Practical application of the Quechers method in the multiresidual determination of pesticides in fruits and wines.

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Introduction

Traditionally the analysis of pesticides has been done by multi-residue methods using liquid gas chromatography and with selective detectors. This leads to the use of different specific techniques with the disadvantage of spending long times of analysis with increased resources and costs.

The last developments aim at the use of faster techniques, with lower costs and that allows the determination of a wide range of active ingredients. One of the developed methods has been known as QuEChERS, which is fast, easy, clean, effective, robust and safe. This extraction procedure together with the technologies of triple quadrupole mass spectrometry, fulfill the objective to have efficient multi-residue methodologies.

Methods

Extraction Procedure

- •15 g fruit extracted with Acetonitrile (1% Acetic Acid)
- •Add $MgSO_4$ and NaOAc
- •Shake and Centrifuge

Clean up Procedure

- •Add PSA and $MgSO_4$ to extract
- •Shake and Centrifuge
- •The final extract is concentrated and changed to toluene and methanol
- •Then transfer to vials for analysis by GC-MS/MS and LC-MS/MS

LC-MS/MS Conditions

- •HPLC: Alliance 2695
- •Detector: Quattro Premier
- •Column: Xterra C18
- •Solvent A: Metanol-5mM Formic Acid
- •Solvent B: Water-5mM Formic Acid
- •Injection: 10uL
- •Ion Mode: ESI
- •Energy: Optimized for each pesticide for MRM function

GC-MS/MS Conditions

- •GC: Agilent 6890
- •Detector: Quattro Micro GC
- •Column: RTX5 30m
- •Injection: 2uL
- •Ion Mode: EI
- •Energy: Optimized for each pesticide for MRM function

Results

This method has been applied to the determination of 180 pesticides in a single injection per instrument, followed by a qualitative and quantitative identification. In addition this method has been validated in a work range between 10 to 1000 ng/g obtaining satisfactory recoveries and repeatability.

Table 1. List of the 180 pesticides and there limit of detection

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MULTI-RESIDUE PESTICIDE SCREENING

Pesticide	LD mg/Kg	N°	Pesticide	LD mg/Kg	N°	Pesticide	LD mg/Kg	N°	Pesticide	LD mg/Kg
ACEPHATE	0,005	46	DDD pp	0,005	91	FLUVALINATE	0,005	136	PENDIMETHALIN	0,005
ACETAMIPRID	0,005	47	DDE op	0,005	92	FOLPET	0,005	137	PERMETHRIN	0,005
ACETOCHLOR	0,005	48	DDE pp	0,005	93	FONOFOS	0,005	138	PHORATE	0,005
ACRINATHRIN	0,005	49	DDT op	0,005	94	FORMOTHION	0,005	139	PHOSALONE	0,005
ALACHLOR	0,005	50	DDT pp	0,005	95	HEPTACHLORO	0,005	140	PHOSPHAMIDON	0,005
ALDICARB	0,005	51	DELTAMETHRIN	0,005	96	HEPTACHLORO EPOXIDE	0,005	141	PIRAZOPHOS	0,005
ALDRIN	0,005	52	DEMETON-S	0,005	97	HEPTENOPHOS	0,005	142	PIRIMETHANIL	0,005
ATRAZINE	0,005	53	DIAZINON	0,005	98	HEXACHLOROBENZENE	0,005	143	PIRMICARB	0,005
AZINPHOS ETHYL	0,005	54	DICHLOBENIL	0,005	99	HEXACONAZOLE	0,005	144	PIRIMIPHOS ETHYL	0,005
AZINPHOS METHYL	0,005	55	DICHLOFLUANID	0,005	100	HEXAZINONE	0,005	145	PIRIMIPHOS METHYL	0,005
AZOXYSTROBIN	0,005	56	DICHLORVOS	0,005	101	HEXYTIAZOX	0,005	146	PROCHLORAZ	0,005
BENOMYL	0,005	57	DICLORAN	0,005	102	IMAZALIL	0,005	147	PROCYMIDONE	0,005
BHC ALPHA	0,005	58	DICOFOL op	0,005	103	IMIDACLOPRID	0,005	148	PROFENOFOS	0,005
BHC BETA	0,005	59	DICROTOPHOS	0,005	104	PHOSMET	0,005	149	PROPARGITE	0,005
BHC DELTA	0,005	60	DIELDRIN	0,005	105	INDOXACARB	0,005	150	PROPICONAZOLE	0,005
BIFENTHRIN	0,005	61	DIFECONAZOLE	0,005	106	IPRODIONE	0,005	151	PROPOXUR	0,005
BITERTANOL	0,005	62	DIMETHENAMID	0,005	107	ISOFENPHOS	0,005	152	PROPYZAMIDE	0,005
BOSCALID	0,005	63	DIMETHOATE	0,005	108	KRESOXIM METHYL	0,005	153	PYRACLOSTROBIN	0,005
BROMACIL	0,005	64	DIPHENYLAMINE	0,005	109	LENACIL	0,005	154	PYRIDABEN	0,005
BROMOPHOS ETHYL	0,005	65	DISULFOTON	0,005	110	LINDANE	0,005	155	QUINALPHOS	0,005
BROMOPHOS METHYL	0,005	66	DODINE	0,005	111	MALATHION	0,005	156	QUINOMETHIONATE	0,005
BROMOPROPYLATE	0,005	67	ENDOSULFAN I	0,005	112	METALAXYL	0,005	157	QUINOXIFENO	0,005
BUPROFEZIN	0,005	68	ENDOSULFAN II	0,005	113	METAMITRON	0,005	158	QUINTOZENE	0,005
CADUSAFOS	0,005	69	ENDOSULFAN SULFATE	0,005	114	METHAMIDOPHOS	0,005	159	SIMAZINE	0,005
CAPTAFOL	0,005	70	ENDRIN	0,005	115	METHIDATHION	0,005	160	SPINOSAD	0,005
CAPTAN	0,005	71	EPTC	0,005	116	METHIOCARB	0,005	161	TEBUCONAZOLE	0,005
CARBARYL	0,005	72	ESFENVALERATE	0,005	117	METHYL PARATHION	0,005	162	TEBUFENOZIDE	0,005
CARBENDAZIM	0,005	73	ETHION	0,005	118	METOLACHLOR	0,005	163	TERBACIL	0,005
CARBOFURAN	0,005	74	ETHOPROFOS	0,005	119	METOMYL	0,005	164	TETRACONAZOLE	0,005
CARBOPHENOTHION	0,005	75	FENAMIPHOS	0,005	120	METOXYCHLOR	0,005	165	TETRADIFON	0,005
CHLORDANE CIS	0,005	76	FENARIMOL	0,005	121	METOXYFENOZIDE	0,005	166	THIABENDAZOLE	0,005
CHLORDANE TRANS	0,005	77	FENBUCONAZOLE	0,005	122	METRIBUZIN	0,005	167	THIACLOPRID	0,005
CHLORDENE	0,005	78	FENCLORPHOS	0,005	123	MEVINPHOS	0,005	168	THIAMETHOXAM	0,005
CHLORFENSON	0,005	79	FENHEXAMID	0,005	124	MIREX	0,005	169	TOLYLFLUANID	0,005
CHLORFENVINPHOS	0,005	80	FENITROTHION	0,005	125	MONOCROTOPHOS	0,005	170	TOXAPHENE	0,005
CHLOROBENZILATE	0,005	81	FENOXYCARB	0,005	126	MYCLOBUTANIL	0,005	171	TRIADIMEFON	0,005
CHLOROTHALONIL	0,005	82	FENTHION	0,005	127	NAPROPAMIDE	0,005	172	TRIADIMENOL	0,005
CHLORPYRIFOS ETHYL	0,005	83	FENVALERATE	0,005	128	NUARIMOL	0,005	173	TRIAZOPHOS	0,005
CHLORPYRIFOS METHYL	0,005	84	FIPRONIL	0,005	129	OMETHOATE	0,005	174	TRICHLORFON	0,005
CYANAZINE	0,005	85	FLUDIOXINIL	0,005	130	OXADIAZON	0,005	175	TRIFLOXYSTROBIN	0,005
CYFLUTHRIN	0,005	86	FLUFENOXURON	0,005	131	OXAMYL	0,005	176	TRIFLURALIN	0,005
CYHALOTRINE L	0,005	87	FLUMETRALIN	0,005	132	OXYFLUORFEN	0,005	177	TRIFORINE	0,005
CYPERMETHRIN	0,005	88	FLUQUICONAZOLE	0,005	133	PACLOBUTRAZOL	0,005	178	TRIFUMIZOLE	0,005
CYPRODINIL	0,005	89	FLUSILAZOLE	0,005	134	PARATHION ETHYL	0,005	179	VAMIDOTHION	0,005
DDD op	0,005	90	FLUTRIAFOL	0,005	135	PENCONAZOLE	0,005	180	VINCLOZOLIN	0,005

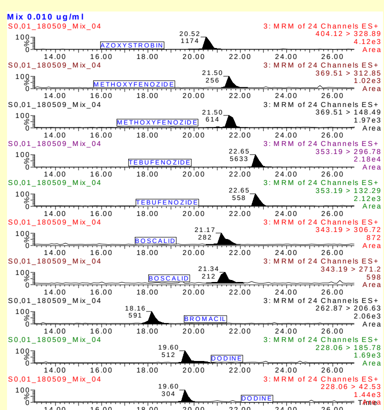

Figure 1. Chromatogram of a Standard mixture at 0.01µg/ml

The method presented is part of the provision of this Laboratory and has been applied to different matrices like grapes, kiwi, apple, pear, raspberry, peach, wines and juices among others.

As an example Figure 2. shows the results of the method of grape samples for analysis of carbaryl, the inyected sequence, cromatograms MRM, ion relationship, calibration curve and percentage of recovery.

Figure 3 Corresponds to the control chart and percentage of recovery of the method for Carbaryl analysis in grape samples, applied in differets dates of analysis. Prooving that the method chosen meets the objetives sets.

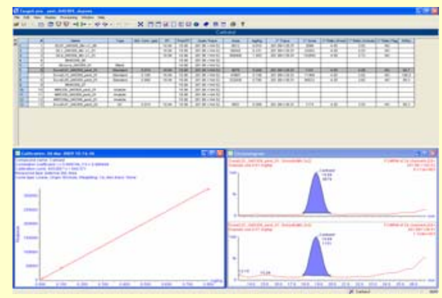

Figure 2. Carbaryl procedure results in grape samples.

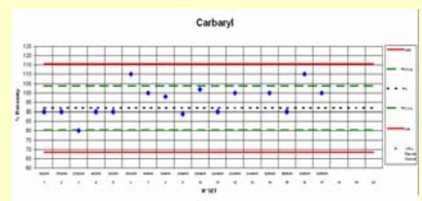

Figure 3. Control charts of the percentage of Carbaryl recovery in grape samples.

Conclusions

As conclusion of the present work we verified that the method proposed is applicable to the routine analysis in a wide range of pesticides and in different matrices, being used in the benefit of the services offered by Corthorn Quality Laboratory (Chile) obtaining short times of response and delivery of results with confirming analyzes that satisfy the needs of the clients.

In addition, this method could be extended for other matrices and analytes.

Literature cited

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For further information

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