

Table 2. Average recovery (%) and RSD (% , in parenthesis) for the GC-TOF MS method applied to orange, apple, carrot and tomato samples (n=6) at three spiked levels (0.01, 0.05 and 0.5 mg/Kg). Limit of quantification (LOQ) objective^a in mg/Kg.

Compound	Family	Orange				LOQ	Apple				LOQ	Carrot				LOQ	Tomato				LOQ
		0.01	0.05	0.5	LOQ		0.01	0.05	0.5	LOQ		0.01	0.05	0.5	LOQ		0.01	0.05	0.5	LOQ	
Alachlor	HERB chloroacetanilide	- ^e	81 (11)	102 (15)	0.05	-	81 (10)	83 (8)	0.05	-	114 (9)	89 (5)	0.05	-	78 (10)	93 (6)	0.05				
Aldrin	INS OC cyclodiene	<u>44</u> ^f (28)	70 (6)	72 (7)	0.05	77 (19)	102 (10)	86 (8)	0.01	88 (11)	88 (8)	91 (4)	0.01	79 (14)	70 (6)	92 (2)	0.01				
Atrazine	HERB chlorotriazine	72 (8)*	92 (5)	73 (6)	0.05	-	-	86 (4)	0.5	88 (11)*	104 (5)	98 (3)	0.05	106 (7)	84 (3)	91 (6)	0.01				
Bifenthrin	INS pyrethroid ester	71 (15)	81 (4)	77 (8)	0.01	87 (5)	80 (7)	87 (5)	0.01	-	105 (9)	88 (4)	0.05	<u>130</u> (20)	80 (13)	105 (3)	0.05				
Buprofezin	INS chitin synthesis inhibitors	-	101 (17)	70 (11)	0.05	-	100 (19)	87 (4)	0.05	-	106 (10)	90 (5)	0.05	-	84 (12)	83 (7)	0.05				
<i>trans</i> -Chlordane	INS OC cyclodiene	-	70 (6)	75 (5)	0.05	-	93 (8)	93 (7)	0.05	-	98 (7)	93 (5)	0.05	-	72 (8)	83 (1)	0.05				
Chlorfenvinphos	INS OP organophosphate	-	78 (17)	81 (10)	0.05	-	<u>60</u> (14)	86 (6)	0.5	-	106 (6)	91 (7)	0.05	-	82 (7)	94 (7)	0.05				
Chlorothalonil	FUNG aromatic	-	-	70 (13)	0.5	-	-	97 (8)	0.5	-	72 (10)	<u>125</u> (6)	0.05	-	-	-	-				
Chlorpropham	HERB carbanalite	<u>53</u> (17)	<u>42</u> (24)	96 (12)	0.5	-	-	74 (11)	0.5	75 (30)	96 (13)	100 (7)	0.01	81 (20)	77 (6)	93 (8)	0.01				
Chlorpyrifos ethyl	INS OP pyridine organophosphate	74 (<u>37</u>)	76 (14)	84 (4)	0.05	^b	<u>53</u> (11)	85 (5)	0.5	92 (16)	98 (5)	98 (4)	0.01	108 (9)	81 (5)	83 (2)	0.01				
Chlorpyrifos methyl	INS OP pyridine organophosphate	78 (14)	77 (6)	71 (7)	0.01	104 (18)	82 (7)	78 (6)	0.01	92 (13)	101 (8)	89 (3)	0.01	95 (6)	76 (4)	93 (5)	0.01				
Cyprodinil	FUNG anilinopyrimidine	88 (9)	84 (5)	86 (5)	0.01	73 (11)	72 (3)	91 (6)	0.01	101 (8)	104 (5)	95 (6)	0.01	^b	^b	^b	-				
<i>p,p'</i> -DDE	INS OC	72 (19)	72 (5)	83 (6)	0.01	85 (9)	85 (3)	91 (4)	0.01	89 (9)	94 (5)	86 (5)	0.01	91 (3)	73 (3)	90 (5)	0.01				
<i>p,p'</i> -DDD	INS OC	77 (5)	84 (4)	91 (4)	0.01	75 (16)	87 (6)	93 (7)	0.01	93 (9)	99 (6)	79 (3)	0.01	103 (3)	<u>63</u> (3)	<u>66</u> (5)	0.01				
<i>p,p'</i> -DDT	INS OC	80 (8)*	83 (5)	76 (6)	0.05	69 (12)	90 (12)	92 (8)	0.01	89 (14)	96 (6)	90 (4)	0.01	105 (8)	79 (4)	78 (5)	0.01				
Diazinon	INS OP pyrimidine organothiophosphate	85 (18)	82 (18)	73 (10)	0.01	76 (20)	80 (8)	81 (10)	0.01	89 (19)*	101 (7)	93 (4)	0.05	101 (18)	78 (7)	79 (3)	0.01				
Dichlorvos	INS OP organophosphate	81 (11)	74 (10)	79 (<u>25</u>)	0.01	69 (27)	96 (9)	86 (17)	0.01	61 (12)	85 (10)	98 (17)	0.01	96 (7)	73 (8)	100 (4)	0.01				
Dieldrin	INS OC cyclodiene	<u>56</u> (36)	100 (10)	97 (8)	0.05	-	97 (10)	96 (7)	0.05	92 (12)	93 (6)	94 (6)	0.01	91 (14)	70 (6)	99 (2)	0.01				
α -Endosulfan	INS OC cyclodiene	-	91 (13)	73 (6)	0.05	-	71 (<u>34</u>)	93 (11)	0.5	93 (22)	99 (7)	93 (7)	0.01	94 (20)	76 (9)	96 (5)	0.01				
β -Endosulfan	INS OC cyclodiene	-	82 (14)	77 (15)	0.05	-	75 (<u>41</u>)	94 (7)	0.5	89 (21)	110 (7)	102 (11)	0.01	65 (24)	82 (7)	94 (2)	0.01				
Endosulfan sulfate	INS OC cyclodiene	70 (28)	99 (15)	94 (9)	0.01	-	91 (12)	94 (5)	0.05	105 (16)	102 (6)	93 (5)	0.01	91 (21)	71 (2)	96 (4)	0.01				
Endrin	INS OC cyclodiene	-	79 (9)	82 (10)	0.05	-	91 (13)	92 (5)	0.05	-	103 (10)	94 (5)	0.05	-	74 (5)	103 (4)	0.05				
Ethion	INS OP aliphatic organothiophosphate	-	80 (9)	75 (10)	0.05	-	70 (8)	89 (5)	0.05	96 (16)	104 (6)	90 (3)	0.01	120 (10)	85 (3)	91 (6)	0.01				
Fenarimol	FUNG pyrimidine	82 (24)*	96 (10)	105 (7)	0.05	-	100 (7)	106 (2)	0.05	109 (4)*	101 (8)	107 (5)	0.05	98 (3)*	90 (3)	113 (6)	0.05				
Fenitrothion	INS OP phenyl organothiophosphate	-	78 (17)	105 (13)	0.01	-	-	70 (5)	0.5	110 (10)	110 (8)	82 (2)	0.01	99 (18)	84 (5)	78 (7)	0.01				
Fenthion	INS OP phenyl organothiophosphate	80 (24)	82 (9)	79 (5)	0.01	70 (9)	70 (9)	81 (5)	0.01	96 (8)	96 (7)	83 (3)	0.01	108 (8)	77 (3)	80 (4)	0.01				
Fenvalerate I	INS pyrethroid ester	-	118 (17)	104 (9)	0.05	-	103 (19)	92 (10)	0.05	-	112 (12)	99 (11)	0.05	-	90 (8)	95 (3)	0.05				
Fenvalerate II	INS pyrethroid ester	-	80 (<u>28</u>)	116 (11)	0.5	-	100 (20)	80 (4)	0.05	-	78 (12)	85 (6)	0.05	-	88 (13)	87 (8)	0.05				
HCB	FUNG aromatic	<u>52</u> (22)	<u>63</u> (8)	74 (10)	0.5	111 (21)	103 (12)	79 (11)	0.01	78 (9)	84 (9)	90 (7)	0.01	81 (11)	70 (9)	96 (4)	0.01				
α -HCH	INS OC	-	78 (13)	70 (18)	0.05	80 (23)	87 (15)	87 (14)	0.01	85 (18)	100 (11)	102 (10)	0.01	103 (24)	74 (9)	<u>127</u> (4)	0.01				

Table 2. (cont).

Compound	Family	Orange				LOQ	Apple				LOQ	Carrot				LOQ	Tomato				LOQ
		0.01	0.05	0.5			0.01	0.05	0.5			0.01	0.05	0.5			0.01	0.05	0.5		
β -HCH + lindane	INS OC	<u>52</u> (30)	83 (15)	79 (12)	0.05	77 (25)	78 (8)	100 (9)	0.01	72 (17)	94 (5)	104 (10)	0.01	88 (22)	77 (5)	^c	0.01				
Heptachlor	INS OC cyclodiene	<u>48</u> (25)	98 (8)	70 (11)	0.05	102 (25)	102 (7)	83 (8)	0.01	71 (16)	97 (12)	88 (5)	0.01	79 (22)	70 (6)	90 (2)	0.01				
Isodrin	INS OC cyclodiene	-	70 (13)	86 (6)	0.05	73 (11)	70 (18)	90 (6)	0.01	85 (26)	91 (8)	97 (4)	0.01	75 (30)	74 (7)	81 (3)	0.01				
Malathion	INS OP aliphatic organothiophosphate	-	77 (10)	105 (7)	0.05	-	<u>68</u> (25)	85 (6)	0.5	79 (30)	105 (8)	91 (4)	0.01	85 (24)	88 (5)	86 (6)	0.01				
Methidathion	INS OP thiaziazole organothiophosphate	-	79 (12)	89 (9)	0.05	-	-	78 (7)	0.5	-	98 (15)	86 (4)	0.05	-	82 (4)	88 (9)	0.05				
Metholachlor	HERB chloroacetanilide	90 (16)	81 (9)	70 (10)	0.01	85 (9)	71 (6)	83 (7)	0.01	99 (9)	102 (8)	93 (3)	0.01	105 (6)	86 (3)	84 (3)	0.01				
Methoxychlor	INS OC	-	89 (5)	91 (9)	0.05	-	87 (8)	86 (7)	0.05	76 (12)	99 (8)	87 (4)	0.01	96 (16)	83 (3)	84 (7)	0.01				
Metribuzin	HERB triazinone	86 (11)*	88 (16)	79 (12)	0.05	-	84 (6)	90 (4)	0.05	89 (2)*	70 (13)	99 (3)	0.05	-	93 (5)	99 (6)	0.05				
Oxadixyl	FUNG anilide	-	91 (20)	85 (6)	0.05	<u>68</u> (14)*	89 (9)	88 (6)	0.05	<u>109</u> (18)*	120 (12)	93 (5)	0.05	101 (20)	90 (3)	90 (2)	0.01				
Parathion ethyl	INS OP phenyl organothiophosphate	-	83 (20)	70 (11)	0.05	-	<u>47</u> (16)	78 (7)	0.5	-	95 (8)	89 (8)	0.05	-	80 (2)	93 (3)	0.05				
Parathion methyl	INS OP phenyl organothiophosphate	74 (18)	86 (10)	96 (5)	0.01	70 (23)	75 (12)	81 (6)	0.01	90 (14)	96 (6)	85 (4)	0.01	100 (11)	82 (5)	83 (4)	0.01				
Pendimethalin	HERB dinitroaniline	-	103 (15)	70 (12)	0.05	-	99 (17)	95 (5)	0.05	-	106 (10)	86 (5)	0.05	112 (9)	78 (4)	112 (3)	0.01				
Phorate	INS OP aliphatic organothiophosphate	-	98 (16)	78 (20)	0.05	-	95 (10)	84 (11)	0.05	-	102 (14)	101 (7)	0.05	-	80 (9)	<u>129</u> (6)	0.05				
Phosmet	INS OP phtalimide	-	76 (20)	95 (14)	0.05	-	-	70 (12)	0.5	101 (12)	111 (8)	90 (5)	0.01	103 (17)	88 (2)	81 (17)	0.01				
Pirimicarb	INS dimethylcarbamate	101 (17)	85 (9)	70 (14)	0.01	96 (11)	94 (10)	84 (8)	0.01	^d	113 (7)	92 (3)	0.05	^d	87 (4)	78 (4)	0.05				
Pirimiphos methyl	INS OP pyrimidine organothiophosphate	<u>62</u> (39)	76 (6)	71 (11)	0.05	<u>69</u> (37)	85 (7)	86 (6)	0.05	99 (11)	99 (7)	92 (4)	0.01	108 (8)	78 (4)	79 (2)	0.01				
Propiconazole I	FUNG conazole	<u>96</u> (15)*	83 (12)	92 (6)	0.05	-	84 (15)	90 (4)	0.05	98 (17)	109 (6)	96 (3)	0.01	108 (7)	95 (4)	94 (4)	0.01				
Propiconazole II	FUNG conazole	<u>91</u> (12)*	85 (11)	90 (6)	0.05	-	102 (6)	92 (3)	0.05	102 (13)	107 (6)	97 (2)	0.01	108 (11)	88 (3)	101 (3)	0.01				
Propyzamide	HERB amide	79 (5)	77 (13)	70 (8)	0.01	-	-	88 (7)	0.5	96 (7)	100 (6)	96 (4)	0.01	101 (7)	81 (5)	83 (5)	0.01				
Pyriproxyfen	INS juvenile hormone mimics	<u>80</u> (23)*	84 (15)	120 (10)	0.05	-	93 (6)	92 (6)	0.05	-	117 (9)	99 (2)	0.05	-	86 (3)	88 (5)	0.05				
Quinalphos	INS OP quinoxaline organothiophosphate	-	78 (11)	88 (6)	0.05	-	77 (12)	82 (4)	0.05	-	103 (8)	101 (2)	0.05	-	91 (3)	88 (4)	0.05				
Terbutylazine	HERB chlorotriazine	76 (18)	79 (16)	71 (6)	0.01	69 (21)	91 (10)	93 (6)	0.01	90 (7)	103 (7)	96 (3)	0.01	100 (9)	83 (4)	85 (6)	0.01				
Tetradifon	ACAR bridged diphenyl	78 (14)	89 (4)	116 (13)	0.01	69 (19)	94 (6)	98 (4)	0.01	104 (7)	102 (4)	102 (5)	0.01	96 (16)	86 (4)	90 (3)	0.01				
Trifluralin	HERB dinitroaniline	<u>55</u> (32)	94 (8)	85 (19)	0.05	<u>78</u> (12)*	104 (13)	74 (9)	0.05	91 (14)	101 (11)	86 (8)	0.01	93 (22)	72 (5)	101 (4)	0.01				

^a LOQ objective is the lowest level that was validated in spiked samples with satisfactory accuracy and precision; ^b data not available due to the poor calibration; ^c data not available due to the detector saturation; ^d data not available due to the presence of an interfering peak; ^e - means not detected; ^f underlined, values out of the acceptance interval; INS=insecticide; HERB=herbicide; FUNG=fungicide; ACAR=acaricide; OP=organophosphate; OC=organochloride.

* In these cases (always at 0.01 mg/kg) the compound could be quantified, but *Q/q* ratio was out of tolerance due to the poor sensitivity for the confirmatory transitions.