

Organochlorine pesticides determination in strawberries and jam using QuEChERS extraction and GC-MS/MS

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↳ Introduction

Minimize the negative effects of conventional cultivation

Conventional	<ul style="list-style-type: none"> • high productivity • deplete natural resources • degrade the environment • threaten human health
IPM	<ul style="list-style-type: none"> • reduce agricultural pollution • appropriate cropping techniques • ally insects and natural pesticides
Organic farming	<ul style="list-style-type: none"> • Without pesticides



Material & Methods

Equipment



GC-ECD-2010-*Shimadzu* coupled with the autosampler HTA 300 series

GC column: Teknokroma TRB-5MS (30 m x 0.25mm x 0.25 μ m)

Injector (splitless mode): 250°C
 ECD detector : 300°C
 Carrier gas: He
 Make up gas: N₂

Column programm		
Rate	Temperature	Hold Time
	65	2
8	160	
2	235	
15	250	



Trace GC ultra *Thermo* gas chromatograph (GC) with a Polaris Q ITMS detector.

GC column: 30 m x 0.25 mm x 0.25 μ m film thickness SLB™-5MS fused-silica column.

Injector (splitless mode): 240°C
 Transfer line: 250°C.
 Carrier gas: He

Column programm		
Rate	Temperature	Hold Time
	40	1
30	220	5
10	270	1

Material & Methods

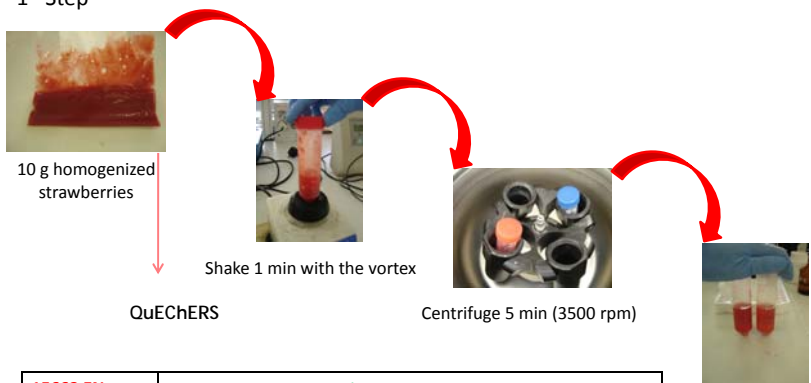
Sample preparation



Homogenized strawberries

Material & Methods

1st Step



10 g homogenized strawberries

QuEChERS

Shake 1 min with the vortex

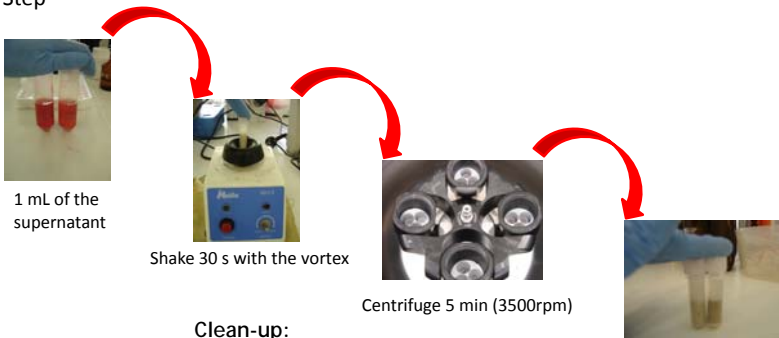
Centrifuge 5 min (3500 rpm)

15662 EN	4 g MgSO ₄ , 1.0 g NaCl, 1.0 g Na ₃ Citrate 2H ₂ O, 0.5 g Na ₂ HCitrate 1 ½ H ₂ O
15662 EN x 1.5	6 g MgSO ₄ , 1.5 g NaCl, 1.5 g Na ₃ Citrate 2H ₂ O, 0.75 g Na ₂ HCitrate 1 ½ H ₂ O
AOAC	6 g MgSO ₄ , 1.5 g NaAce

add 10 mL of acetonitrile

Material & Methods

2nd Step



1 mL of the supernatant

Clean-up:

Shake 30 s with the vortex

Centrifuge 5 min (3500rpm)


AOAC	150 mg MgSO ₄ ; 50 mg PSA; 50 mg C18
AOAC	150 mg MgSO ₄ ; 50 mg PSA
Other	150 mg MgSO ₄ ; 150 mg PSA; 50 mg C18

Inject 2 µL in GC

→ Results

GC-ECD

OCPs	15662 EN (%) n=3	15662 EN x 1.5 (%) n=3	AOAC -1 (%) n=3	AOAC -2 (%) n=3	AOAC -3 (%) n=3
HCB	133	123	134	131	129
Lindane	157	150	155	134	140
Aldrin	94	84	71	87	85
4.4' DCBP	97	93	100	84	93
Endosulfan I	93	102	98	96	95
Dieldrin	94	99	93	94	92
p-p' DDE	62	48	39	47	52
Endrin	107	123	114	114	113
Endosulfan II	107	117	115	108	109
p-p' DDD	106	107	96	98	97
o-p' DDT	88	94	80	85	86
Methoxychlor	82	91	81	82	85



→ Material & Methods

QuEChERS - EN 15662

4 g MgSO₄,

1.0 g NaCl,


1.0 g Na₃Citrate 2H₂O,

0.5 g Na₂HCitrate 1 ½ H₂O


Clean-up: 150 mg PSA
150 mg MgSO₄
50 mg C18

↳ Results


Strawberries - Recoveries



Pesticides	Spiking levels		
	0.03 µg/kg (n=3)	0.09 µg/kg (n=3)	0.18 µg/kg (n=3)
HCB			
Lindan			
Aldrin			
4,4' DCBP	>99 %	>80 %	>91 %
α-Endosulfan			
Dieldrin			
p-p' DDE	51 %	46 %	54 %
Endrin			
β-Endosulfan			
p-p' DDD	>94 %	>89 %	>108 %
o-p' DDT			
Methoxychlor			




↳ Material & Methods





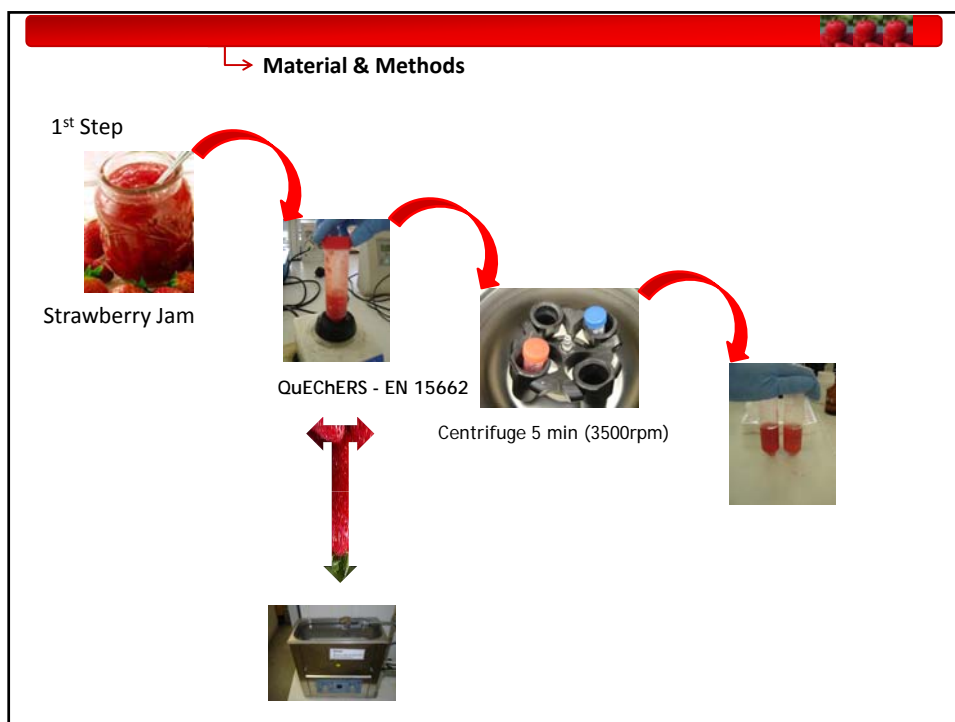
QuEChERS - EN 15662

4 g MgSO₄, 1.0 g NaCl,
1.0 g Na₃Citrate 2H₂O,
0.5 g Na₂HCitrate 1 ½ H₂O

Clean-up: 150 mg PSA
150 mg MgSO₄
50 mg C18


Strawberry jam - Recoveries		Results	
			Jam (%) (n=3)
 <p>QuEChERS EN 15662</p>	HCB	47	
	Lindan	43	
	Aldrin	62	
	4,4-DCBP	77	
	Endosulfan I	59	
	Dieldrin	62	
	p-p' DDE	49	
	Endrin	48	
	Endosulfan II	69	
	p-p' DDD	77	
	o-p' DDT	67	
	Methoxychlor	95	


Strawberry jam - Recoveries		Results	
		Jam (%) (n=3)	Homogenized jam (%) (n=3)
 <p>QuEChERS EN 15662</p> 	HCB	47	56
	Lindan	43	60
	Aldrin	62	77
	4,4-DCBP	77	80
	Endosulfan I	59	76
	Dieldrin	62	77
	p-p' DDE	49	66
	Endrin	48	65
	Endosulfan II	69	87
	p-p' DDD	77	101
	o-p' DDT	67	91
	Methoxychlor	95	98

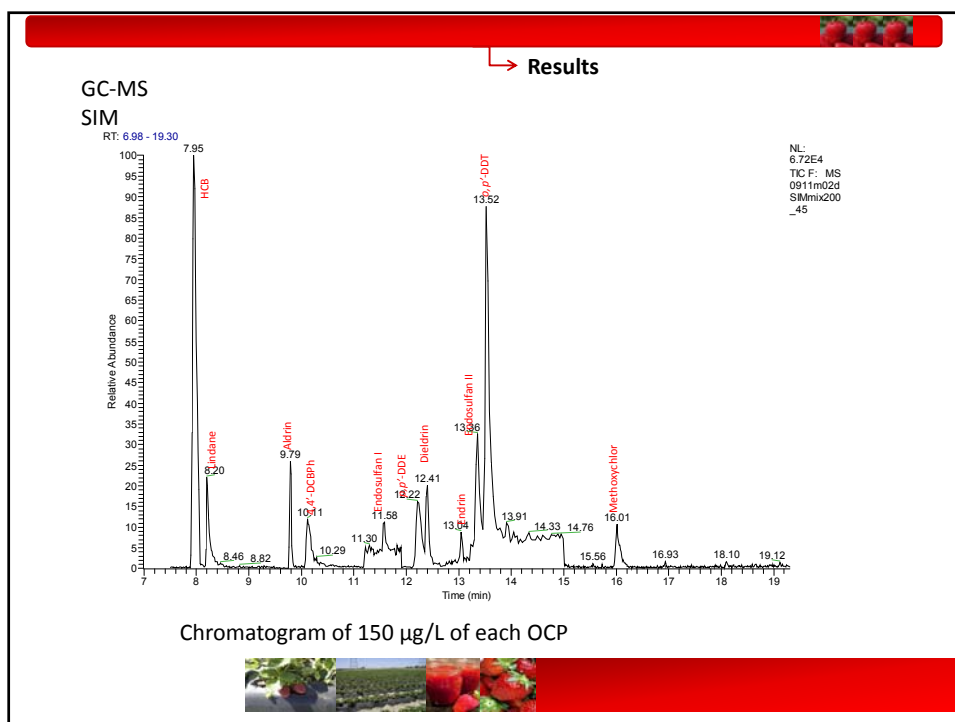
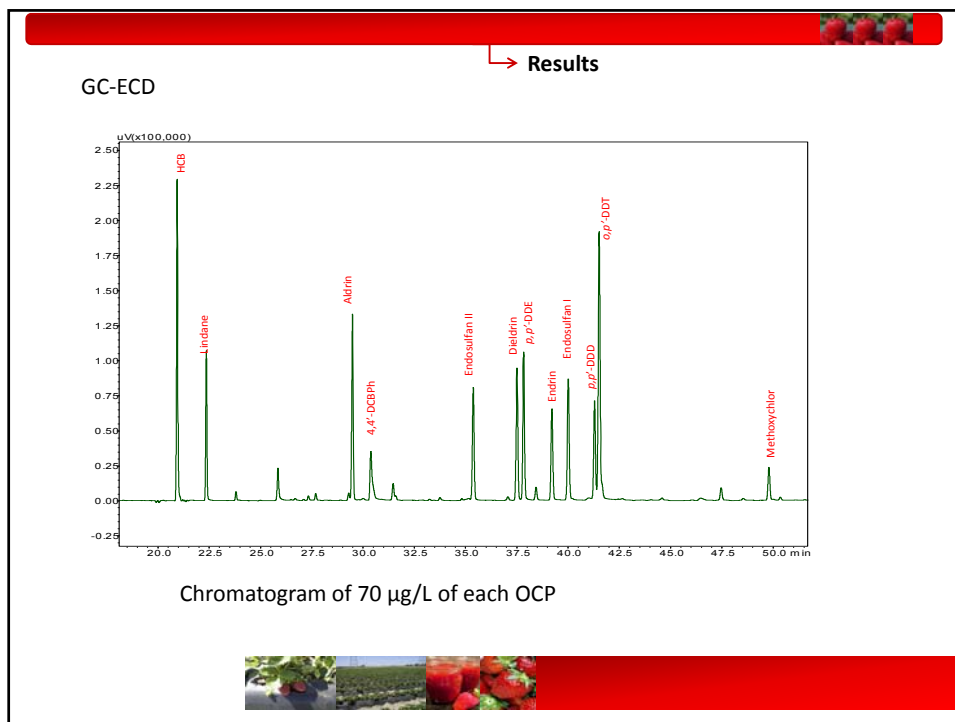


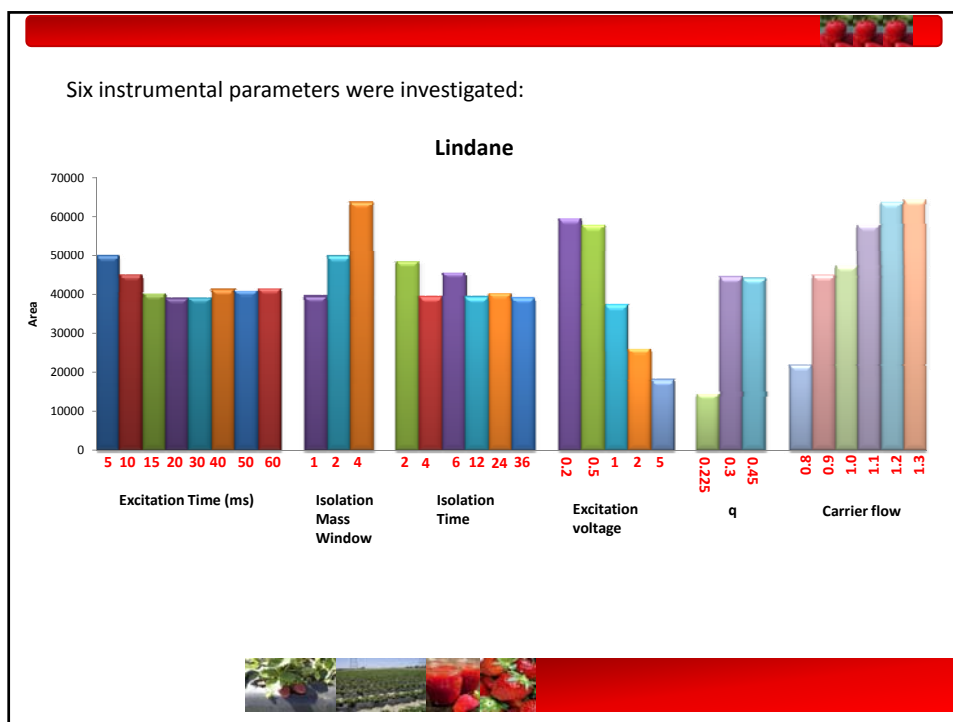
Results

Strawberry jam - Recoveries

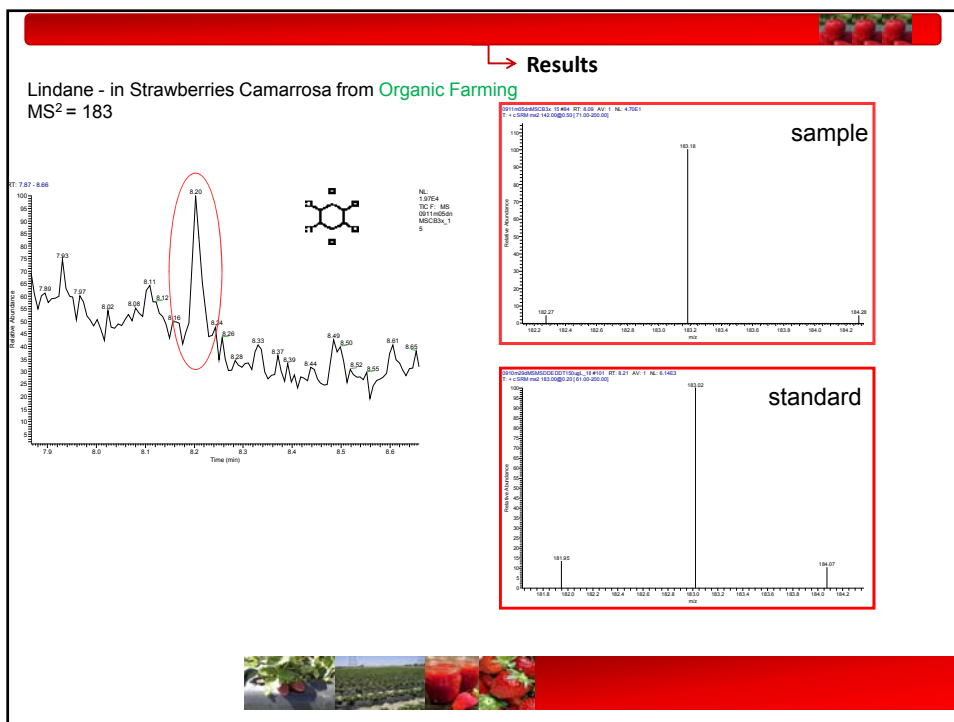
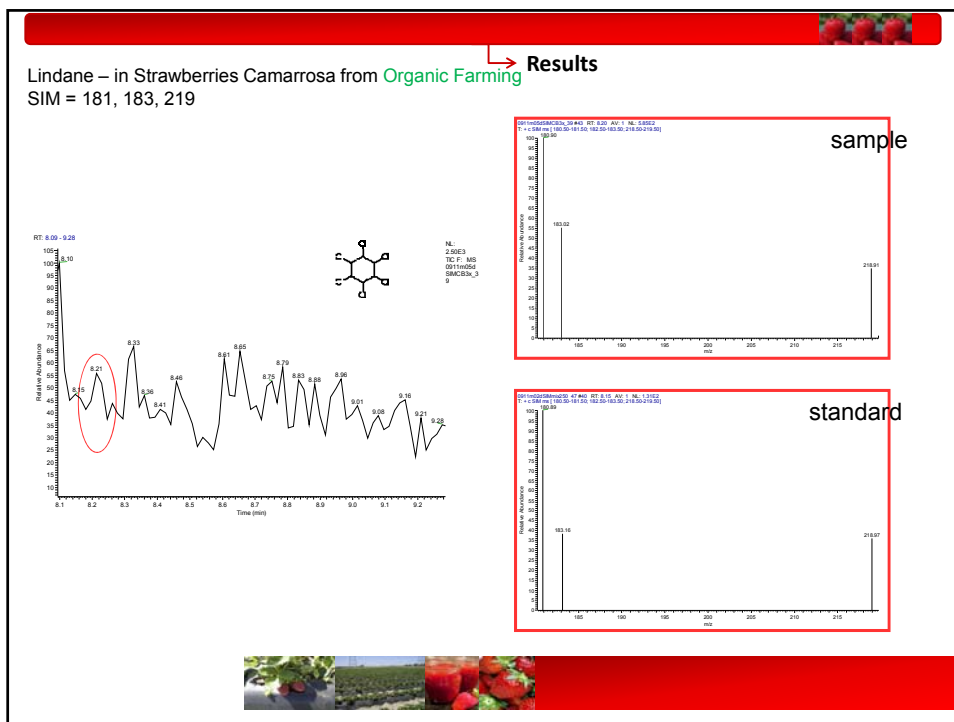
	Jam (%) (n=3)	Homogenized jam (%) (n=3)	Homogenize jam Ultrasonic bath (%) (n=3)
	HCB	47	56
	Lindan	43	60
	Aldrin	62	77
QuEChERS EN 15662	4,4-DCBP	77	80
	Endosulfan I	59	76
	Dieldrin	62	77
	p-p' DDE	49	66
	Endrin	48	65
	Endosulfan II	69	87
	p-p' DDD	77	101
	o-p' DDT	67	91
	Methoxychlor	95	98

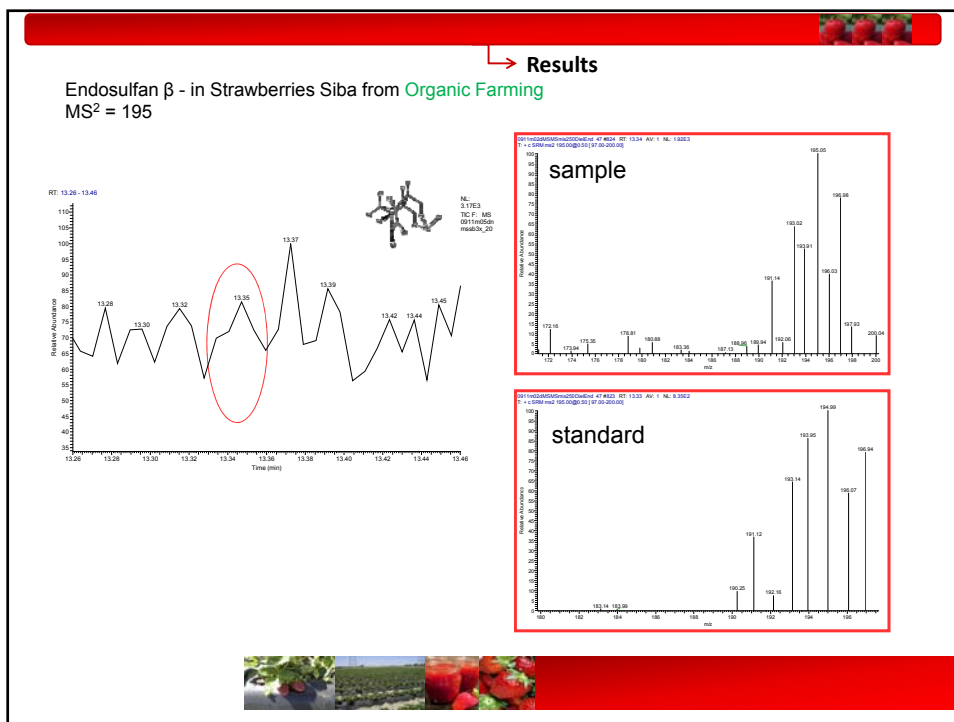
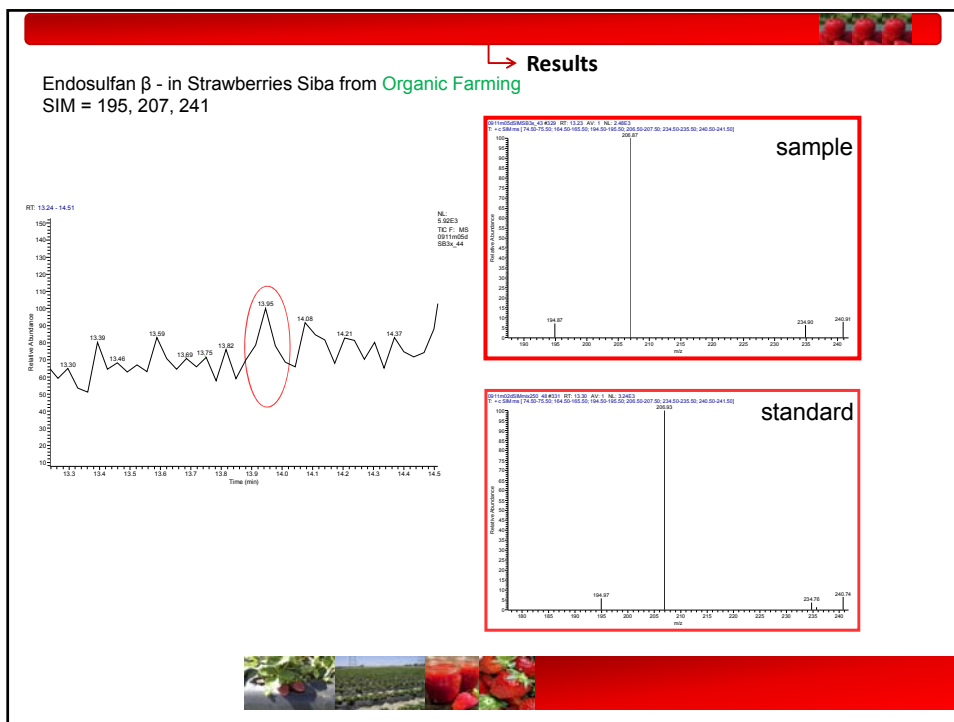






Segment	Time retention	SRM	Results			
			Precursor ion MS (m/Z)	LOD ECD (µg/Kg)	LOD GC-MS (µg/Kg)	LOD GC-MS/MS (µg/Kg)
HCB	1	142, 284, 286	142	7.44	9.20	7.65
Lindane	2	181, 183, 219	183	7.08	9.10	9.03
Aldrin	3	66, 263, 293	263	5.05	8.20	5.99
4.4' DCBP	4	111, 139, 250	139	8.08	9.30	9.00
Endosulfan I	5	195, 207, 241	195	8.58	9.90	8.76
p-p' DDE	6	176, 246, 318	318	5.61	9.50	7.50
Dieldrin		79, 263, 277	243	4.48	9.60	8.02
Endrin	7	81, 263, 281	245	7.14	8.70	7.80
Endosulfan II	8	195, 207, 241	195	5.61	8.60	7.64
o-p' DDT		165, 235, 354	235	6.18	9.90	6.02
Methoxychlor	9	227, 237	227	8.68	9.32	7.86





Results					
Strawberries samples	Organic farming ($\mu\text{g}/\text{Kg}$)			IPM $\mu\text{g}/\text{Kg}$	
	Siba	Camarosa	Festival	Camarosa	Festival
HCB	nd	nd	nd	nd	nd
Lindan	13	27.3	3.86	14.6	3.73
Aldrin	nd	1.19×10^{-3}	1.38	0.65	nd
Endosulfan I	nd	nd	nd	nd	nd
Dieldrin	nd	nd	nd	nd	nd
p-p' DDE	nd	nd	0.11 < LOD	0.12 < LOD	0.1 < LOD
Endrin	4.94	nd	nd	0.13 < LOD	nd
Endosulfan II	7.02	5.34	1.97	3.52	3.44
p-p' DDD	0.37 < LOD	0.38 < LOD	0.09 < LOD	0.33 < LOD	0.22 < LOD
o-p' DDT	0.68 < LOD	0.54 < LOD	0.15 < LOD	0.11 < LOD	0.04
Methoxychlor	1.26	1.38	0.65 < LOD	1.36	0.92 < LOD

MRL = 10 $\mu\text{g}/\text{Kg}$

Results									
Strawberry jam	Commercial products				Traditional products				Organic farming products
	$\mu\text{g}/\text{Kg}$				$\mu\text{g}/\text{Kg}$				
	C ₁	C ₂	C ₃	C ₄	T ₁	T ₂	T ₃	T ₄	OF ₁
HCB	1.11	0.962	nd	nd	nd	nd	nd	nd	nd
Lindan	0.901	1.34	nd	nd	nd	0.873	nd	nd	nd
Aldrin	0.382	nd	nd	nd	0.489	nd	nd	nd	nd
Endosulfan I	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dieldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd
p-p' DDE	nd	nd	nd	nd	nd	nd	nd	nd	nd
Endrin	nd	nd	nd	nd	nd	nd	nd	nd	nd
Endosulfan II	nd	nd	nd	nd	nd	nd	nd	nd	nd
p-p' DDD	nd	nd	nd	nd	nd	nd	nd	nd	nd
o-p' DDT	nd	nd	nd	nd	nd	nd	nd	nd	nd
Methoxychlor	nd	nd	nd	nd	nd	nd	nd	nd	nd


↳ Conclusions

- Good calibration curves linearity were achieved
- The sample preparation procedures can be applied to strawberries for organochlorine pesticide analysis
- An additional step is required for the extraction of organochlorine compounds in jams
- GC-ECD in the method is more suitable for quantification of lower levels, never excusing confirmation by GC-MS
- The GC-MS/MS method can be used for quantification and confirmation with satisfactory sensitivity
- Compared to a GC-MS/SIM method, the GC-MS/MS method provides better sensitivity and confirmation
- Lindane was found in organic and IPM at higher concentration than MRLs


Acknowledgements

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Thank you for listening!

