Multi-Residue Method for Determination of 350 Pesticides in Food Extracts by utilizing new GC-MS/MS technology

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Introduction

Traditionally pesticide residues in foods have been monitored with multi-residue methods using gas chromatography (GC), such. For methods with a very wide scope, generic sample preparation procedures are usually employed. Inherent to this approach is that clean up of extracts is only possible to a limited extent. Whereas single quadrupole and ion trap MS instruments are suitable for simple matrices, these detection systems provide insufficient selectivity for complex food matrices. When applying such methods to complex matrices like baby food, herbs and spices, enhanced selectivity in detection is required to make up for the low selectivity in sample preparation.

This poster shows the analysis of pesticides in fruit and vegetable extracts using the **Agilent 7000A Triple Quadrupole GC/MS system in MRM mode** and in combination with Retention Time Locking combined with **Agilent Capillary Flow Technology** to provide backflushing.

Experimental

An Agilent 7890A GC fitted with an HP5-MS Ultra Inert column (30m x 0.25mm ID x 0.25µm;19091S-433UI) was connected to an Agilent 7000A. Cold splitless injections (1µL) were made by using a PTV inlet and an 7683 auto-liquid sampler. The analytical method employed was the **Agilent RTL Pesticide method, locked to Chlorpyriphos-methyl** (16.59 minutes) and Helium as Carrier Gas. The QQQ was operated in MRM mode, each target analyte was measured using two transitions, one for quantitation, one as a qualifier. The list of target analytes is shown in Table 1. Samples and Matrix standards were prepared using the **QuEChERS technique.**

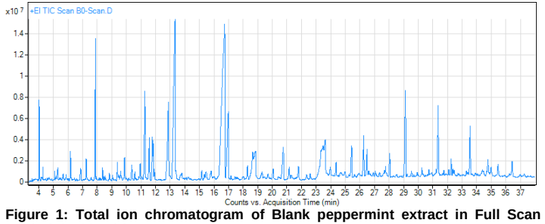

Figure 1: Total ion chromatogram of Blank peppermint extract in Full Scan mode (50-500 m/z).

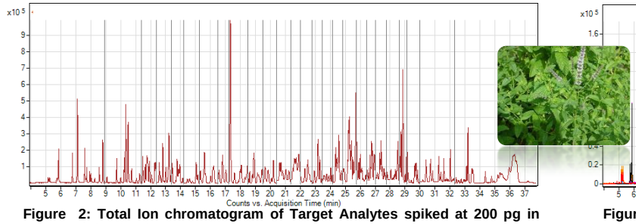

Figure 2: Total Ion chromatogram of Target Analytes spiked at 200 pg in peppermint extract.

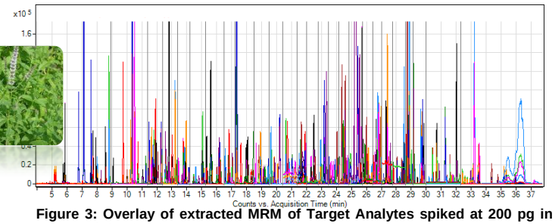

Figure 3: Overlay of extracted MRM of Target Analytes spiked at 200 pg in peppermint extract.

Table 1: Target Analytes Measured in Food Extract Samples

2,4-Dimethylaniline	Butafenacil	Cymiazole	Dioxathion	Fenpropidin	Hexaconazole	Methyl paraoxon	Phorate Sulfoxide	Quizalofop-ethyl	Triadimenol
Acephate	Cadusafos	Cypermethrin I-IV	Diphenamid	Fenson	Hexazinone	Methyl parathion	Phosalone	Resmethrine I+II	Triazophos
Acetochlor	Captafol	Cyproconazole	Diphenylamine	Fensulfothion	Imazalil	Metolachlor	Phosmet	S421	Trichlorfon
Acrinathrin	Captan	Cyprodinil	Dipropetryn	Fenthion	Indoxacarb	Metribuzin	Phosphamidon I + II	Silafluofen	Trichloronate
Alachlor	Carbaryl	DDD, o,p'-; p,p'-	Disulfoton	Fenthion oxon	Iprobenfos	Mevinphos	Picolinafen	Simazine	Tricyclazole
Aldrin	Carbofuran	DDE, o,p'-; p,p'-	Disulfoton sulfone	Fenthion sulfoxide	Iprodione	Mirex	Pirimicarb	Simetryn	Trifloxystrobin
Allethrin	Carbophenothion	DDT, o,p'-; p,p'-	Disulfoton Sulfoxide	Fenthion-sulfone	Isazophos	Molinate	Pirimicarb desmethyl	Spirodiclofen	Triflumizole
Allethrin	Carbosulfan	Decachlorobiphenyl	Ditalimfos	Fenvalerate I + II	Isocarbophos	Monocrotophos	Pirimiphos-ethyl	Spiroxamine I + II	Trifluralin
Ametryn	Chinomethionat	Deltamethrin	DNOC	Fipronil	Isodrin	Myclobutanil	Pirimiphos-methyl	Sulfentrazone	Triticonazole
Amitraz	Chlordane, cis-; trans-	Demeton-S- methyl	Edifenphos	Flonicamid	Isofenphos	Napropamide	Prochloraz	Sulfotep	Vamidothion
Atrazine	Chlorfenapyr	Desmetryn	Endosulfan - α; -β	Fluazifop-p-butyl	Isofenphos-methyl	Nitralin	Procymidone	Sulprofos	Vinclozolin
Atrazine-desethyl	Chlorfenson	Dialifos	Endosulfan sulfate	Fluazinam	Isopropalin	Nitrapyrin	Profenofos	Tebuconazol	Zoxamide
Azaconazole	Chlorfenvinphos, trans-	Diazinon	Endrin	Flubenzimine	Isoxadifen-ethyl	Nitrofen	Profluralin	Tebufenpyrad	
Azinphos-ethyl	Chlormefos	Dichlobenil	Endrin aldehyde	Fluchloralin	Isoxathion	Nitrothal-isopropyl	Promecarb	Tebupirimifos	
Azinphos-methyl	Chloroneb	Dichlofenthion	EPN	Flucythrinate I + II	Jodfenphos	Norflurazon	Prometon	Tecnazene	
Benalaxyl	Chloropropylate	Dichlofluanid	Etaconazole I + II	Fludioxonil	Lenacil	Nuarimol	Prometryn	Tefluthrin, cis-	
Bendiocarb	Chlorothalonil	Dichlorvos	Ethalfluralin	Flufenacet	Leptophos	Ofurace	Propachlor	Telodrin	
Benfluralin	Chlorpropham	Diclobutrazol	Ethiofencarb	Flumioxazin	Lindane	Omethoate	Propanil	Temephos	
Benfuracarb	Chlorpyrifos	Diclofop methyl	Ethion	Fluotrimazole	Malaoxon	Oxadiazon	Propazine	Terbufos	
Benzoylprop ethyl	Chlorpyrifos-methyl	Dicloran	Ethofenprox	Flusilazole	Malathion	Oxadixyl	Propetamphos	Terbumeton	
BHC α-; β-; γ-	Chlorthal-dimethyl	Dicofol, o,p-; p,p'-	Ethoprophos	Fluthiacet-methyl	Mecarbam	Oxyfluorfen	Propham	Terbuthylazine	
Bifenox	Chlorthion	Dicrotophos	Ethoxyquin	Flutriafol	Mefenpyr-diethyl	Paclobutrazol	Propiconazole I + II	Terbutryne	
Bifenthrin	Chlorthiophos	Dieldrin	Etridiazole	Fluvalinate-tau-I + II	Mepanipyrim	Paraoxon	Propoxur	Tetrachlorvinphos	
Biphenyl	Chlozolinate	Diethofencarb	Etrimfos	Folpet	Mepronil	Parathion	Propyzamide	Tetraconazole	
Bitertanol I	Climbazol	Difenoconazol I + II	Famphur	Fonofos	Metalaxyl	Penconazole	Prothiofos	Tetradifon	
Bromacil	Clomazone	Diflufenican	Fenamiphos	Formothion	Metamitron	Pencycuron	Prothoate	Tetramethrin I + II	
Bromocyclen	Cloquintocet-mexyl	Dimepiperate	Fenarimol	Fosthiazate I + II	Metazachlor	Pendimethalin	Pyrazophos	Tetramethrin II	
Bromophos	Coumaphos	Dimethenamid	Fenazaquin	Fuberidazole	Methacrifos	Pentachloroanisole	Pyrethrin I +II	Tetrasul	
Bromophos-ethyl	Crimidine	Dimethoate	Fenbuconazole	Furalaxyl	Methamidophos	Permethrin I + II	Pyridaphenthion	Thiometon	
Bromopropylate	Cyanazine	Dimoxystrobin	Fenchlorphos	Furathiocarb	Methidathion	Perthane	Pyrifenox I+II	Thionazin	
Bromuconazole I + II	Cyanofenphos	Diniconazole	Fenhexamid	Heptachlor	Methiocarb	Phenthoate	Pyrimethanil	Tolclofos-methyl	
Bupirimate	Cyanophos	Dinitramine	Fenitrothion	Heptachlor epoxide	Methoprene II	Phenylphenol, o-;p-	Quinalphos	Tolylfluanid	
Buprofezin	Cyfluthrin I-IV	Dinoseb	Fenoxycarb	Heptenophos	Methoprotryne	Phorate	Quinoxyfen	Transfluthrin	
Butachlor	Cyhalothrin I (lambda)	Dioxacarb	Fenpropathrin	Hexabromobenzene	Methoxychlor	Phorate Sulfone	Quintozene	Triadimefon	

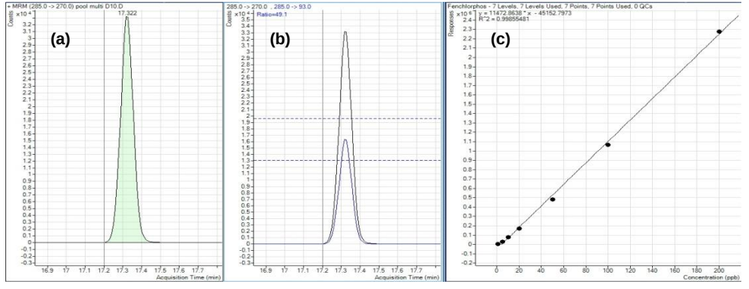

Figure 4 Quantifier ion (a), Overlay of Qualifier and Quantifier Ions (b) at 10 pg on column in Peppermint Matrix, for Fenchlorphos, Calibration Curve for Fenchlorphos 1 ppb – 200 ppb (c).

Results

Matrix-matched calibration standards were prepared in blank Peppermint extracts (TIC scan Figure 1) over the range of 1 – 200 ppb. Figure 2 shows the TIC chromatogram acquired in scan mode of the MRM mode for 350 pesticides, as extracted MRM in Figure 3. Each MRM segment is indicated by a grey marker line. Linearity was also tested with seven levels between 1 and 200 ppb for 350 pesticides. An Example for Peak shape. Overlay of qualifier and Quantifier Ion and shape of the Calibration curve is shown in Figure 4 for Fenchlorphos.

Overall the correlation coefficients of the external standard calibration curve were 0.99 on average. The LOD was estimated based on the calculated S/N of the 10 pg standard. For the majority of pesticides, **LODs were below 2 pg on column** (based on S/N >3:1 Peak to Peak).

Conclusion

• Agilent's 7000A Triple Quadrupole GC/MS in combination with the 7890 GC is a **sensitive and rugged tool method** we developed also meets the performance and identity confirmation criteria defined by the stringent EU regulations.

• Excellent selectivity has been achieved to allow **unambiguous confirmation of identity for these 350 pesticides** even in very complex food matrices and generic sample clean up by QuEChERS.

• For this new GC/MS/MS method, the **Agilent Retention Time Locking (RTL)** database was used to calibrate the retention times of all pesticides. Therefore, the presented GC/MS/MS method can be easily transferred to other Agilent 7000 Triple Quadrupole systems with **minimum effort and time**.