

Analytical and Bioanalytical Chemistry

Electronic Supplementary Material

Screening and quantification of pesticide residues in fruits and vegetables making use of gas chromatography–quadrupole time-of-flight mass spectrometry with atmospheric pressure chemical ionization

M.I. Cervera, T. Portolés, F.J. López, J. Beltrán, F. Hernández

Table S1. Pesticides found in the screening of 34 fruit and vegetable samples. Mass errors (in ppm) for the m/z ion at the LE function

| Compounds | Courgette | | | | Strawberry | | | | Lettuce | | | | Apple | | | | Orange | | | | Red pepper | | | | Tomato | | | | | | Carrot | | | | | | | | | | | | | | | | |
|---------------------|------------------|-----|------------------|------------------|------------------|------------------|-----|------------------|------------------|------------------|------------------|-----|------------------|-----|------------------|------------------|------------------|------------------|------------------|-----|------------------|------------------|-----|------------------|--------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|----|----|-----|--|------------------|------------------|-----|--|--|--|--|-----|------------------|-----|------------------|
| | S1 | S2 | S3 | S4 | S1 | S2 | S3 | S4 | S1 | S2 | S3 | S4 | S1 | S2 | S3 | S4 | S1 | S2 | S3 | S4 | S1 | S2 | S3 | S4 | S1 | S2 | S3 | S4 | S5 | S6 | S1 | S2 | S3 | S4 | | | | | | | | | | | | | |
| 2-Phenylphenol | | | | | | | | | 2.2 ^a | | 3.7 ^a | | 4.1 ^a | | 1.7 | | | | | | | | | | | | | | | 4.2 ^a | | | | | | | | | | | | | | | | | |
| Diphenylamine | | | | | | | | 1.1 ^a | 2.9 ^a | 1.0 ^a | 0.6 ^a | 3.1 | 1.7 ^a | 2.4 | 2.7 | 0.2 ^a | | 0.2 ^a | | | | | | | | 5.0 ^a | 3.0 ^a | 4.6 ^a | 1.3 ^a | 5.2 ^a | 4.6 ^a | 2.4 ^a | | | | | | | | | | | | | | | |
| Terbutylazine | | | | | | | | | | | | | | | | 4.6 ^a | | 3.0 ^a | | | | | | | | | | | | | | 2.2 ^a | | | | | | | | | | | | | | | |
| Chlorothalonil | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Tefluthrin | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Chlorpyrifos methyl | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Metalexyl | | | | | | | | | 0.4 ^a | | 3.4 ^a | | 1.7 | | | | | | | | | | | | | | | | | | | | | | 1.4 | | | | | | | | | | | | |
| Malathion | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Chlorpyrifos | | | | | | | | | | | | | | | | | 1.1 ^b | 0.5 ^c | 3.3 ^b | 2.1 | 3.0 ^b | 0.0 ^c | 1.5 | 0.3 ^a | 3.5 | 5.0 | | | | | | | | | | | | 5.0 ^a | 0.7 | | | | | | | | |
| Cyprodinil | | | | | | | | | | | | | | | | | 6.6 ^a | | | | 2.0 ^a | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Fipronil | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 2.6 ^a | 5.0 | | | | | | | | | |
| Thiabendazole | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Procymidone | | | | | | | | | | | | | | | | | 2.8 ^a | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Imazalil | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Fenhexamid | 2.0 ^e | 1.8 | 3.7 ^a | 3.2 ^a | 1.6 ^a | 3.7 ^a | 0.1 | 0.5 ^c | 1.0 ^a | | 5.0 | | 2.2 ^a | | 1.8 ^a | | 5.4 ^a | | | | 1.0 | 3.2 ^a | 2.4 | 0.7 ^a | 0.9 | | 0.0 ^a | | | | 2.9 ^a | 4.3 ^a | | | | | | | | | | | | | | | |
| Phosmet | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Iprodione | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Fenarimol | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| lambda-Cyhalothrin | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Cypermethrin I | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 1.6 | | | |
| Cypermethrin II | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.6 | | |
| Cypermethrin III | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.0 | | |
| Cypermethrin IV | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.8 | | |
| Azoxystrobin | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.5 ^b | 0.7 | 4.4 ^a |

Unless specified, positives were confirmed by the presence of the Q m/z ion at LE and at least one fragment ion (q) at HE, both with mass errors < 5 ppm. q/Q ratio was also within maximum tolerance deviation admitted

^a Only the Q ion at LE (mass error < 5 ppm) was observed.

^b The fragment ion at HE presented mass error > 5 ppm.

^c Both Q and q ions were observed, but q/Q ratio was out of tolerance.

Table S2. List of compounds searched in the widened screening method

| Compounds | | | | |
|-----------------------|-------------------------|----------------------|---------------------------|--------------------|
| Acephate | Bixafen | Chlorfenson | <i>p,p'</i> -DDE | Diniconazole |
| Acequinoxy | Boscalid | Chlorfenvinphos | <i>p,p'</i> -DDD | Dinitramine |
| Acetamiprid | Bromocyclen | Chloridazon | <i>p,p'</i> -DDT | Dinobuton |
| Acetochlor | Bromofenvinphos | Chlormephos | DEF | Dinocap |
| Aclonifen | Bromophos | Chloroneb | Deltamethrin | Dinoseb |
| Acrinathrin | Bromophos ethyl | Chloropropylate | Demeton | Dinoterb |
| Alachlor | Bromopropilate | Chlorothalonil | Demeton-S-methyl | Dioxathion |
| Aldicarb | Bromuconazole | Chlorotuluron | Dialifos | Diphenylamine |
| Aldicarb sulfone | Bupimirate | Chlorpropham | Diazinon | Disulfoton |
| Aldrin | Buprofezin | Chlorpyrifos | 4,4'-Dibromobenzophenone | Disulfoton sulfone |
| Allethrin | Butachlor | Chlorpyrifos methyl | Dicamba | Ditalimfos |
| Ametryn | Butamifos | Chlorsulfuron | Dicapthon | Diuron |
| Amidithion | Butralin | Chlorthal dimethyl | Dichlobenil | DNOC |
| Ancymidol | Cadusafos | Chlorthion | Dichlofenthion | Edifenphos |
| Anilazine | Captafol | Chlorthiophos | Dichlofluanid | alpha-endosulfan |
| Anthraquinone | Captan | Chlozolinate | Dichloran | beta-endosulfan |
| Aramite | Carbaryl | Cinidon-ethyl | 4,4'-Dichlorobenzophenone | Endosulfan ether |
| Atrazine | Carbendazim | Clodinafop propargyl | Dichlorprop | Endosulfan sulfate |
| Atrazine desethyl | Carbetamide | Clomazone | Dichlorvos | Endrin |
| Atrazine desisopropyl | Carbofuran | Coumaphos | Diclobutrazol | EPN |
| Azaconazole | Carbophenothion | Crotoxyphos | Diclofop methyl | Epoxyconazol |
| Azamethiphos | Carbophenothion methyl | Crufomate | Dicofol | Etaconazole |
| Azinphos ethyl | Carbosulfan | Cyanazine | Dicrotophos | Ethalfuralin |
| Azinphos methyl | Carboxin | Cyanofenphos | Dieldrin | Ethiofencarb |
| Azoxystrobin | Carfentrazone ethyl | Cyanophos | Dienochlor | Ethion |
| Benalaxyl | Chinomethionat | Cycloxydim | Difenoconazole | Ethiprole |
| Benfluralin | Chlorantraniliprole | Cyfluthrin | Diflufenican | Ethofumesat |
| Benoxacor | Chlorbenside | lambda-Cyhalothrin | Dimefox | Ethoprophos |
| Bentazone | Chlorbenzilate | Cymoxanil | Dimethachlor | Ethoxyquin |
| Benzoylprop ethyl | <i>trans</i> -Chlordane | Cypermethrin | Dimethenamide | Etofenprox |
| Bifenox | Chlordecone | Cyphenothrin | Dimethipine | Etoxazole |
| Bifenthrin | Chlorethoxyfos | Cyproconazole | Dimethoate | Etridiazole |
| Binapacryl | Chlorfenapyr | Cyprodinil | Dimethomorph | Etrimfos |
| Bitertanol | Chlorfenprop methyl | Cyprofuram | Dimoxystrobin | Famophos |

Table S2. (Continued)

| Compounds | | | | |
|-----------------------|----------------------|-------------------|---------------------|-----------------------|
| Famoxadone | Fluopyram | Iodofenphos | Methabenzthiazuron | Pentachlorobenzene |
| Famphur | Fluorodifen | Ioxynil | Methacriphos | Pentachlorophenol |
| Fenamidone | Fluotrimazole | Ioxynil octanoate | Methamidophos | Pentanochlor |
| Fenamiphos | Fluquinconazole | Iprobenfos | Methidathion | Permethrin |
| Fenarimol | Flurenol butyl | Iprodione | Methiocarb | Perthane |
| Fenbuconazole | Flurochloridone | Iprovalicarb | Methiocarb sulfone | Phenkapton |
| Fenchlorazole ethyl | Flurprimidol | Isazophos | Methomyl | Phenothrin |
| Fenchlorphos | Flurtamone | Isobenzan | Methoprene | Phenthroate |
| Fenfluthrine | Flusilazole | Isocarbofos | Methoxychlor | 2-Phenylphenol |
| Fenhexamid | Flutriafol | Isodrin | 2,4-D-Methylester | Phorate |
| Fenitrothion | tau-Fluvalinate | Isofenphos | 2,4,5-T-Methylester | Phosalone |
| Fenobucarb | Folpet | Isofenphos methyl | Metolachlor | Phosfolane |
| Fenoxyprop ethyl | Fonofos | Isomethiozin | Metrafenon | Phosmet |
| Fenoxy carb | Formothion | Isopropalin | Metribuzin | Phosphamidon |
| Fenpropathrin | Fosalone | Isoxaben | Mevinphos | Picloram methyl ester |
| Fenpropimorph | Furathiocarb | Isoxadifen ethyl | Mirex | Picolinafen |
| Fenpyroximate | Furfural | Isoxathion | Molinate | Picoxystrobin |
| Fenson | Halfenprox | Ketoendrin delta | Monocrotophos | Pirazofos |
| Fensulfothion | Haloxyfop methyl | Kresoxim methyl | Monuron | Pirimicarb |
| Fensulfothion sulfone | HCB | Lactofen | Myclobutanil | Pirimiphos ethyl |
| Fenthion | alpha-HCH | Lenacil | Nitralin | Pirimiphos methyl |
| Fenvalerate | beta-HCH | Leptophos | Nitrofen | Plifenate |
| Fipronil | gamma-HCH | Lufenuron | Omethoate | Prallethrin |
| Flamprop isopropyl | delta-HCH | Malaoxon | Oxadixyl | Prochloraz |
| Flamprop methyl | Heptachlor | Malathion | Oxyfluorfen | Procymidone |
| Fluazifop-p-butyl | Heptachlor epoxide A | Mecarbam | Paclobutrazol | Profenofos |
| Flubenzimine | Heptachlor epoxide B | Mecoprop | Paraoxon ethyl | Profluralin |
| Fluchloralin | Heptenophos | Mepanipyrim | Paraoxon methyl | Prometryn |
| Flucythrinate | Hexachlorobutadiene | Mephosfolan | Parathion ethyl | Propachlor |
| Fludioxonil | Hexaconazole | Merphos | Parathion methyl | Propanil |
| Flufenoxuron | Hexythiazox | Metalaxyd | Penconazole | Propargite |
| Flumethrine | Imazalil | Metamitron | Pendimethalin | Propazine |
| Flumetralin | Imibenconazole | Metazachlor | Pentachloranisol | Propetamphos |
| Fluopicolide | Indoxacarb | Metconazole | Pentachloroaniline | Propham |

Table S2. (Continued)

| Compounds | | |
|-------------------------|------------------------|-----------------|
| Propiconazole | Tebupirimfos | Trietazine |
| Propisochlor | Tecnazene | Trifloxystrobin |
| Propoxur | Teflubenzuron | Triflumizole |
| Propyzamide | Tefluthrin | Triflumuron |
| Prosulfocarb | Temephos | Trifluralin |
| Prothioconazole-desthio | TEPP | Triticonazole |
| Prothiophos | Terbacil | Vamidothion |
| Prothoat | Terbufos | Vinclozolin |
| Pymetrozine | Terbumeton | |
| Pyraclofos | Terbumeton desethyl | |
| Pyraclostrobin | Terbutylazine | |
| Pyraflufen ethyl | Terbutylazine desethyl | |
| Pyrazophos | Terbutryn | |
| Pyridaben | Tetrachlorvinphos | |
| Pyridaphenthion | Tetraconazole | |
| Pyrifenoxy | Tetradifon | |
| Pyrimethanil | Tetramethrin | |
| Pyrimidate | Tetrasul | |
| Pyriproxyfen | Thiabendazole | |
| Quinalphos | Thiometon | |
| Quinoxifen | Thionazin | |
| Quintofos | Thiophanate methyl | |
| Quintozene | Tolclofos methyl | |
| Quizalofop ethyl | Tolyfluanid | |
| Resmethrin | Transfluthrin | |
| Sebutylazin | Triadimefon | |
| Silafluofen | Triadimenol | |
| Simazine | Triallate | |
| Spirodiclofen | Triamiphos | |
| Spiromesifen | Triazophos | |
| Sulfotep | Tribufos | |
| Sulprofos | Trichlorfon | |
| Swep | Trichloronat | |
| Tebuconazole | Tridiphane | |

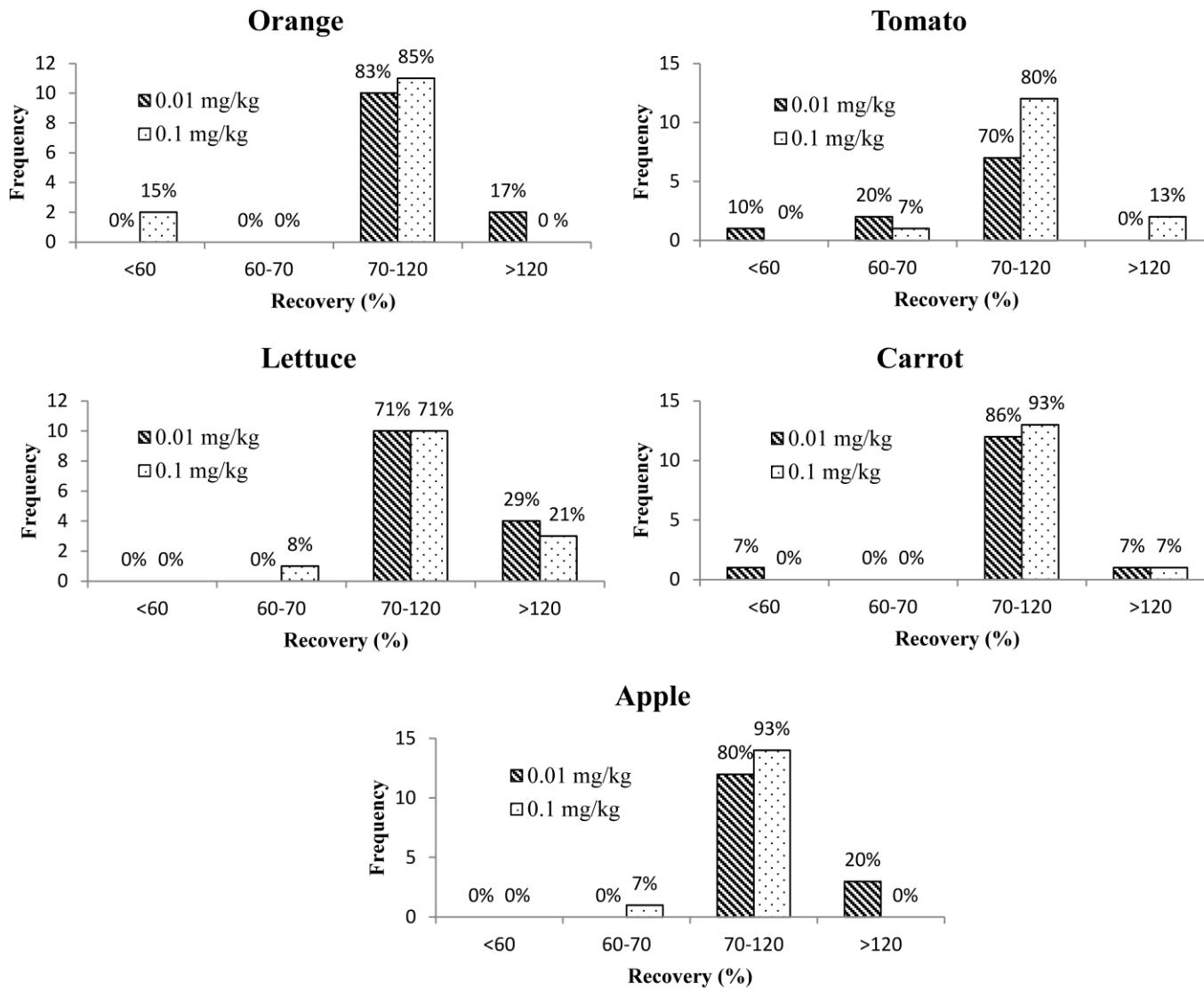


Figure S1. Histograms for recoveries experiments at 0.01 mg/kg and 0.1 mg/kg for the five validated matrices: orange, tomato, lettuce, carrot and apple.