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National Food Institute
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Validation Report 40

Determination of pesticide residues in wheat, rivce, rye, and oat by LC-MS/MS and GC-MS/MS

(QuEChERS method)

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January 2023

CONTENT:

1. Introduction

This report describes the validation of the QuEChERS method combined with GC-MS/MS and LC-MS/MS. The method was tried validated for 62 pesticides and metabolites by both gas and liquid chromatography combined with triple quadrupole in four different cereal matrixes (wheat, rice, rye and oat). The pesticides and/or metabolites included in the validation study are shown in Appendix 3.

2. Principle of analysis

Sample preparation

Blank samples of wheat, rice, rye, and oat were milled with a sieve at 1 mm and stored at -80°C. Five gram was weighted accurately in a 50 mL polypropylene PP tube. Ceramic homogenizers were inserted in each tube before adding 10 mL of cold water and 10 mL of acetonitrile. Samples were mechanically shaken for 5 minutes by a Ginogrinder. Prepared mixture of salts, containing 4 g $MgSO_4$, 1 g NaCl, 1 g Na_3 citrate dihydrate and 0.5 g Na_2H citrate sesquihydrate, were added to the samples. Tubes were shaken mechanically for another minute and then centrifuged for 10 minutes at 4500 rpm. Eight millilitre of supernatant were transferred in a clean tube and placed in -80°C freezer for at least 1 hour. After freezing-out the samples were removed from freezer, thawed and centrifuged at 5°C for 10 minutes at 4500 rpm.

Appropriate amount of extract was transfer for the LC analyses and another 6 mL extract were transferred to a 15 ml single use centrifuge tube containing 150 mg PSA and 900 mg $MgSO_4$, shaken 30 seconds and centrifuged five minutes at 4500 rpm. After centrifugation step 4 ml was transfer in a clean 15 ml tubes containing 40 µl of 5% formic acid and analysed on GC.

GC-MS/MS parameters

For gas chromatographic separation, a Thermo Scientific™ Trace™ 1310 Gas Chromatograph coupled to a Thermo Scientific™ TriPlus™ RSH autosampler was used. The samples were injected in a programmable temperature vaporizer (PTV) mode through a PTV baffle liner 2×2.75×120 mm for Thermo GCs (Siltek). The injection volume was 1 µL and the injection temperature was set to 70°C. Helium as used as carrier gas at a flow of 1.2 $ml.min^{-1}$. The analytes were separated on a TG-5SILMS (capillary column of 30 m long, 0.25 mm inner diameter and a film thickness of 0.25 µm). The oven temperature program was as follows: 60°C for 1.5 min, up to 90°C at 25°C/min for 1.5 min, up to 180°C at 25°C /min, then up to 280°C at 5 °C/min and finally up to 300°C at 10°C/min and for 12 min. The total runtime was 42 min. For the mass spectrometric analysis, a Thermo Scientific™

TSQ^{TM} 8000 Evo was used. The instrument has been upgraded with and Advanced Electron ionisation source, (AEI). The AEI source was operated with an electron energy of 50 eV. The analyses were performed by a triple quadrupole operating in the SRM mode (Selected Reaction Monitoring). The source temperature was set at 300°C, and the transfer line, at 280°C.

LC-MS/MS parameters

For liquid separation, a LC system Thermo Ultimate 3000 and the mass spectrometer Bruker EVOQ. The analytes were separated on a Accuity UPLC BEH C18 1.7 µm, 2.1*100 mm reversed-phase column. The injection volume was **2** µl. The eluents consisted of milli-q water with 0,1% formic acid and 5 mM ammonia solution (A eluent) and methanol (B eluent) and a flow rate of 0.4 ml/min was applied. The analytes were separated using a gradient elution program. In this program the column is equilibrated with 2% B eluent before injection. At the time of injection the B eluent is increased to 35% within 0.1 min and then increased further reaching 98% at a run time of 7 min. The 98% of B eluent is then maintained for 3 minutes before the proportion is lowered again to 2% within 0.1 min and maintained until a total run time of 13 min in order to prepare the column for the next injection. The mass spectrometer was operated in multiple reaction monitoring mode and using both + and negative electrospray ionization.

3. Validation

Validation design

The method was validated for 55 compounds (pesticides or/and metabolites) in four different matrices (wheat, rice, rye, and oat). The validation was performed on 5-6 replicates at each of the four cereals matrices, and at four spiking levels of 0.002, 0.005, 0.01 and 0.05 mg/kg. Extraction of a blank sample were included for all commodities.

Calibration curves and linearity

Linearity study was performed by using matrix-matched calibration curve prepared in 5 concentrations for each one of the compounds within the range of 0.33 to 100 µg/L. The calibration curves were fitted to linear function and the deviation of the back–calculated concentration of the calibration standards from the true concentrations were within ±20%.

All quantifications were performed using bracketing matrix matched calibration curves.

Specificity

The ion ratios for sample extracts were within ±30% (relative) of average of relevant calibration standards from same sequence. The ion ratios may vary slightly depending on concentration level and in some cases the average of calibration standard was based on the lower calibration levels for the low spike samples.

Accuracy – Recovery

Recovery values were calculated as average recovery of 5-6 replicates for each level (0.002, 0.005, 0.01, and 0.05 mg/kg) and matrices. Accepted recovery range was between 70 and 120% (following SANTE document)[3]. Values outside this range have been accepted if the precision data was satisfactory.

Precision – repeatability and internal reproducibility

Repeatability and internal reproducibility were calculated for all pesticides and degradation products on all four spiking levels (0.002, 0.005, 0.01 and 0.05 mg/kg) as given in ISO 5725-22. Accepted values were ≤ 20%.

Limit of quantification, LOQ

The Limit of quantification (LOQ) was determined as the lowest spiked level for which the acceptance criteria were met (average relative recovery between 70 and 120% and precision lower than or equal to 20%), and ion ratios for sample extracts were within ±30% (relative) of average of relevant calibration standards.

4. Results and conclusion

A total of 54 compounds were successfully validated using QuEChERS method. Nine compounds were validated on both GC-MS/MS and LC-MS/MS, 13 compounds were only validated ong GC-MS/MS and 36 only on LC-MS/MS. All the validation data for the pesticides and/or metabolites and four different matrices are presented in appendix 2. Seven compounds (chloridazon-desphenyl, diclofop, dithianon, eugenol, MCPA, MCPB and thymol) did not fulfil the criteria for validation using the above levels and method conditions.

An LOQ of 0.002 mg/kg was achieved for 29 compounds. An LOQ of 0.005 was achieved for three compounds (azadiractin, PCP and pinoxaden metabolite SYN505164 -1), and an LOQ of 0.01 mg/kg was obtaeined for chloramben.

Twenty-two compounds included in this study were previously validated and an LOQ of 0.005 mg/kg was demonstrated. However, to lower the LOQs, these compounds were included in this validation and the LOQs were succefully lowered from 0.005 mg/kg to 0.002 mg/kg, except fenoxaprop-P, for which, the lowest LOQ still remains at 0.005 mg/kg.

Some compounds did not have the same sensitivity in all the matrices. Azadiractin was validated in wheat, rice and rye a LOQ 0.005 mg/kg, but it could not be validated in oat. Chloramben was validated in rice and rye (LOQ 0.001 mg/kg) but not in wheat and oat. Cyprazine, flupyradifurone, hexaconazole could not be validated in wheat, although they were validated in the other matrices at LOQ 0.002 mg/kg. Trifloxysulfuron (sodium) had a LOQ of 0.002 for wheat and rye but it could not be validated for rice and oat.

The majority of the combined uncertainties were lower than 50%.

5. References

1. EN 15662:2008. Foods of plant origin - Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE - QuEChERS-method

2. ISO 5725-2:1994. Accuracy (trueness and precision) of measurement methods and results – Part 2. Basic method for the determination of repeatability and reproducibility of standard measurement method. First edition. December 1994.

3. Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed, Document SANTE/ 11312 /2021.

Appendix 1A. GC-MS/MS conditions

Retention time, Rt, precursor mass, product mass, and collision energy (CE).

Pesticide	Rt	Precursor	Product	CE	Precursor	Product	CE
2-phenylphenol	9.7	170.0	115.0	35.0	170.0	141.0	25.0
Benfluralin	10.92	292.0	159.7	20.0	292.0	206.1	10.0
Bifenazate	22.24	258.0	196.1	12.0	258.0	199.1	12.0
Chlormephos	9.02	154.0	65.0	16.0	154.0	121.0	5.0
Dazomet	11.66	162.0	44.0	18.0	162.0	89.0	6.0
Dichlofenthion	13.33	222.9	205.0	12.0	250.9	223.0	8.0
Dieldrin	18.02	262.8	192.9	30.0	276.9	206.9	20.0
Disulfoton	12.57	185.9	96.9	16.0	186.0	153.0	5.0
Endosulfan-alpha	17.19	158.9	123.0	12.0	194.7	125.0	22.0
Ethalfluralin	10.72	276.0	202.0	14.0	276.0	248.1	8.0
Ethoxyquin	11.73	174.1	131.2	18.0	174.1	146.1	12.0
Fenchlorphos	13.94	124.9	47.0	12.0	124.9	79.0	6.0
Flonicamid	10.17	146.0	126.0	8.0	174.0	69.0	36.0
Fluacrypyrim	19.42	189.1	101.1	25.0	189.1	129.1	10.0
Furalaxyl	16.26	146.1	105.1	10.0	152.1	122.1	5.0
Orbencarb	14.3	100.1	72.1	5.0	125.0	89.0	10.0
Propazine	11.9	214.1	94.0	15.0	214.1	172.1	5.0
Quinoxyfen	20.21	237.0	208.0	26.0	271.8	237.1	12.0
Simetryn	13.73	170.1	111.1	15.0	170.1	155.1	5.0
Tetrasul	19.64	251.9	173.0	34.0	251.9	181.9	32.0

Appendix 2B. LC-MS/MS conditions;

Ionisation mode, retention time, Rt, precursor mass, product mass, and collision energy(CE).

Pesticide	ESI mode	Rt	Precursor	Product	CE	Precursor	Product	CE
Azadiractin	+	4.3	703.5	585.0	-12.0			
Azadiractin -	-	4.3	765.5	719.3	10.0			
Bensulfuron Methyl	+	4.9	411.0	119.0	-33.0	411.0	149.0	-17.5
Bifenazate	+	5.7	301.0	170.0	-17.0	301.0	198.0	-8.0
Bifenazate-Diazene	+	6.7	299.0	213.1	-8.0	299.0	196.1	-21.0
Chloramben	-	2.7	204.0	159.9	4.0	204.0	35.3	11.0
Chlortoluron	+	4.4	213.0	72.0	-16.0	213.0	46.0	-12.0
Chromafenozide	+	5.7	395.0	175.0	-18.0	395.0	339.0	-7.0
Cyanazine	+	3.8	241.0	214.0	-14.0	241.0	104.0	-28.0
Cymoxanil	+	3.1	199.0	128.0	-6.0	199.0	111.0	-16.0
Cyprazine	+	4.9	228.0	186.0	-14.0	228.0	108.1	-22.0
Desmethy-Chlorpirifos-Methyl	-	4.8	308.0	197.9	9.0	306.0	195.9	9.0
Dichlorvos	+	4.1	221.0	109.0	-16.0	238.0	221.0	-4.0
Dinotefuran	+	2.0	203.0	129.0	-10.0	203.0	157.0	-5.0
Disulfoton	+	6.8	275.0	61.0	-19.0	275.0	89.0	-5.5
Ethoxyquin	+	5.3	218.0	148.0	-20.0	218.0	174.0	-26.0
Fenoxaprop-P	-	6.6	333.0	152.0	18.0	333.0	260.9	9.0
Fenuron	+	2.9	165.0	72.0	-16.0	165.0	46.0	-14.0
Flupyradifurone	+	3.0	289.7	126.0	-15.0	289.7	91.2	-36.0
Furathiocarb	+	7.2	383.0	195.0	-15.0	383.0	252.0	-10.0
Halosulfuron-methyl	+	6.0	435.0	83.0	-43.0	435.0	182.0	-20.0
Hexaconazole	+	6.8	314.0	70.0	-12.5	314.0	159.7	-24.5
Lufenuron	-	7.5	509.0	339.0	11.5	509.0	326.0	18.0
Mefenacet	+	5.9	299.0	148.1	-11.0	299.0	120.2	-21.0
Metaflumizone	-	7.3	505.0	302.0	14.0	505.0	117.0	39.0
Metamitron	+	3.0	203.0	104.0	-17.0	203.0	145.0	-13.0
Monuron TCA	+	4.0	199.0	99.1	-19.0	199.0	72.0	-14.0
Neburon	+	6.7	275.0	88.0	-14.0	275.0	88.2	-21.0
Neburon	-	6.4	273.0	159.9	16.0	273.0	185.9	16.0
Novaluron	+	7.1	493.0	158.0	-20.0	493.0	141.0	-50.0
Orbencarb	+	6.8	258.0	125.0	-20.0			
Paraoxon metil	+	3.7	248.0	109.0	-25.0	248.0	202.0	-25.0
PCP	-	7.6	263.0	35.3	19.0	265.0	35.3	19.0
Pinoxaden Metabolite SYN502836 -1	-	3.0	345.0	173.0	30.0	345.0	158.0	39.0
Pinoxaden Metabolite SYN505164 -1	-	3.0	331.0	185.0	28.0	331.0	203.0	24.0
Propazine I	+	4.9	230.0	188.0	-14.0	230.0	146.0	-20.0
Propazine II	+	5.5	230.0	188.0	-14.0	230.0	146.0	-20.0
Quinoxyfen	+	7.6	308.0	161.9	-47.0	308.0	197.0	-31.0
Simetryn	+	4.3	214.0	68.2	-28.0	214.0	124.1	-17.0

Pesticide	ESI mode	Rt	Precursor	Product	CE	Precursor	Product	CE
Tebufenozide	+	6.4	353.0	133.0	-17.0	353.0	297.0	-7.5
Terbacil	-	4.3	215.0	158.9	13.0	215.0	42.3	23.0
Triazoxide	+	4.6	248.2	68.1	-37.0	248.2	95.0	-25.0
Trichlorfon	+	2.9	274.0	109.0	-19.5	274.0	127.0	-18.0
Triclopyr	-	5.5	254.0	196.0	11.0	254.0	218.0	6.0
Trifloxysulfuron (sodium)	+	4.8	460.0	178.0	-16.0	460.0	278.9	-14.0

Appendix 2. Validation results

Recoveries (Rec), repeatability (RSD_r), internal reproducibility (RSDR), expanded uncertainty (U) without correcting for recoveries and Limit of Quantification (LOQ) for pesticides validated on four cereal commodities, wheat (W) rice(Ri), rye (Ry) and oat(O), using QuEChERS.

	Pesticide	Spike level 0.002 mg/kg					Spike level 0.005 mg/kg					Spike level 0.01 mg/kg					Spike level 0.05 mg/kg					LOQ	Matrices
		Rec %	RSDr %	RSDR %	U %	Cu %	Rec %	RSDr %	RSDR %	U %	Cu %	Rec %	RSDr %	RSDR %	U %	Cu %	Rec %	RSDr %	RSDR %	U %	Cu %		
GC	**2-phenylphenol***	90	9	15	36	15	93	5	20	44	21	81	17	27	68	28	79	10	24	64	24	0.002	W, Ri, Ry,O
LC	**Azadiractin**	-	-	-	-	-	103	12	19	40	20	84	16	17	48	18	91	8	9	27	10	0.005	W[1], Ri, Ry[1]
LC	**Azadiractin (-)**	-	-	-	-	-	99	14	13	28	14	84	20	22	56	23	91	9	20	44	20	0.005	W[1], Ri
GC	**Benfluralin**	97	8	37	76	38	100	9	30	62	31	82	8	46	101	47	68	4	56	132	58	0.002	W, Ri, Ry,O
LC	**Bensulfuron Methyl***	95	14	19	40	19	98	10	22	44	22	92	16	18	41	19	92	11	14	32	14	0.002	W, Ri, Ry,O
LC	**Bifenazate**	89	6	-	-	-	63	7	-	-	-	50	13	-	-	-	41	6	-	-	-	0.002	Ri
GC	**Bifenazate***	97	4	15	31	15	92	6	21	45	21	88	9	12	34	12	85	7	15	43	15	0.002	W, Ri, Ry,O
LC	**Bifenazate-**	116	9	20	53	21	130	5	33	91	34	127	11	30	81	30	114	27	42	90	43	0.002	W, Ri, Ry,O
LC	**Chloramben**	-	-	-	-	-	-	-	-	-	-	97	20	40	83	42	72	9	14	63	14	0.01	Ri, Ry
GC	**Chlormephos**	85	15	27	64	28	101	10	20	41	20	106	12	14	31	14	107	11	14	31	14	0.002	W, Ri, Ry,O
LC	**Chlortoluron**	89	12	21	48	21	108	12	20	43	20	102	14	18	36	18	100	13	16	32	16	0.002	W, Ri, Ry,O
LC	**Chromafenozide**	92	11	19	43	20	98	6	6	13	6	94	13	12	28	13	103	10	19	39	19	0.002	W, Ri, Ry,O
LC	**Cyanazine**	88	9	18	44	18	100	8	18	36	18	102	14	14	30	15	97	15	15	31	15	0.002	W, Ri, Ry,O
LC	**Cymoxanil***	100	9	18	37	18	92	9	13	32	14	96	14	20	42	20	96	7	15	33	16	0.002	W, Ri, Ry,O
LC	**Cyprazine**	93	6	8	22	9	97	8	8	18	8	97	12	12	26	13	98	8	8	18	8	0.002	Ri, Ry,O
GC	**Dazomet**	86	7	34	76	35	75	4	20	64	20	68	9	11	68	12	68	8	11	68	11	0.002	W, Ri, Ry,O
LC	**Desmethy-Chlorpirifos-Methyl**	83	18	21	55	22	78	14	18	58	19	68	20	20	76	20	74	10	14	59	14	0.002	W, Ri, Ry,O
GC	**Dichlofenthion***	104	4	17	35	17	98	6	15	30	15	92	7	11	28	11	85	5	7	32	7	0.002	W, Ri, Ry,O
LC	**Dichlorvos***	88	15	22	51	22	98	7	13	26	13	94	12	12	27	12	94	9	9	23	9	0.002	W, Ri, Ry,O
GC	**Dieldrin**	92	7	16	36	16	94	7	18	38	18	87	7	8	31	8	84	5	9	38	10	0.002	W, Ri, Ry,O

	Pesticide	Spike level 0.002 mg/kg					Spike level 0.005 mg/kg					Spike level 0.01 mg/kg					Spike level 0.05 mg/kg					LOQ	Matrices
		Rec %	RSDr %	RSDR %	U %	Cu %	Rec %	RSDr %	RSDR %	U %	Cu %	Rec %	RSDr %	RSDR %	U %	Cu %	Rec %	RSDr %	RSDR %	U %	Cu %		
LC	**Dinotefuran***	113	8	13	37	13	96	12	16	34	16	101	14	17	35	17	92	7	9	25	9	0.002	W[1], Ri, Ry,O
GC	**Disulfoton**	94	5	26	55	27	88	5	20	47	20	82	9	16	48	16	81	5	9	43	9	0.002	W, Ri, Ry,O
LC	**Disulfoton**	81	10	33	77	34	95	11	13	29	13	85	14	15	42	15	88	11	10	32	11	0.002	W, Ri, Ry,O
GC	**Endosulfan-alpha**	96	6	19	41	20	94	6	17	36	17	89	8	10	30	11	86	4	5	31	5	0.002	W, Ri, Ry,O
GC	**Ethalfluralin**	98	19	28	57	29	111	11	48	100	49	74	10	38	94	39	75	5	58	128	59	0.002	W, Ri, Ry[1],O
GC	**Ethoxyquin**	75	5	33	84	33	56	11	51	137	52	45	13	39	135	40	37	15	59	174	60	0.002	W, Ri, Ry,O
LC	**Ethoxyquin**	-	-	-	-	-	92	8	9	25	9	53	13	12	98	12	35	31	47	163	49	0.005	Ry,O
GC	**Fenchlorphos***	108	17	19	42	20	94	10	14	31	14	82	10	11	42	11	90	5	20	46	20	0.002	W, Ri,O
LC	**Fenoxaprop-P***	-	-	-	-	-	108	14	17	39	18	90	17	18	41	18	89	8	15	38	15	0.005	W[1], Ri,
LC	**Fenuron**	93	8	17	38	18	99	8	18	37	19	98	12	18	37	18	96	8	13	28	13	0.002	W, Ri, Ry,O
GC	**Flonicamid***	118	3	22	58	22	102	6	10	21	10	97	7	16	33	16	91	6	15	35	15	0.002	W, Ri, Ry,O
GC	**Fluacrypyrim**	104	7	13	27	13	105	5	18	37	18	96	7	10	21	10	95	5	16	35	17	0.002	W, Ri, Ry,O
LC	**Flupyradifurone**	101	11	12	26	13	99	10	9	18	9	103	14	14	30	15	101	7	8	17	9	0.002	Ri, Ry,O
GC	**Furalaxyl**	105	3	18	38	18	105	5	19	40	20	96	8	12	25	12	94	4	16	34	16	0.002	W, Ri, Ry,O
LC	**Furathiocarb***	94	10	11	25	11	93	6	14	33	15	92	11	17	39	18	100	5	17	35	17	0.002	W, Ri, Ry,O
LC	**Halosulfuron-methyl**	97	8	17	36	18	102	6	15	32	16	95	14	16	34	16	93	9	13	30	13	0.002	W, Ri, Ry,O
LC	**Hexaconazole**	84	10	19	50	19	106	10	16	35	16	101	14	16	33	17	102	8	13	28	14	0.002	Ri, Ry,O
LC	**Lufenuron***	82	17	20	54	20	85	8	17	46	17	88	17	22	50	22	94	5	20	43	20	0.002	W, Ri, Ry,O
LC	**Mefenacet**	84	8	19	51	20	105	8	20	42	21	104	13	19	39	19	101	14	18	37	18	0.002	W, Ri, Ry,O
LC	**Metaflumizone***	94	11	21	44	21	99	11	13	27	13	93	11	15	34	15	95	7	18	37	18	0.002	W, Ri, Ry,O
LC	**Metamitron***	99	11	17	35	17	103	9	12	24	12	99	12	12	24	12	94	7	7	18	7	0.002	W, Ri, Ry,O
LC	**Monuron TCA**	91	9	19	42	19	100	8	19	38	19	99	13	17	35	18	96	8	13	27	13	0.002	W, Ri, Ry,O
LC	**Neburon**	90	16	15	37	15	103	13	14	29	14	95	15	17	36	17	90	8	12	32	13	0.002	W, Ri, Ry,O[1]
LC	**Neburon**	82	17	19	53	19	84	13	14	43	15	88	15	20	47	20	90	16	17	40	18	0.002	W, Ri, Ry,O
LC	**Novaluron***	103	10	10	21	10	104	9	19	39	19	98	18	20	41	21	98	15	18	37	19	0.002	W, Ri, Ry,O
GC	**Orbencarb**	98	6	14	28	14	97	7	14	30	15	90	9	10	28	10	87	4	13	37	14	0.002	W, Ri, Ry,O
LC	**Orbencarb**	78	13	26	68	26	112	7	23	53	24	109	14	19	43	20	101	24	23	48	24	0.002	W, Ry,O

	Pesticide	Spike level 0.002 mg/kg					Spike level 0.005 mg/kg					Spike level 0.01 mg/kg					Spike level 0.05 mg/kg					LOQ	Matrices
		Rec %	RSDr %	RSDR %	U %	Cu %	Rec %	RSDr %	RSDR %	U %	Cu %	Rec %	RSDr %	RSDR %	U %	Cu %	Rec %	RSDr %	RSDR %	U %	Cu %		
LC	**Paraoxon metil***	93	14	16	36	16	87	12	18	45	19	88	15	19	47	20	90	8	20	46	21	0.002	W, Ry,O
LC	**PCP****	-	-	-	-	-	113	16	16	43	17	88	19	18	45	19	80	16	20	57	20	0.005	W, Ri, Ry,O
LC	**Pinoxaden Metabolite SYN502836 -1**	-	-	-	-	-	94	12	17	37	17	93	14	21	45	21	80	9	17	53	17	0.005	W, Ri, Ry,O[2]
LC	**Pinoxaden Metabolite SYN505164 -1**	-	-	-	-	-	105	19	17	37	18	96	12	20	41	20	85	13	14	41	15	0.005	W, Ri[2], Ry,O[2]
GC	**Propazine**	103	11	12	26	13	102	7	13	26	13	95	9	8	20	9	91	5	11	30	11	0.002	W, Ri, Ry,O
LC	**Propazine I**	91	11	19	42	19	107	7	18	40	19	103	10	15	31	15	99	7	9	19	9	0.002	W, Ri, Ry,O
LC	**Propazine II**	97	8	11	24	12	105	6	16	34	16	101	12	15	31	15	97	9	12	26	13	0.002	W, Ri, Ry,O
GC	**Quinoxyfen***	101	4	13	27	14	94	6	16	35	17	86	8	9	33	9	83	4	10	39	10	0.002	W, Ri, Ry,O
LC	**Quinoxyfen***	81	9	18	53	18	93	14	16	35	16	94	12	15	34	16	97	9	19	39	19	0.002	W, Ri, Ry,O
GC	**Simetryn**	107	11	17	37	17	99	7	15	30	15	90	8	11	29	11	89	5	15	38	15	0.002	W, Ri, Ry,O
LC	**Simetryn**	105	12	12	27	12	95	8	13	27	13	100	12	16	32	16	98	9	11	22	11	0.002	W, Ri, Ry,O
LC	**Tebufenozide***	98	11	14	29	14	104	9	18	37	18	99	14	17	35	18	94	10	16	35	17	0.002	W, Ri, Ry,O
LC	**Terbacil**	86	20	20	50	21	97	12	19	40	20	94	16	19	41	19	93	8	11	27	11	0.002	W, Ri, Ry,O
GC	**Tetrasul***	83	6	19	52	20	76	5	18	60	18	69	8	13	67	13	67	5	6	68	6	0.002	W, Ri, Ry,O
LC	**Triazoxide***	87	18	17	43	17	90	12	20	46	20	91	14	14	33	14	92	7	7	21	7	0.002	W, Ri, Ry,O
LC	**Trichlorfon***	104	12	13	27	13	99	9	10	21	11	98	12	13	26	13	94	8	10	24	11	0.002	W, Ri, Ry,O
LC	**Triclopyr***	96	18	26	54	27	89	15	21	49	22	80	12	14	50	14	85	8	11	37	11	0.002	W, Ri, Ry,O
LC	**Trifloxysulfuron (sodium)**	81	11				105	16	15	33	16	102	13	17	35	18	92	9	10	26	10	0.002	W,Ry[1]

***revalidated at a lower LOQ (0.002 mg/kg)**

**** PCP- pentachlorophenol**

[1] LOQ = 0.01 mg/kg

[2] LOQ = 0.05 mg/kg

Appendix 3: Flowchart of the QuEChERS method for cereal samples