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Stability Study of Five Pesticides in the Preparation of Home-Made Fruit Jams and Establishment of a Processing Factor

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Introduction

The presence of certain pesticide residues in raw and processed foods is a consumer concern due to the fact that residues may have negative health effects. The main route for exposure to pesticide residues for consumers is food. Therefore, a proper monitoring and risk assessment of pesticide residues in both raw and processed products is crucial for better consumer protection [1]. The goals of this study were to monitory the stability of 5 pesticides (which have known metabolites) after the preparation of home-made fruit jams from spiked fruit samples and compare the pesticide residues concentration in the home-made jams with pesticide concentration in the raw fruits, both spiked at the same concentration (the pesticide concentration found in the jams/pesticide concentration found in the raw fruits).

Experimental Conditions

Thereby a mixture of the pesticides, namely carbendazim, chlorpyrifos, imidacloprid, iprodione and propargite, was spiked to six different types of fruits (apple, grape, orange, peach, pear and strawberry) at 500 μg kg^{-1}. Home-made jams were prepared with these samples by cooking the crushed spiked fruits with sugar and water (ratio, 25:25:10), in an open pan for 30 min. The QuEChERS extraction method was applied either to blank fruits, to the fruits spiked at 500 μg kg^{-1} and to the home-made jams (also spiked at 500 μg kg^{-1}). The figure 1, below, shows the scheme used for the preparation of the home-made fruit jams and the QuEChERS extraction procedure used.

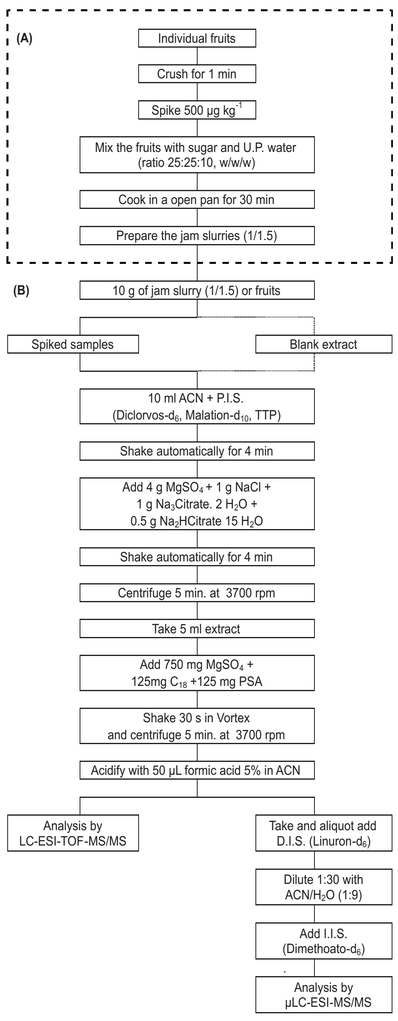

Fig. 1. Home-made fruit jams preparation scheme (A) and QuEChERS citrate extraction procedure (B).

The acetonitrile extracts of the jams were analyzed by LC-ESI-QTOF-MS/MS to ascertain the presence of metabolites of the 5 pesticides. Moreover, all the samples (blank fruits, spiked fruits and home-made jams) were analyzed by μLC-ESI-MS/MS for the establishment of a processing factor (the pesticide concentration found in the jams/pesticide concentration found in the raw fruits).

Table 1. Chromatographic parameters of the LC-ESI-QTOF-MS/MS method.

Compound	t_R (min)	Neutral Mass	$(M+H)^+$	Description
3,5,6-Thrichloro-2-pyridinil		196.9202	197.9275	Metabolite of chlorpyrifos
Benzimidazole		118.0531	119.0604	Metabolite of carbendazim
Carbendazim	0.98	191.0695	192.0768	Pesticide
Chlorpyrifos	8.95	348.9263	349.9336	Pesticide
Cyclohexanol-2-(4-Tert Butyl-Phenoxy)		248.1776	249.1849	Metabolite of propargite
Dichloroaniline, 3,5-		510.6684	511.6757	Metabolite of iprodione
Imidacloprid	3.17	255.0523	256.0596	Pesticide
Imidacloprid, Olefin		253.0367	254.0439	Metabolite of imidacloprid
Imidaclorpid-5 hidroxi		271.0472	272.0545	Metabolite of imidacloprid
Iprodione	6.90	329.0334	330.0407	Pesticide
Propargite	9.27	350.1552	351.1625	Pesticide

Results

To verify the correct execution of the QuEChERS extraction method and the μLC-ESI-MS/MS injection, recoveries (%) and RSD (%) were calculated and are shown in table 2. The home-made jams acetonitrile extracts were also analysed by LC-ESI-QTOF-MS/MS and, as demonstrated in the Figure 2, none of the five pesticides metabolites was detected.

Table 2. Average recoveries (%), RSD (%) and matrix effect (%) for the 5 spiked pesticides in all matrices.

Pesticide	Fruits - Group 1							Fruits - Group 2							Jam		
	Apple		Pear		Peach		ME[b] (%)	Grape[a]	Orange		Strawberry		ME[c] (%)	Peach Jam		ME (%)
	Average Recovery (%)	RSD (%)	Average Recovery (%)	RSD (%)	Average Recovery (%)	RSD (%)		Average Recovery (%)	Average Recovery (%)	RSD (%)	Average Recovery (%)	RSD (%)		Average Recovery (%)	RSD (%)	
Carbendazim	78	1	69	13	60	2	-2	96	64	3	67	16	-21	86	3	-31
Chlorpyrifos	95	1	93	6	84	9	-11	99	70	19	90	6	-10	94	8	6
Imidacloprid	88	1	84	2	81	14	-7	79	77	13	63	10	-2	102	1	-20
Iprodione	92	1	108	29	117	30	1	104	87	1	78	7	-2	91	6	48
Propargite	81	4	92	3	81	9	-26	75	58	19	74	7	-12	92	2	18

[a]RSD is not calculated due the fact that there w as just one replicate. [b]Calibration standards w ere prepared in apple balnk extract. [c]Calibration standards w ere prepared in blank orange extract.

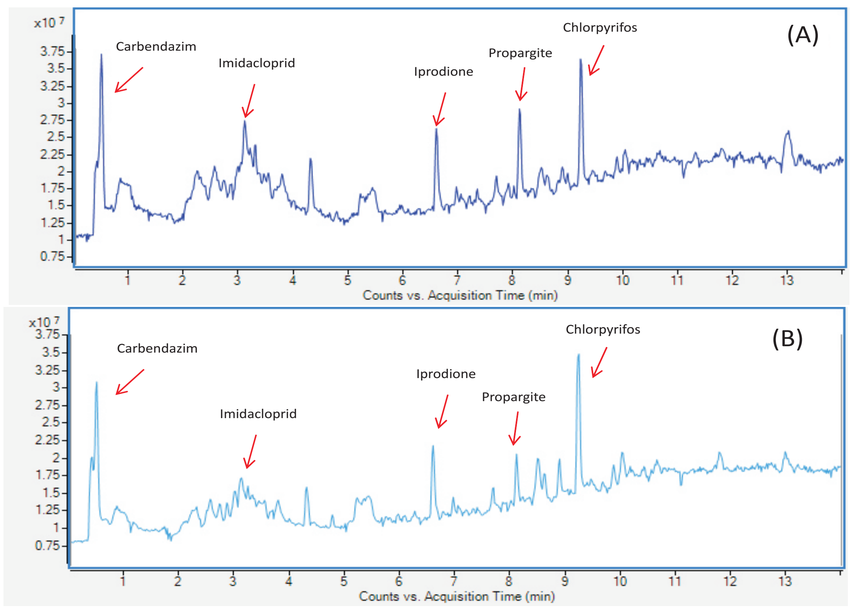

Figure 2. Total ion chromatograms obtained by analysis via LC-ESI-QTOF-MS/MS of (A) apple acetonitrile extract spiked with the mixture of the 5 studied pesticides at 500 μg kg^{-1} and (B) home-made apple jam acetonitrile extract, also spiked at 500 μg kg^{-1}.

By the comparison of the pesticides concentrations found in the jams and in the spiked fruits could be seen a decrease of the pesticide levels in the jams. The percentages of the pesticides that remained present in the home-made jams, calculated from the samples, presented variations depending on the pesticide and the fruit used for the preparation of the jam. But the average percentage of carbendazim, chlorpyrifos, imidacloprid, iprodione and propargite that remained in the jams, was 50%, 30%, 50%, 50% and 40%, respectively. Thus, the factors of ½, 3/10, ½, ½, 2/5, respectively, could by established in the preparation of the home-made fruit jams (Table 3).

Table 3. Stablished processing factor for studied jams

	Processing Factor						
Pesticide	**Strawberry Jam**	**Peach Jam**	**Orange Jam**	**Pear Jam**	**Apple Jam**	**Grape Jam**	**Average**
Carbendazim	0,5	0,6	0,4	0,6	0,6	0,4	0,5
Chlorpyrifos	0,3	0,3	0,4	0,2	0,3	0,2	0,3
Imidacloprid	0,7	0,7	0,6	0,6	0,6	-	0,6
Iprodione	0,6	0,5	0,6	0,4	0,5	0,5	0,5
Propargite	0,4	0,4	0,7	0,3	0,4	0,3	0,4

Conclusions

In this study the stability of 5 pesticides was demonstrated due the fact that none of the pesticides metabolites was detected in the home-made jams prepared from crushed spiked fruits. Moreover, a processing factor have been established for each pesticides and the decrease in concentration of the pesticides was shown in the preparation of the home-made jam samples.

ACKNOWLEDGEMENT

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[1] Martin, L., Mezcua, M., Ferrer, C., et al., Food Addit. Contam. 2013, 30, 466-476 .