

Optimization of matrix solid-phase dispersion (MSPD) for the determination of pesticide multi-residues in onion by LC-ESI-MS/MS

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Introduction



Pesticides constitute an important group of chemical compounds that have to be controlled due to high toxicity and their widespread use in agricultural practice. The control of pesticide residues in foods is very important for consumer's safety and to respect the low detection levels required by regulations. MSPD found suitable application for the preparation, extraction and fractionation from solid and semi-solid matrices. The technique has several advantages when compared to traditional methods such as the extraction liquid-liquid. In this research, a method based on MSPD and liquid chromatography coupled to electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS) was optimized to analyze residues of dimethoate, metalaxyl-M, tebuconazole, azoxystrobin and difenoconazole in onion samples. The matrix was chosen because of its economic and social importance in Rio Grande-RS, a city in the south of Brazil. The pesticides were selected after interviews were made with farmers in the region to identify the compounds often applied in crops and by their chemical properties, such as polarity.

Chromatographic conditions in LC-ESI-MS/MS: analytical column Waters X Terra® MS C18 (3.0 x 50 mm, 3.5 µm); mobile phase acetonitrile and water (54:46, v/v), acidified with 0.1% formic acid; injection volume of 10 µL.

Table 1 Pesticides analysed by LC-ESI-MS/MS positive ionization mode, transitions (m/z), collision energy (eV), cone voltage (V) and retention time.

Pesticides	Retention time (min)	Transitions (m/z)	Collision Energy (eV)	Cone Voltage (V)
Dimethoate	0.66	230>125	20.0	16.0
		230>190	10.0	16.0
Metalaxyl-M	0.97	280>192	17.0	16.0
		280>220	17.0	16.0
Azoxystrobin	1.51	404>372	20.0	20.0
Tebuconazole	1.69	308>70	20.0	40.0
		308>88	50.0	33.0
Difenoconazole	2.84	406>251	31.0	31.0
		406>337	20.0	32.0

Experiment

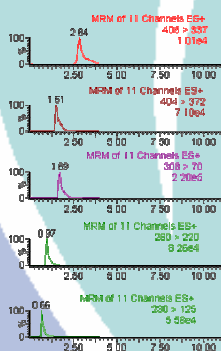


Figure 1. MRM chromatogram

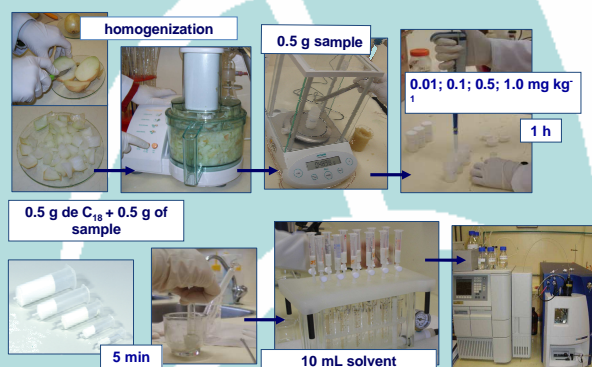


Figure 2. Scheme of the optimized methods

Results and Discussion

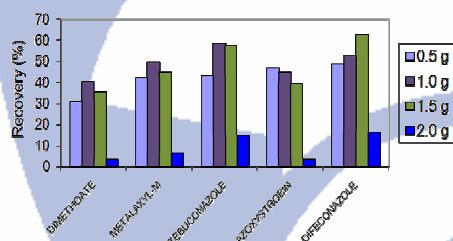


Figure 3. Choice of the quantity of adsorbent (Conditions: adsorbent: C18, eluent: acetonitrile).

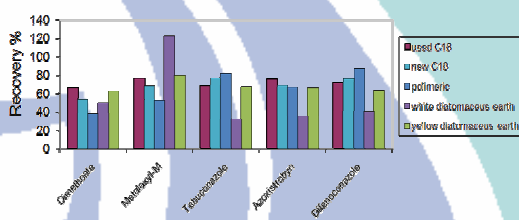


Figure 4. Choice of the kind of adsorbent (Conditions: eluent: acetonitrile; quantity of adsorbent: 1.0 g)

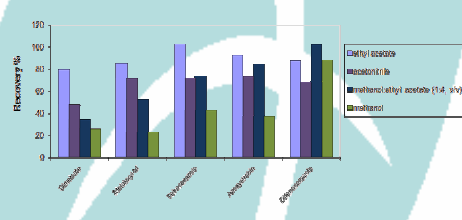


Figure 5. Choice of the elution solvent (Conditions: 1.0 g of used C18)

Table 2. Linearity and limit of quantification of the instrument (LOQi) and of the method (LOQm)

Pesticides	LC-ESI-MS/MS			r
	Linear range (mg L ⁻¹)	LOQi (mg L ⁻¹)	LOQm (mg Kg ⁻¹)	
Dimethoate	0.0005 – 1.0	0.005	0.1	0.9986
Metalaxyl-M	0.0005 – 1.0	0.005	0.1	0.9995
Azoxystrobin	0.0005 – 1.0	0.0005	0.01	0.9990
Tebuconazole	0.0005 – 1.0	0.0005	0.01	0.9995
Difenoconazole	0.0005 – 1.0	0.0005	0.01	0.9994

Conclusions

The method based on MSPD and LC-ESI-MS/MS was suitable for the analysis of dimethoate, metalaxyl-M, azoxystrobin, tebuconazole and difenoconazole residues in onion samples. The main advantages are small quantity of sample, low consumption of organic solvents, minimization of costs by using diatomaceous earth and the use and reuse of C18-bonded silica.