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Multiresidue pesticide determination using QUECHERs pretreatment method and LC-MS/MS instrumentation

Introduction

Multiresidue determination of selected pollutants is of utmost importance in environmental samples. The application of chemical substances throughout the lifetime cycle of crops have been proven to increase overall productivity and inhibit the formation and development of parasites, nevertheless it poses a great threat to ecosystems. This experimental method describes the pretreatment of food samples (fruit and vegetable) for the determination of pesticide residues in trace quantities using Ultra Pressure Chromatography coupled with tandem MS.

The present work includes a convenient experimental procedure based on the innovative method of QuEChERS. This method is suitable for the analysis of multiple classes of pesticide residues in foods and has been given an acronymic name, QuEChERS, that reflects its major advantages (Quick, Easy, Cheap, Effective, Rugged, Safe). The QuEChERS method is effective for the analysis of pesticides in fresh fruits and vegetables, resulting in much faster sample analysis and significant reduction in solvent usage and hazardous waste production.

Materials

QuEChERS dispersive sample preparation kit, DisQuETM-AOAC (acetate) consists of 50 mL plastic centrifuge tubes containing anh. MgSO4 and sodium acetate followed by 2 mL mini-centrifuge tubes containing anh. $MgSO_4$ and SiO_2. The DisQuETM-CEN (citrate) consists of 50 mL plastic centrifuge tubes containing anh. MgSO4, NaCl, sodium citrate tribasic dehydrate and sodium hydrogencitrate sesquihydrate followed by 2 mL mini-centrifuge tubes containing anh. $MgSO_4$, and SiO_2. Other chemicals and solvents needed were: acetic acid (purity 100%, Merck), methanol LC-MS (purity ≥ 99,9 %, Merck), acetonitrile LC-MS and formic acid (purity 98-100%, Merck).

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Table 1: Pesticides used for preparation of standard solution and quantification.

Pesticide name	Purity
Acetamiprid Pestanal	99,90%
Atrazine Pestanal	97,50%
Azinphos- methyl Pestanal	98,90%
Azoxystrobin Pestanal	99,90%
Boscalid Pestanal	99,90%
Carbaryl Pestanal	99,80%
Chlorpyrifos Pestanal	99,90%
Clothianidin Pestanal	99,90%
Cyprodinil Pestanal	99,80%
Imazalil Pestanal	99,70%
Imidacloprid Pestanal	99,90%
Metalaxyl Pestanal	99,00%
Oxamyl Pestanal	99,60%
Pirimicarb Pestanal	99,00%
Pyraclostrobin Pestanal	99,90%
Pyrimethanil Pestanal	99,90%
Thiamethoxam Pestanal	99,70%
Triadimenol Pestanal	98,40%

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Sample Pretreatment

Weigh an amount (gr) of sample in a 50 mL tube

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Add the suitable solvent (acetonitrile, methanol, etc.)

⇩

1. Shake vigorously 1 min

2. Vortex 1 min

⇩

Centrifugation 3 min/ 3000 rpm

⇩

Take an aliquot to 2 mL tube

⇩

Add the extra sorbent if needed(activated carbon)

⇩

1. Shake vigorously 30 sec

2. Vortex 30 sec

⇩

Centrifugation 3 min/ 3000 rpm

⇩

Take aliquot to vial

⇩

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LC-MS/MS analysis

The chromatographic conditions are: Acquity UPLC BEH 1,7 μm, 2,1x100 mm column, gradient elution with ultra pure water:MeOH 0,1% formic acid (98:2, water phase) and MeOH 0,1% formic acid (organic phase), 0,45mL min^{-1} flow. The analysis time was 10 min. For the MS/MS detection the MRM mode will be employed in positive mode electrospray ionization, using nitrogen as the dessolvation/nebulising gas, argon (99,9995% pure) as the collision gas. The source temperature is set to 120°C and the dessolvation temperature to 450°C. For each pesticide, two characteristic MRM transitions will be identified and the cone voltage, as well as the collision energy for each transition, will be optimized.

Standard curves and standard solutions

The pesticides used, in order to prepare the standard solutions and quantify the obtained detection results are summarized in table 1. 10 mg (solid state) or appropriate volume (liquid state) of each pesticide are dissolved in MeOH and diluted in 10 mL volumetric flasks, ending up in final pesticide solutions of 1000 mg L^{-1} concentration (stock solution). A stock mixed solution of the pesticides (conc. 10 mg L^{-1}) will be prepared by transferring 1 mL of each pesticide stock solution into a 100 mL volumetric flask and diluting with MeOH. Finally a standard mixed solution of the pesticides (conc. 1 mg L^{-1}) will be prepared by adding 1 mL of stock mixed solution into a 10 mL volumetric flask and diluting with MeOH.

Quality control of analytical results

Quantification and quality check will be based on L.O.D, L.O.Q, Matrix Suppression and R^2 values, as described in the 96/23/2002 EU Directive on the Quality of Analytical Results.

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