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Abstract. A sorbent material based on silica particles modified with poly(N-vinylimidazole) (SiO_2-PVI) has been evaluated for the treatment of samples by matrix solid-phase dispersion (MSPD). The extraction of four organophosphorus pesticides was done from a spiked tomato and the extracts were analyzed by gas chromatography coupled to mass spectrometry. Six elution solvents were evaluated and acetone was selected due to better recovery of the four pesticides and low background signal in the chromatograms. A factorial design 2^4 was used for selection of extraction conditions. The factors were contact time, acetone volume, treatment (with or without freeze-drying) and adsorbent (SiO_2 or SiO_2-PVI). The best recoveries were obtained using 15 minutes of contact, 2 mL of solvent and sorbent without freeze-drying. The recoveries were between 60 and 83% for SiO_2-PVI in spiked tomato with 0.2 and 0.8μg/g.

1. Introduction

The development, evaluation and application of new adsorbents in matrix solid-phase dispersion (MSPD) are scarce. The current adsorbents based on organic functionalized silica have a relatively low retention of polar compounds and low chemical stability in extreme pH conditions (pH<2 and pH>8)[1, 2]. The retention can improve by modification the surface of sorbents with polar groups, for example, the poly(N-vinylimidazole) to get polar interactions[3,4,5]. In recent years there has been a growing interest in the development of new hybrid materials and their application as adsorbents for the removal of different types of pollutants. In this sense, polymethacrylic acid (PMAA) was grafted onto the surface of silica gel particles (PMAA/SiO_2) for the adsorption of phenol [6].

Researchers have reported studies on compounds derived from silica, which have been successfully applied as adsorbents in the removal of pollutants such as aromatic compounds and some heavy metals. An et al. [7] researched macromolecules grafted to polyacrylamide (PAM) on the surface of particles of silica gel using 3-methacryloxypropyl trimethoxysilane (MPS) as coupling agent. They developed a new adsorbent material PAM/SiO_2 for removal of 2,4,6-trinitrotoluene (TNT).There have also been studies on their use as columns for the detection of some heavy metals using the method of solid phase extraction.

Organophosphorus pesticides (OPPs) are synthetic substances most used to protect crops and hives. Nevertheless, OPPs are toxic to human being. Exposure to even small amounts of OPPs can be fatal

and death is usually caused by respiratory failure. For this reason, analysis of OPPs residues is necessary to protect consumer's health and guarantee the quality of vegtables like tomato [8].

In this work, a sorbent material based on silica particles modified with poly(N-vinylimidazole) shell (SiO_2-PVI) has been evaluated for the treatment of samples by matrix solid phase dispersion (MSPD). The extraction of four organophosphorus pesticides (parathion-methyl, malathion, dichlofenthion and fensulfothion) was done from a fortified tomato and the extracts were analysed by gas Chromatography coupled to mass spectrometry.

2. Experimental

2.1. Chemicals and materials

SiO_2 from Sigma-Aldrich and SiO_2-PVI was obtained as previously reported. Analytical grade anhydrous sodium sulfate (Na_2SO_4) and solvents (ethyl ether, dichloromethane, acetonitrile, ethyl acetate, acetone, 2-propanol, isooctane) were from J. T. Baker (Mallinckrodt Baker, Phillipsburg, NJ, USA). Pesticide standards (at least 97% pure) [methyl parathion (MPT), malathion (MLT), dichlofenthion (DCF) and fensulfothion(FSF)] were from ChemService (West Chester, PA, USA).

Individual stock solutions were prepared in ethyl acetate (1000 ppm) and stored at -18ºC. Working standard solutions were prepared by diluting the stock solutions with ethyl acetate. Finally, calibration standards were prepared by diluting the stock solution with the extract of tomato free of pesticides.

2.2. Spiking procedure

The preparation of the spiked tomato was as follows: 200μL of a standard mixture (0.1 or 0.4 μg/mL) of organophosphorus pesticides (MPT, MLT, DCF, FSF) were added to 0.1 g of tomato respectively to reach a concentration of 0.2 and 0.8 μg/g. Finally, it was left to stand (15 min) to allow the incorporation of the pesticides in the matrix of the tomato.

2.3. Experimental design

An unreplicated factorial design 2^4 for each pesticide was used and four factors with two levels were evaluated: (1) contact time (A: 0 min, 15 min), (2) volume of solvent (B: 1 mL, 2 mL), (3) particles treatment (C: without freeze-dried, with freeze-dried), (4) type of adsorbent (D: SiO_2, SiO_2-PVI). The recovery percent (%R) of pesticides in tomato extracts was the variable response. The results were interpreted using an analysis of variance (ANOVA) [9].

2.4. MSPD extraction

First, a 0.1 g of tomato was placed in a glass mortar. Immediately, 0.5g of Na_2SO_4 was added and disgregated with the pestle. Next, 0.4 g of the particles (SiO_2 or SiO_2-PVI) were added and dispersed to obtain an homogenous mixture. Subsequently, it was transferred to a polypropylene column (100 x 20 mm ID) with a filter paper disc at the bottom. After that, the mixture was compacted slightly to remove air bags. The end of the column was blocked with a polypropylene cap and 2 mL of acetone were loaded. Then, the entrance of the column was closed and the mixture with the solvent was left to stand (15 min); it was eluted dropwise. The eluent was evaporated to 1 mL with gentle air flow and 0.1 g of Na_2SO_4 was added. Finally, the sample was centrifuged (14500 rpm, 4 min) and the supernatant was transferred into a vial for GC-MS analysis.

2.5. Instrumentation and chromatographic conditions

The extracts of the pesticides were analysed with a gas chromatograph (6890N, Agilent Technologies) coupled to a mass spectrometer (5973 N, Agilent Technologies). Helium (purity 99.999) was used as carrier gas (1 mL/min). A fused-silica column Equity-5™ (5% phenyl-95% polydimethylsiloxane; 30 m × 0.25 mm ID, 0.25 μm), supplied by SUPELCO (Bellefonte, PA, USA) was employed. The inlet temperature was 250ºC and 1 μL of the extract was injected in a splitless mode (0.7 min). The oven temperature as programmed as follows: 120ºC (initial temperature), increase of temperature to 280ºC

at 10ºC/min and holding 4 min. The eluent from the GC column was transferred into the MSD via a transfer line (at 280ºC). Typical conditions were optimized through the autotune software option. The electron impact mode (70eV) was used as ionization source (250ºC) and masses were monitored between 50-400 m/z (SCAN mode). The temperature of the quadrupole was 150ºC. The analysis was performed in the selected ion monitoring (SIM). The mass-charge ratio (m/z) for the ions monitored of each pesticide were 97, 223, 279 for DCF; 109, 125, 263 for MPT; 125, 158, 173 for MLT and 265, 293, 308 for FSF.

2.6. Efficiency of the MSPD extraction with SiO_2-poly(N-vinylimidazole)

Recovery experiments were done at two spiked levels (0.2 and 0.8 μg/g) to evaluate the efficiency of the SiO_2-poly(N-vinylimidazole) in MSPD. Recoveries were calculated through external calibration and pesticide standards were prepared by dilution with bee pollen extracts to minimize matrix effect. The precision of extractions was evaluated as the relative standard deviation (RSD). Tomato at each spiked level was analysed at least twice.

3. Results and discussion

The chromatogram obtained from a mixture of pesticides is showed in figure 1. It can be seen that all the chromatographic signals were resolved at the base line.

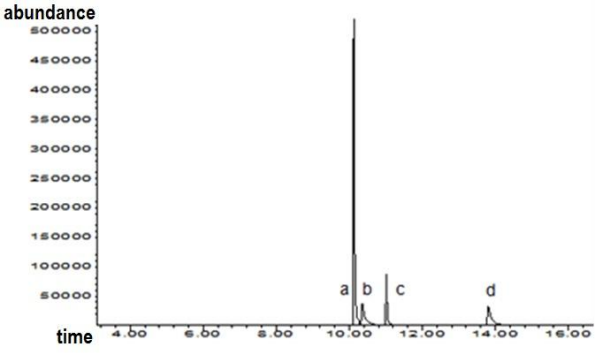

Figure 1. GC/MS-SCAN chromatogram acquired from a standard mixture of organophosphorus pesticides to 2 μg/mL. a: DCF, b: MPT, c: MLT, d: FSF

Solvent	Relative analytical signal for pesticides			
	DCF	**MPT**	**MLT**	**FSF**
Ethylacetate	0.35	0.02	0.12	0.04
Ethyl ether	0.20	0.96	0.47	0.10
Dichlometane	0.33	1.00	0.82	0.01
2-Propanol	0.37	0.14	0.29	1.00
Acetonitrile	0.59	0.03	0.17	0.56
Acetone	1.00	0.88	1.00	0.99

n=2

Table 1. Relative analytical signal for the pesticides (0.5 μg/g) obtained from the tomato extract in different solvents and analyzed by GC/MS-SIM.

Dichloromethane, ethyl ether, ethyl acetate, acetone, 2-propanol and acetonitrile were tested for the elution of pesticides. As is showed in table 1, acetone was chosen as the solvent of elution because of the high relative analytical signal achieved for pesticides. In addition, chromatograms acquired from acetone extracts presented a lower number of chromatographic signals as is showed in figure 2.

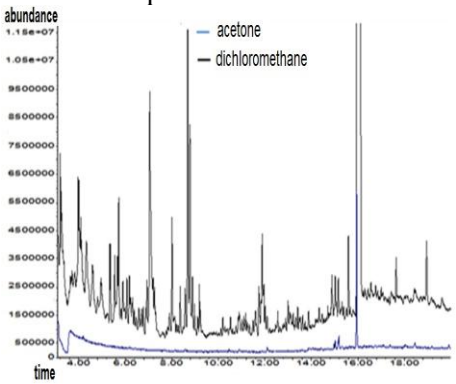

Figure 2. GC/MS-SCAN chromatogram acquired from extracts of tomato with two different solvents.

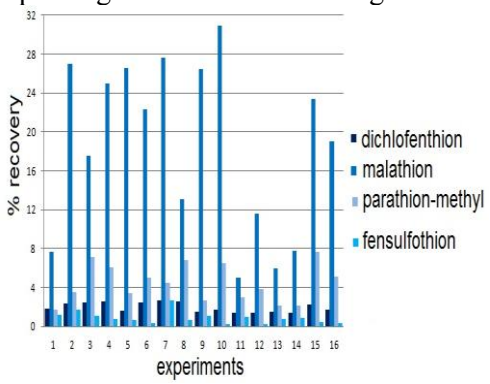

Figure 3. Recoveries obtained in the 16 experiments for each pesticide, using SiO_2-PVI as adsorbent.

Once the solvent elution was selected, an experimental design was used to find the combination of extraction conditions to extract pesticides from spiked tomato by MSPD with materials based on silicon. The graph of the recoveries obtained for three pesticides in each experiment is observed in figure 3. The best extraction conditions were: 15 min of contact time, 2 mL of solvent volume, adsorbent SiO_2-PVI without lyophilize (experiment 15). These conditions gave to the best recovery for DCF and MPT and the fourth better recovery for FSF.

The calibration process was done with matrix-match standard solutions at 0.0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10 and 0.12 μg/mL. In table 2, the calibration function and the coefficient of determination (R^2) are showed. In all cases, the determination coefficient was higher than 0.99, which indicates a good linearity.

Table 2. Recoveries and relative standard deviations (RSD) for the pesticide extraction by MSPD using SiO_2-PVI

Pesticide	Calibration function	R^2	Spiked level, μg/g	Recovery, %	RSD, %
DCF	A = 1000000C - 3902.7	0.9985	0.2	68	12
			0.8	83	13
MPT	A = 266753C - 834.47	0.9977	0.2	73	11
			0.8	77	9
MLT	A = 665493 - 5061.3	0.9961	0.2	60	18
			0.8	68	11
FST	A = 403883C - 180.71	0.9974	0.2	73	13
			0.8	78	9

A: analytical signal (peak area); C: pesticide concentration (μg/mL)

Recoveries obtained for the organophosphorous pesticides by MSPD extraction with SiO_2-poly(N-vinylimidazole) were at least 60%. The highest recovery was achieved with DCF at 0.8 μg/g followed by MPT and FST that presented recoveries higher than 70% at both spiked level. The lowest recoveries were obtained for MLT at both spike levels and for DCF at 0.2 μg/g. For most of the pesticides the presicion of the extraction was lower than 20%.

Recoveries achieved in our work agrees with results of Torres and co-workers [10] for MLT, MPT and diazinon in tomato (spike level: 0.1 μg/g) by MSPD with C18 and ethyl acetate as solvent elution. However, our values are relatively low in comparison with those obtained by Menezes and co-workers [11] for MPT (95%) from tomato (spike level: 1.0 μg/g) with alumina and dichloromethane.

4. Conclusions.

A material based on SiO_2-PVI was applied for the extraction of organophosphorous pesticides from spiked tomato by MSPD. Recoveries and precision were acceptable (60%, RSD<20%) at two spiked levels this suggest that SiO_2-PVI has potential to be applied as adsorbent in MSPD.

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