

# QuEChERS optimization

## GC-MS/MS determination of pesticides in feedingstuffs

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Validation for wheat, lupine and rapeseed cake

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# QuEChERS method

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- **prEN 15662:2007**

Foods of plant origin – Determ. of pesticides residues using GC-MS and/or LC-MS/MS following acetonitrile extraction and cleanup by dispersive SPE – QuEChERS-method

- **Accredited SOP**

certificate No. 470/2007 (CAI, EN ISO 17025:2005)

- **Instruments**

- **GC-MS/MS** CP3800/V1200 (Varian)
- **LC-MS/MS** HP1200/Esquire 600 (Bruker)
- **LC-MS/MS** Quatro Premier (Waters)

# Sample preparation

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## □ Extraction

- 5 g sample
- + 10 ml AcCN+ 10 ml water
- + ISTD

*Sufficient ratio AcCN: water*

- 1:1 (wheat, pease)
- 1:1,5 (bran, rapeseed)
- 1:2 (lupin)
- add buffer-salt mixture
- shake
- centrifuge

## □ Extract cleaning

- Aliquot for LC/MS
- **Aliquot for GC/MS**
  - Freezing out
  - Dispersive SPE (PSA, GCB, ODS)
  - Extract stabilization (formic acid)

# GC/MS Determination

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- Internal standard: TCP
- Injection ISTD: PCB185
- Matrix calibration
- MS mode
  - SIM (screening)
  - MS/MS (evaluation)

# Method validation

Analytes	MS/MS	Recovery (RSD) (%)		
		Wheat	Lupin	Rapeseed cake
<b>Bifenthrin</b>	181→166	88 (3,5)	71 (1,0)	95 (7,1)
<b>Cypermethrin</b>	163→127	105 (3,7)	82 (1,9)	95 (10,3)
<b>Cyproconazole</b>	222→125	93 (0,9)	108 (1,6)	101 (0,1)
<b>Deltamethrin</b>	253→174	101 (6,8)	75 (6,8)	105 (6,5)
<b>Diazinon</b>	304→179	100 (5,3)	115 (3,5)	103 (7,4)
<b>Difenoconazole</b>	323→265	100 (7,8)	108 (4,1)	112 (0,4)
<b>Fenhexamid</b>	301→266	55,3 (5,4)	87 (19,5)	117 (4,0)
<b>Fluquinconazole</b>	340→298	93 (7,9)	111 (5,9)	107 (3,4)
<b>Chlorpyrifos</b>	314→258	93 (5,9)	94 (2,0)	73 (2,0)
<b>Chlorpyrifos-M</b>	286→271	96 (6,2)	99 (2,3)	89 (4,8)
<b>Iprodione</b>	314→245	109 (7,3)	104 (4,5)	102 (13,8)
<b>Kresoxim-M</b>	206→116	88 (9,2)	119 (4,2)	109 (6,8)
<b>L-cyhalothrin</b>	197→141	98 (2,1)	82 (3,4)	89 (1,3)
<b>Malathion</b>	173→127	94 (8,6)	114 (1,8)	79 (7,1)
<b>Metconazole</b>	250→125	83 (8,6)	112 (19,8)	116 (15,6)
<b>Parathion</b>	291→263	101 (6,1)	96 (2,7)	97 (17,5)
<b>Permethrin</b>	183→168	93 (10,1)	71 (10,0)	92 (7,6)
<b>Pirimicarb</b>	238→166	105 (9,1)	110 (2,3)	116 (7,1)
<b>Pirimifos-M</b>	290→233	96 (6,3)	103 (1,3)	94 (7,5)
<b>Procymidone</b>	283→255	109 (4,3)	117 (5,3)	114 (13,9)
<b>Tebuconazole</b>	250→125	100 (15,3)	103 (3,2)	114 (11,3)
<b>Vinclozolin</b>	285→212	103 (4,8)	118 (3,7)	103 (9,6)

## Cleanup selection

## legume extracts

Analytes	Recovery (RSD) (%)		
	PSA	PSA + GCB	PSA + GCB + ODS
<b>Bifenthrin</b>	50 (4,0)	71 (1,0)	69 (2,2)
<b>Cypermethrin</b>	70 (6,2)	82 (1,9)	93 (3,2)
<b>Cyproconazole</b>	95 (1,6)	108 (1,6)	105 (2,8)
<b>Deltamethrin</b>	71 (1,1)	75 (6,8)	95 (8,4)
<b>Diazinon</b>	92 (3,2)	115 (3,5)	973 (8,3)
<b>Difenoconazole</b>	99 (0,2)	108 (4,1)	108 (5,1)
<b>Fenhexamid</b>	78 (6,0)	87 (19,5)	91 (24,2)
<b>Fluquinconazole</b>	99 (5,0)	111 (5,9)	112 (6,4)
<b>Chlorpyrifos</b>	74 (3,2)	94 (2,0)	78 (9,9)
<b>Chlorpyrifos-M</b>	78 (4,2)	99 (2,3)	87 (6,3)
<b>Iprodione</b>	93 (8,0)	104 (4,5)	95 (1,2)
<b>Kresoxim-M</b>	97 (3,7)	119 (4,2)	107 (6,3)
<b>L-cyhalothrin</b>	70 (4,6)	82 (3,4)	92 (1,53)
<b>Malathion</b>	102 (1,6)	114 (1,8)	113 (6,3)
<b>Metconazole</b>	95 (13,8)	112 (19,8)	90 (12,6)
<b>Parathion</b>	761 (0,3)	96 (2,7)	98 (4,5)
<b>Permethrin</b>	51 (2,8)	71 (10,0)	74 (1,4)
<b>Pirimicarb</b>	106 (7,2)	110 (2,3)	101 (14,81)
<b>Pirimifos-M</b>	85 (2,1)	103 (1,3)	92 (9,9)
<b>Procymidone</b>	108 (2,2)	117 (5,3)	116 (6,8)
<b>Tebuconazole</b>	90 (10,1)	103 (3,2)	106 (5,3)
<b>Vinclozolin</b>	99 (6,1)	118 (3,7)	101 (15,3)

# Cleanup selection for legume extracts

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<b>Pesticide group</b>	<b>Recovery (RSD) (%)</b>		
	<b>PSA</b>	<b>PSA + GCB</b>	<b>PSA + GCB + ODS</b>
<b>Pyrethroids</b>	62 (4)	76 (5)	85 (3)
<b>Organo-P</b>	85 (2)	103 (2)	92 (8)
<b>Triazoles</b>	96 (6)	108 (7)	104 (6)
<b>Dicarboximides</b>	100 (5)	113 (4)	104 (8)
<b><i>Total method</i></b>	<b>85 (4)</b>	<b>100 (5)</b>	<b>96 (7)</b>

# Matrix effects

Matrix effect (%)	Wheat	Lupin	Rapeseed cake	
	MS/MS	MS/MS	MS/MS	SIM
<b>Bifenthrin</b>	89	83	135	162
<b>Cypermethrin</b>	82	100	147	143
<b>Cyproconazole</b>	114	88	160	-
<b>Deltamethrin</b>	109	104	76	174
<b>Diazinon</b>	93	84	144	147
<b>Difenoconazole</b>	110	114	132	172
<b>Fenhexamid</b>	78	143	160	204
<b>Fluquinconazole</b>	96	88	94	101
<b>Chlorpyrifos</b>	86	88	121	131
<b>Chlorpyrifos-M</b>	101	119	115	157
<b>Iprodione</b>	97	147	106	113
<b>Kresoxim-M</b>	83	87	125	150
<b>L-cyhalothrin</b>	108	105	102	92
<b>Malathion</b>	95	102	107	114
<b>Metconazole</b>	118	149	136	149
<b>Parathion</b>	91	156	153	183
<b>Permethrin</b>	103	103	108	130
<b>Pirimicarb</b>	91	102	141	189
<b>Pirimifos-M</b>	70	97	120	130
<b>Procymidone</b>	107	96	224	493
<b>Tebuconazole</b>	108	93	147	157
<b>Vinclozolin</b>	72	98	137	175
<b>Average</b>	<b>96</b>	<b>107</b>	<b>132</b>	<b>166</b>



# Conclusion

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- Suitability of the QuEChERS cleanup for various feed materials
- MS/MS mode for pesticide determination in complex feedingstuffs