

Development and Application of Methods for the Determination of Pesticide Residues in Natural Waters and Sediments, Coupled to GC-MS

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Abstract

The main objectives of this study were to develop rapid and accurate screening multiresidue pesticide methods on the basis of Solid-Phase Extraction (SPE) technique for the determination of 10 pesticides in water samples and on the basis of QuEChERS technique regarding sediments samples. The target compounds were determined by Gas Chromatography-Mass Spectrometry (GC-MS). The method was validated in terms of accuracy, precision, linearity, detection and quantification limits. The recovery percentages obtained for the pesticides in water samples at three different concentration levels, ranged between 73.2 to 101.2%, with relative standard deviations below 9.3%. The corresponding results from the sediment ranged between 69.5 to 122.7% with relative standard deviations below 11.2%. The limits of detection for the pesticides in water and sediment were below 12 ng L⁻¹ and 9 mg kg⁻¹, respectively. The optimized methods were applied in Epirus region (North-Western Greece) to determine the concentration level of the target compounds in sea water and sediment samples. The analytical methodologies exhibited excellent analytical characteristics and proved to be reliable for the estimation of the pollutant load in sea water and sediment samples from marine aquaculture.

Keywords: pesticides, QuEChERS, sediments, SPE, waters

1. Introduction

A number of pesticides are used in aquaculture to treat sea lice or control weeds and algae (Martínez Bueno M.J. et al.). The determination of the residues of pesticides is one of the major challenges for the preservation and sustainability of the environment (Ccanccapa A et al.). It is very important due to the risks that these compounds offer to human health, besides their persistence in the environment and their tendency to bioaccumulation. Pesticides that are more hydrophobic tend to be detected more frequently in sediment (Elizabeth Carazo-Rojas et al.). It is therefore, needed to be monitored for a better knowledge of their fate.

2. Materials and Methods

Analytical standards were purchased by Fisher Scientific (Leicestershire, UK), purity >99.0%. Stock standard

solutions were prepared at a concentration of 5-100 µg/L in methanol and were stored at -20°C. All solvents used were of pesticide residue analysis grade and purchased from Labscan (Dublin, Ireland). Bond Elut C18 cartridges (500 mg, 6 cm³) were purchased from Agilent Technologies (Walbronn, Germany). Regarding QuEChERS extraction method, propylene centrifuge tubes of 50 mL and 15 mL were used. The QuEChERS purchased from Merck (Darmstadt, Germany) and from Sigma-Aldrich (Steinheim, Germany).

3. Solid-Phase extraction (SPE)

Prior to extraction, C18 cartridges were preconditioned with 2 times of 6 mL of ethyl acetate, followed by 6 mL of methanol and 6 mL of deionized water. In order to adjust the conductivity, 2.5 g NaCl were added. MeOH 1 % (v/v) was also added to avoid analyte adsorption in the glass material. Before the cartridges dried out, water samples (250 mL) were passed through the C18 cartridges, at a flow rate of approximately 5 mL/min, using a vacuum manifold that maintained a constant pressure differential between the inlet and the outlet of the cartridge. Once the total sample was percolated, cartridges were rinsed with 6 mL of deionized water. Afterwards, the cartridges were dried under vacuum for 10 min to remove residual water, and analytes were eluted with 2 times of 6 mL of ethyl acetate. The final extract was dried over anhydrous sodium sulfate, evaporated to dryness under a gentle stream of nitrogen and reconstituted in 0.1 mL hexane and stored at -20 °C prior to chromatographic analysis.

4. QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe)

Five grams of freeze-dried sediment sample were weighed into a 50 ml of poly-propylene centrifuge tube. A volume of 10 ml of Acetonitrile was added afterwards and the tube was shaken vigorously by hand for 1 minute. Then 1.5g of NaCl and 4.0g of MgSO₄ were added and the resulting mixture was shaken immediately to prevent the formation of crystalline agglomerates during MgSO₄ hydration. The samples were centrifuges for 5 min at 4000 rpm. Clean up was performed using d-SPE. An aliquot of 1ml of the upper organic layer was transferred

into a 15 ml poly-propylene centrifuge tube containing 150 mg MgSO₄, 50 mg PSA and 50 mg C18. Tubes were vortexed for 1 minute and centrifuged at 4000 rpm for 5 minutes. The final extract was evaporated to dryness under gentle stream of nitrogen and the reconstituted in 0.1 ml of hexane. Prior the injection in GC-MS system, all samples were filtered through syringe membrane filters (poly-tetrafluoroethylene, 0.22 µm)

5. Results And Discussion

The optimum conditions were implemented to verify the applicability of the proposed method for the quantitative determination of target analytes. Quality parameters including, the linear range, the accuracy R (%), the limits of detection (LODs), and limits of quantification (LOQs) the intra-day precision RSD_T (%), inter-day precision RSD_R (%), were investigated. The methods were validated using spiked seawater and sediment samples (previously ensured to be free of the analyte of interest) fortified with the target compounds at three concentration levels. The analytical methods were shown to be linear over a wide range of concentration. The recovery

percentages obtained for the pesticides in water at three different concentration levels, ranged between 73.2 to 101.2%, with relative standard deviations below 9.3%. The corresponding results from the sediment ranged between 69.5 to 122.7% with relative standard deviations below 11.2%. The limits of detection for the pesticides in water and sediment were below 12 ng L⁻¹ and 9 mg kg⁻¹, respectively.

The optimized methods were applied in Epirus region (North-Western Greece) to determine the concentration level of the target compounds in sea water and sediment samples.

6. Conclusions

The proposed methodologies provided good precision, high extraction efficiency and low enough detection levels, confirming the applicability of it for the routine analysis of pesticides in seawaters and sediments in aquaculture monitoring. It possesses the advantages of SPE and QuEChERS such as (fast, simple, highly sensitive) and could be potentially extended to other classes of pesticides.

References

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