

PESTICIDE ANALYSIS IN WATER SAMPLES USING GC-MS PULSED SPLITLESS INJECTION

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Abstract

Pulsed splitless injection was performed on pesticide analysis in water samples using GC-MS and compared to the most frequently used classical hot splitless injection. Fifteen pesticides from different chemical groups like acylalanines (benalaxyl), organophosphorus (chlorpyrifos, malathion, pirimifos methyl), carbamates (methomyl, pirimicarb, propamocarb), triazinone (metribuzin, penconazole), triazoles (triadimenol) anilipirimidines (pyrimethanil), and no classified buprofezin were investigated in this study. A set of experiments in water samples (pH 7) were conducted employing pulsed splitless injection with values of pressure ranging from 10 to 50 psi and purge flow to split vent of 0.5 and 1.5 min and compared to the responses of pesticides when classical hot splitless injection was used. Liquid-liquid extraction of water samples using dichlorometane as solvent, was not efficient for propamocarb because of its higher solubility in water compared to its solubility in dichlorometane. The improvement observed at methomyl was most dramatic. Pulsed splitless injection of 50 psi injection pressure and 1.5 min of split vent, significantly improve the response of methomyl which is difficult to be analyzed in conventional splitless injection. The same pressure but shorter vent time (0.5 min) show significant response improvement of malathion and chlorpyrifos, too. Slightly improvement was observed at pyrimethanil, pirimicarb, metribuzin and penconazole when pressure of 10 psi for 0.5 min is applied. The improvement was not observed at triadimenol and buprofezin.

Key words: pulsed splitless injection, purge flow to split vent, response factor

1. Introduction. Classical hot splitless injection is the most frequently used injection technique when pesticides are analyzed with gas chromatography. However, when it comes to low volatile and thermo labile compounds this kind of injection does not show satisfactory results due to a degradation process that

occurs because of the high temperature in the injector. Many authors emphasize that thermolabile compounds prone to degradation in the injector port should be subjected to the injection enhancement [1-4].

There were attempts to overcome this problem by using different techniques of injection like PTV [5], GC-MS/NP [6]. The research of GODULA et al. [7] showed that pulsed splitless injection technique can significantly improve the performance of classical split/splitless injection recommending that the pulse pressure time should not exceed 1 min and the intensity of the pressure should not be greater than 60 psi because of the losses of volatile compounds.

Pulsed splitless injection is a technique that uses pressure to reduce the volume in the injection liner so the entire injected volume can move to the column very fast. High pressure in the injection port also decreases the possibility of volatile analytes to escape through the septum purge vent. Using this technique the degradation of thermally labile compounds is avoided because of the faster leaving of the hot injection port [8]. The information on its application for analysis of pesticides belonging to different chemical groups is still limited. The literature data shows that no general rules exist for deriving optimal parameters for pulsed splitless injection [3,4,9].

This study deals with the investigation of parameters for pulsed splitless injection for twelve pesticides in order to improve their analysis with GS-MS using hot split/splitless injector when no other types of injectors are available.

2. Materials and methods. 2.1. Apparatus and instrumentation.

Analyses were performed on gas chromatograph Agilent 6890N coupled to a mass spectrometer and equipped with JAS UNIS split/splitless injector series 7683B. Glass wool liner type (JAS 90323L) with single restriction, 88 mm long and 3 mm ID, was used in all experiments. For the separation of analytes DB-5ms Supelco column was used with helium as a carrier gas.

2.2. Chemicals and materials. Certified chemical standards (purity 95–99%) and solvents with HPLC grade were obtained from Sigma Aldrich. Pesticide stock solutions and working standards were prepared in acetone. Hexane was used as solvent for column injection.

2.3. Extraction. The extraction of pesticides from water was made using continuous Liquid-Liquid Extraction (LLE) and dichloromethane (DCM, 40 ml) as a solvent. Water (1 l, HPLC pure) was salted out with sodium chloride (NaCl, 66 g) and the extraction process was carried out using separating funnel. Water was spiked with pesticide standards in concentration of 100 ng/l. Triphenyl phosphate (TPP) was used as an internal standard in concentration of 50 ng/l. The extract was evaporated until dryness and reconstructed in 100 µg/l of hexan.

2.4. GC conditions. Separation conditions are the same for all experiments. The oven temperature ramped from 60 °C for 2 min to 150 °C with increment of 25 °C for 0 min, ramped to 200 with increment of 3 °C for 0 min, ramped to 280 with increment of 20 °C for 10 min, for a total running time of

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Method parameters when the injection pressure of 50 psi for 0.5 min vent time is used

	Quantifier ion	Qualifier ion	RRT	RSD	R%	R^2	Equation	LOD $\mu\text{g/l}$	LOQ $\mu\text{g/l}$
Methomyl	105	58, 88	0.185	11.20	127	0.95	$y = 0.33 \cdot x + 0.0129$	0.55	5.5
Propamocarb	129	58, 188	0.295	–	–	–	–	–	–
Pyrimethanyl	198	199, 77	0.565	3.14	125	0.96	$y = 0.2972 \cdot x - 0.3101$	0.09	0.9
Pirimicarb	166	72, 238	0.601	2.89	109	0.95	$y = 0.2162 \cdot x - 0.2155$	0.01	0.1
Metribuzin	198	103, 144	0.638	2.46	94	0.98	$y = 0.581 \cdot x - 0.0847$	0.08	0.8
Pirimiphos methyl	290	276, 305	0.695	3.47	108	0.96	$y = 0.1107 \cdot x - 0.1031$	0.03	0.3
Malathion	125	173, 93	1.04	8.60	120	0.98	$y = 0.777 \cdot x - 0.0978$	0.54	5.4
Chlorpyrifos	197	97, 199	0.726	6.34	130	0.98	$y = 0.294 \cdot x - 0.197$	0.33	3.3
Penconazole	159	248, 161	0.799	7.14	117	0.97	$y = 0.1749 \cdot x - 0.1845$	0.01	0.1
Triadimenol	112	168, 57	0.822	5.00	120	0.96	$y = 0.0761 \cdot x - 0.0888$	0.19	1.9
Buprofezine	105	106, 172	0.899	2.92	106	0.96	$y = 0.0702 \cdot x - 0.0582$	0.53	5.3
Benalaxyl	148	91, 206	0.966	4.52	112	0.95	$y = 0.158 \cdot x - 0.133$	0.02	0.2

RRT – relative retention time; RSD – relative standard deviation; R – reproducibility;
 R^2 – correlation coefficient; LOD – limit of detection; LOQ – limit of quantification

41.8 min. The temperature of the injector was 250 °C, the temperature of the MS quadrupole was 150 °C and the injection volume was 1 μl .

Pulsed pressure has been tested for optimum performance of the injection, changing the parameters from 10 to 50 psi with the increment of 10 psi and the range of flow to split vent of 0.5 and 1.5 min. To minimize the variations in the injection volume the response of the analytes is measured calculating the response factor (RF) where the target compound response is calculated relative to that of the internal standard [10].

SIM method was created for the analysis of pesticides (Table 1). Blank sample and pure sample in hexan as well as ion extraction technique was used to avoid false positive result.

3. Results and discussion. The extraction was efficient for all investigated pesticides except propamocarb. It is assumed that this pesticide was not extracted from the water. Propamocarb has very high solubility in water (900 g/l) greater than its solubility in DCM (400 g/l) so the extraction efficiency is very low for this pesticide when LLE using DCM as a solvent is used for extraction of propamocarb from water. In order to find the most suitable conditions, RF of the analytes obtained using pulsed splitless injection was compared to the RF obtained with classical hot splitless injection. The purge flow vent time was also investigated. All investigated pesticides except methomyl, benalaxyl and pirimiphos methyl show better result when the vent time was shorter (0.5 min, Fig. 1). Methomyl, malathion, chlorpyrifos and benalaxyl show improvement when pulsed pressure of 50 psi was applied. Pyrimethanil, pirimicarb, metribuzin and penconazole show

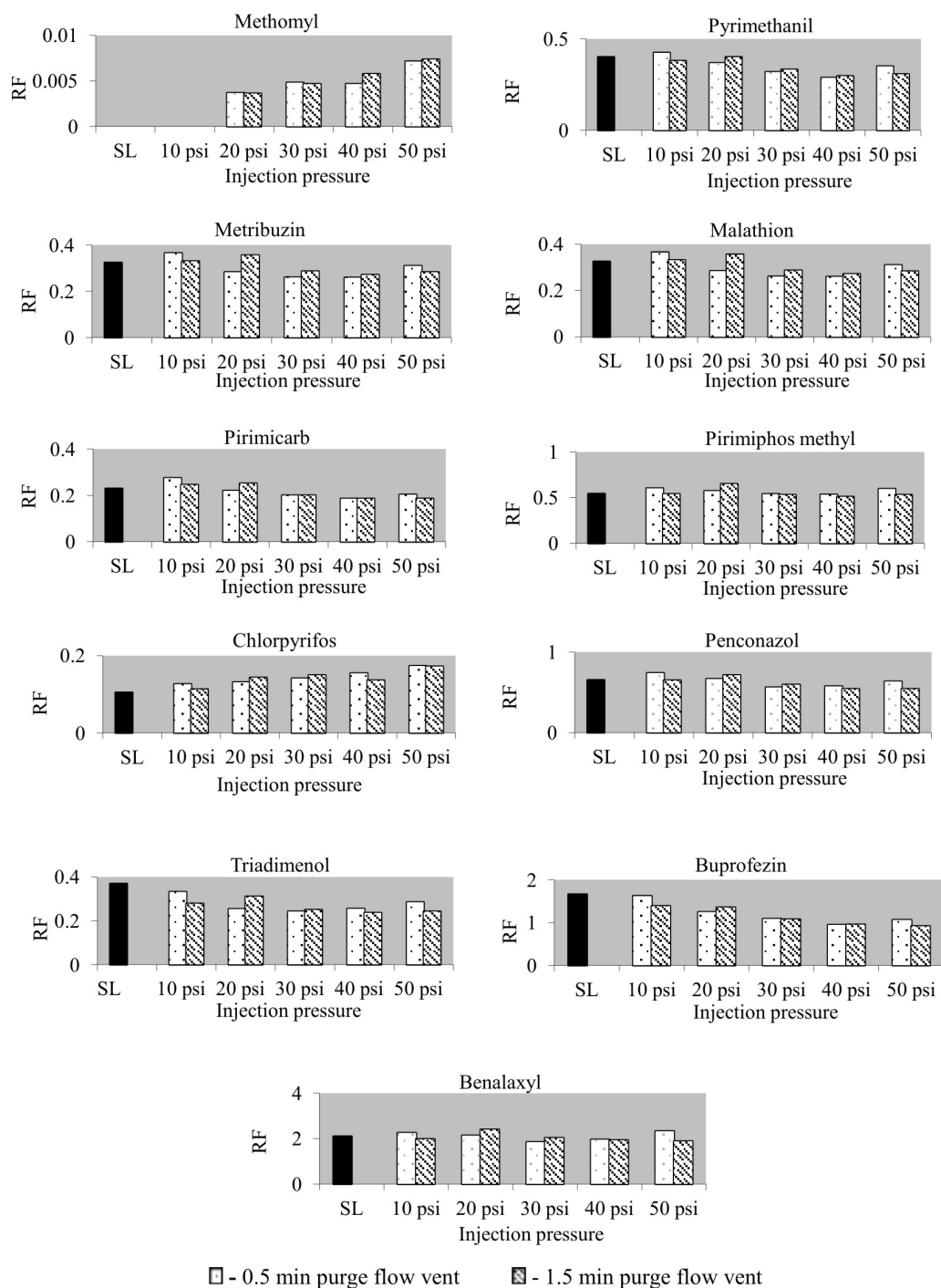


Fig. 1. Response factor (RF) of investigated pesticides when classical hot splitless injection is used (SL) against pulsed splitless injection at 10 psi, 20 psi, 30 psi, 40 psi and 50 psi at 1.5 min and 0.5 min purge flow vent

better result when pulsed pressure of 10 psi was applied. When 20 psi pulsed pressure and 1.5 min purge flow vent was applied, slight improvement was visible for benalaxyl and pirimiphos methyl. Conventional hot splitless injection is better only when triadimenol and buprofezine are determined with GC-MS (Fig. 1). Maximum improvement from the use of pulsed splitless injection, was observed at methomyl.

When classical hot splitless injection as well as low pulsed pressure like 10 psi, is used to inject this pesticide into the column, the peak is not visible even when ion extraction is used. The increase of the pressure results in the improvement of peak visibility showing its maximum at pressure of 50 psi. Other investigated pesticides from the same chemical group like pirimicarb show the improvement when pressure of 10 psi is applied. The improvement was also significant for organophosphorus pesticides malathion and chlorpyrifos (Fig. 1). Other investigated pesticides except triadimenol and buprofezine, show only slight improvement of the RF when pulsed splitless injection was used. For the practice it is important to mention that pulsed splitless injection did not show significant decreasing of the response factor, so the technique can be used for multi pesticide determination.

Considering the obtained results a method using injection pressure of 50 psi for 0.5 min vent time was created. Other method parameters are the same as mentioned before. Relative standard deviation ranged between 2.46 for metribuzin and 11.20 for methomyl (Table 1).

Reproducibility was on the upper limit ranging from 94% for metribuzin to 130% for chlorpyrifos. Such behaviour is not surprising due of the high level of extract concentration. Linearity coefficient was on the lower limit ranging from 0.95 to 0.98 but this is also considered as satisfactory when the calibration is made from the real samples which are subjected to the entire process of extraction and concentration. Limit of detection (LOD) ranged between 0.01 µg/l and 0.55 µg/l and the limit of quantification (LOQ) ranged between 0.1 µg/l and 5.5 µg/l (Table 1).

4. Conclusion. The investigation demonstrated that pulsed splitless injection did not always show significant improvement of the response factor and it is not related to the chemical group to which a pesticide belongs, although the best results are obtained for organophosphorus and carbamate pesticides. In our case pulsed splitless injections show significant improvement for organophosphorus pesticides malathion and chlorpyrifos but the improvement was not significant in the case of other investigated organophosphorus pesticide like pirimiphos methyl. The most dramatic improvement is observed for methomyl. It is useful to consider that if methomyl, chlorpyrifos and malathion are target compounds of the analysis, the detection should consider pulsed splitless injection of 50 psi in order to improve their response. The investigation shows that general conclusion for injector parameters giving the best results for all investigated pesticides is not

possible, however, sample introduction in the column using injection pressure of 0.5 psi for 0.5 min purge flow vent can improve the detectability of thermo labile pesticides without significant negative impact to the detectability of other compounds. It is also recommended not to use DCM as a solvent when performing liquid-liquid extraction of propamocarb from water matrices.

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