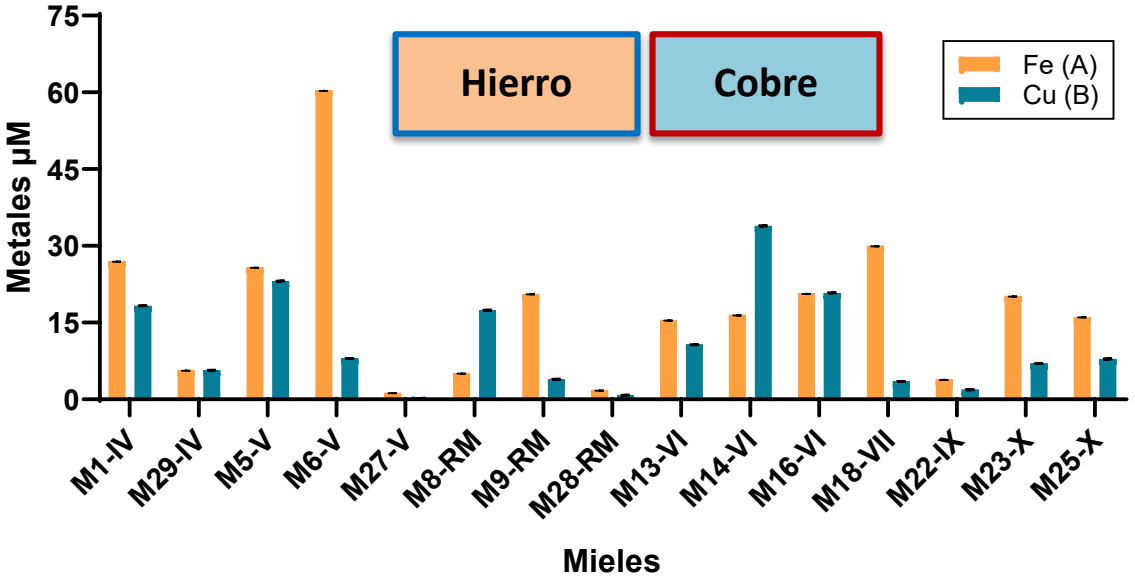
Componente vegetal

Componente vegetal

- Polen y néctar
  - Carbohidratos
    - Sacarosa y almidón
      - **Glucosa**
      - **Fructosa**
  - Minerales
    - **Hierro**
    - **Cobre**
  - Proteína (1/3)
  - Compuestos fenólicos
  - Vitaminas
- Área geográfica
  Flora




Compuestos fenólicos
Flavonoides totales µM
0
1
2
3
4
5
M1-IV
M29-IV
M5-V
M6-V
M27-V
M8-RM
M9-RM
M28-RM
M13-VI
M14-VI
M16-VI
M18-VII
M22-IX
M23-X
M25-X
Mieles


Hierro
Cobre
Fe (A)
Cu (B)
Metales µM
0
15
30
45
60
75
M1-IV
M29-IV
M5-V
M6-V
M27-V
M8-RM
M9-RM
M28-RM
M13-VI
M14-VI
M16-VI
M18-VII
M22-IX
M23-X
M25-X
Mieles

Componente animal

Compuestos de las abejas

Proteínas (2/3)

Enzimas

Invertasa y diastasa

GOX

Defensina-1

Glucosa + O_2

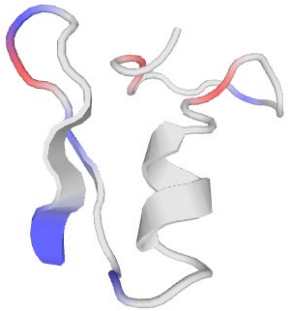
Acido glucónico

+

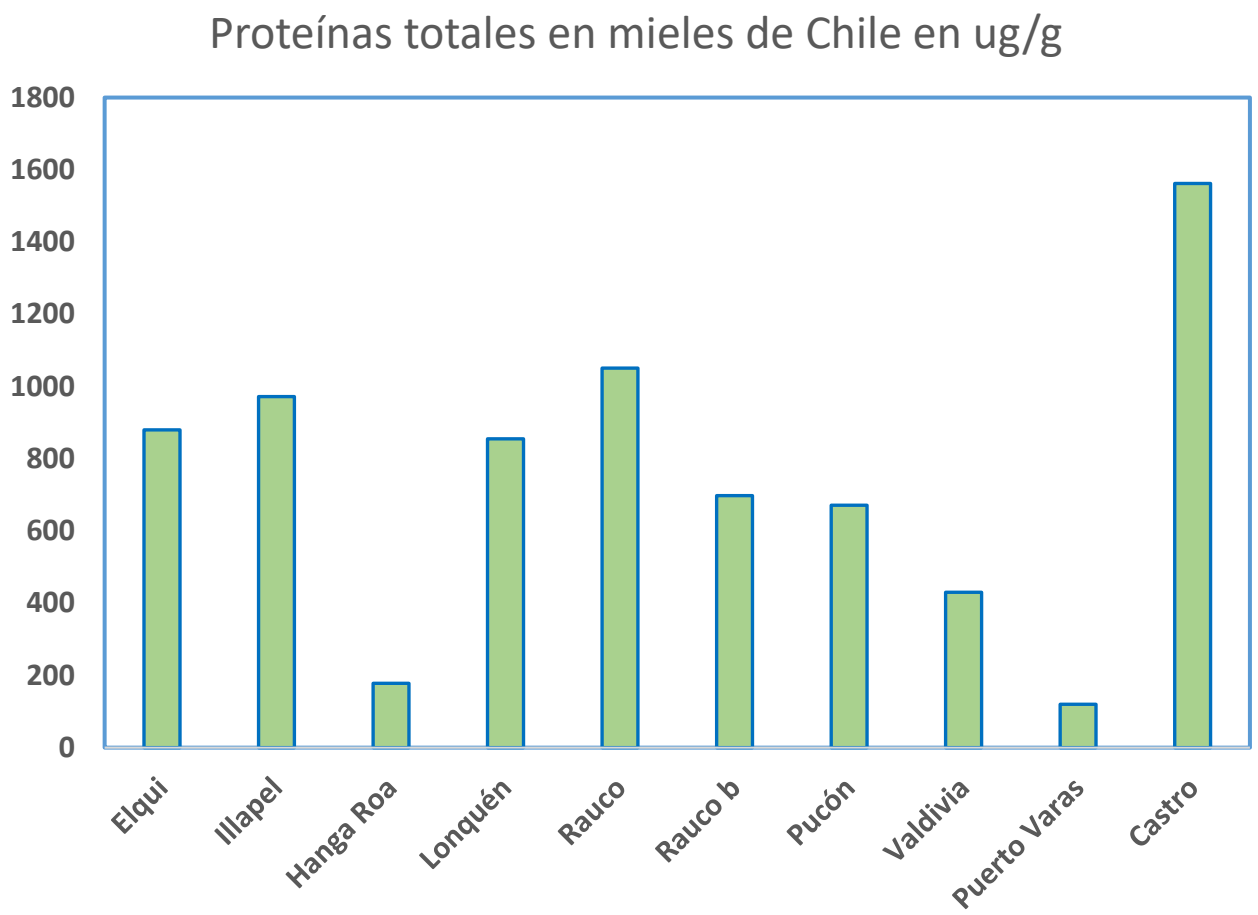
H_2O_2

Medio ácido (pH ≈ 4)

Genética de las abejas



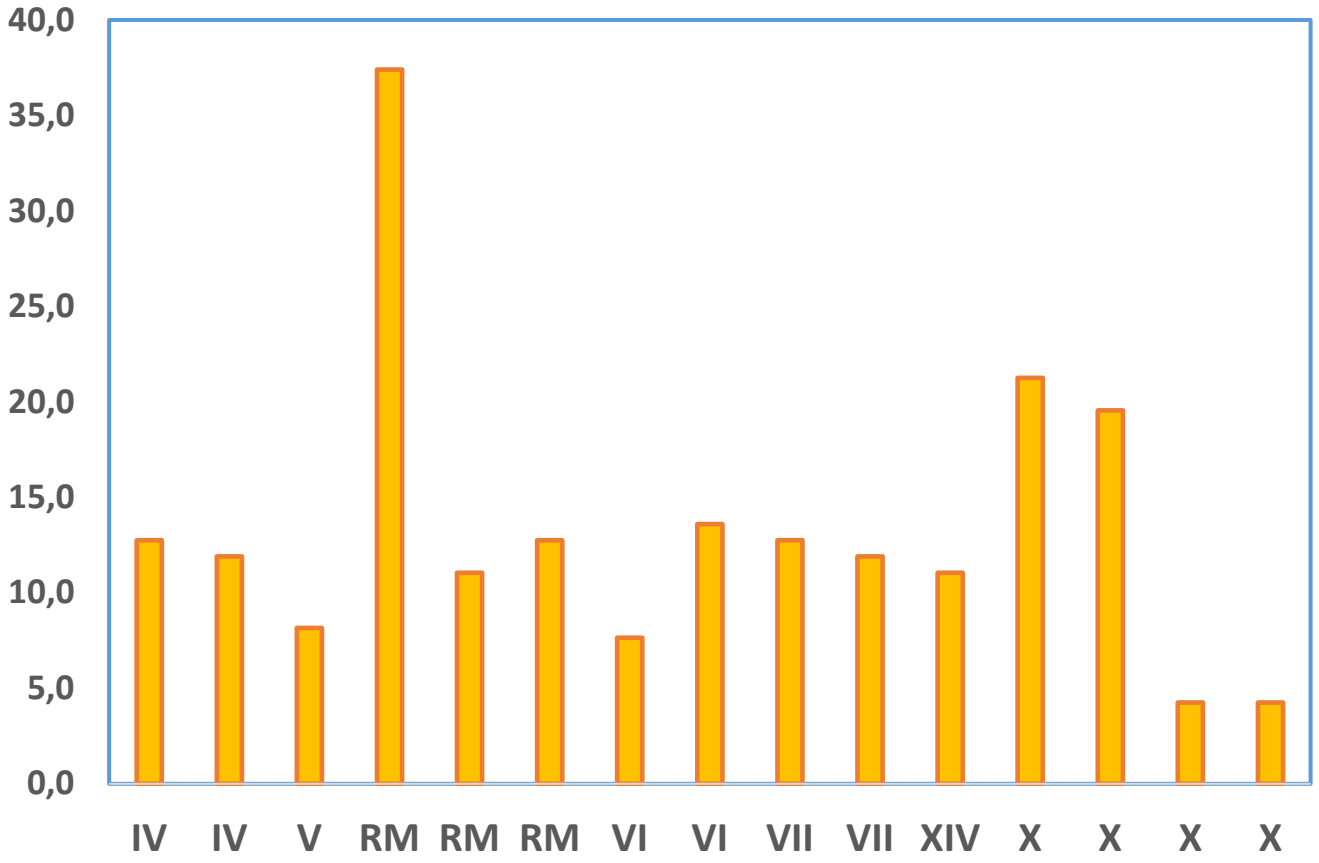
Péptido antibacteriano


Proteínas totales en mieles de Chile en ug/g
1800
1600
1400
1200
1000
800
600
400
200
0
Elqui
Illapel
Hanga Roa
Lonquén
Rauco
Rauco b
Pucón
Valdivia
Puerto Varas
Castro

Generación de peróxido de hidrogeno en mieles provenientes de distintos lugares del mundo.

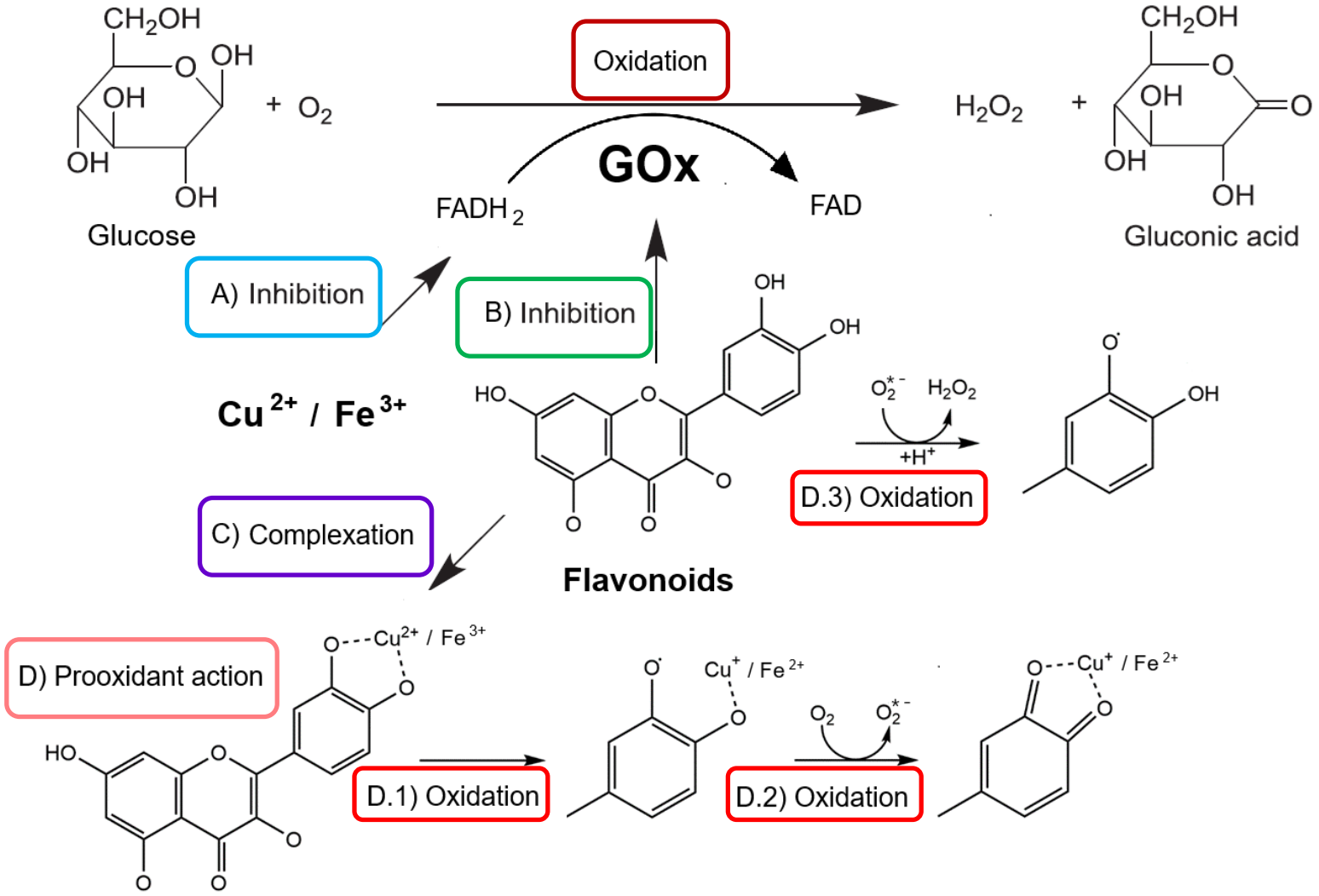
País de Origen	H_2O_2 (ug/g)	Dilución	Condiciones de incubación
Eslovaquia	**1-20**	40% p/v en agua	4 hrs a 37°C
Australia	**0,9-50**	30% p/v en agua	4 hrs a temperatura ambiente
Polonia	**1-51**	25% p/v en agua	1 hr a 37°C
Eslovaquia	**2-54**	40% p/v buffer pH 7	Sin incubación
Córcega	**4-9**	40% p/v en agua	30 min a temperatura ambiente
Portugal	**1-6**	40% p/v en agua	Sin información
Australia	**5-50**	30% p/v en agua	2 hrs a temperatura ambiente
Suiza	**17-68**	40% p/v buffer pH 7	Sin incubación
Canadá	**5-40**	16% p/v buffer pH 7	2 hrs a temperatura ambiente
Japón	**3-15**	10% p/v buffer pH 7	30 min a 37°C
Chile	**5-36**	20% p/v en agua	3 hrs a temperatura ambiente

Generación de H2O2 en mieles de Chile en ug/g



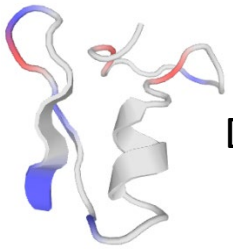
Assessment of role of glucose oxidase, flavonoids, copper and iron on the generation of hydrogen peroxide in honey

Food Research International 202 (2025) 115532



The potential mechanism of enzymatic and non-enzymatic H_2O_2 production in honey by action of GOx and autoxidation of flavonoids in the presence of Cu^{2+} or Fe^{3+}.

https://doi.org/10.1016/j.foodres.2024.115532



Desarrollo de un método analítico para la determinación de defensina-1 en miel.

Miel

Miel 20% m/v en Buffer Fosfato 0.15 M pH 6

12 mL

Procedimiento SPE-WCX

Extractos miel

Juntar extractos
Evaporación 40 °C
Reconstitución 1mL
H_2O MilliQ

Extracto concentrado

100 µL

20 µL

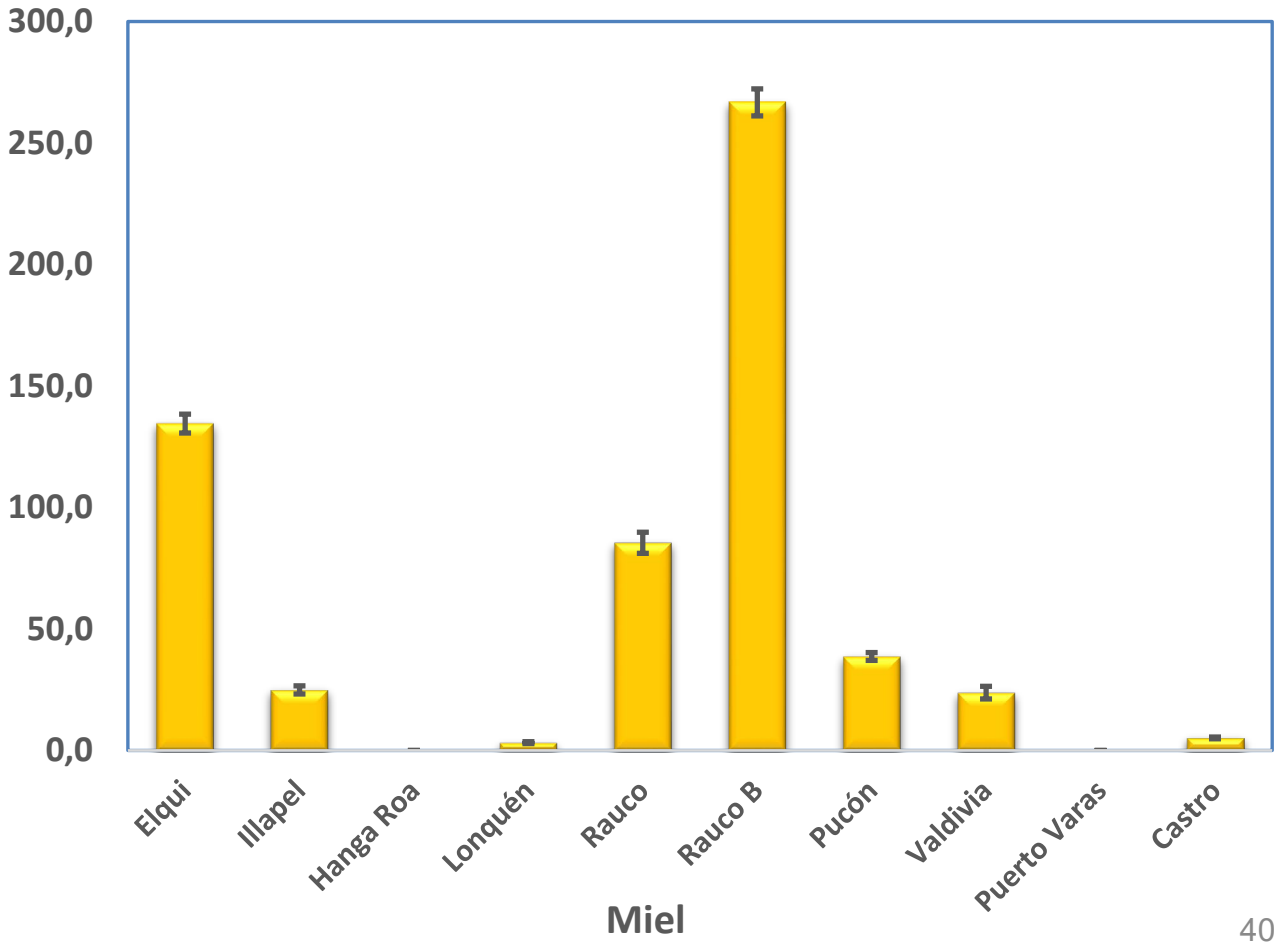
HPLC-FLD

Miel 20% m/v en Agua MilliQ

Determinación proteínas totales
Método de Bradford

Péptido antibacteriano

Concentraciones de defensina-1 en mieles de Chile en ug/g



Química Analítica

- Apoya **regulaciones sanitarias y ambientales**.
- Sustenta políticas públicas de **seguridad alimentaria y sostenibilidad**.
- Permite tomar decisiones basadas en **datos confiables y trazables**.
- Contribuye al desarrollo de **tecnologías limpias y alimentos seguros**.

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Ministerio de Ciencia, Tecnología, Conocimiento e Innovación
Gobierno de Chile

Proyectos Fondecyt 1190217 y 1240481