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Identification of pesticide residues in order to ensure food security of cereals grown in Transylvania by gas chromatography/mass spectrometry

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Abstract

The Protocol requires the extraction of pesticides using acetonitril extraction and purification using the solid phase extract (D-SPE) with C18 as sorbent material (octadecil), followed by gas chromatographic determination coupled with mass spectrometry (GC-MS). The identified compounds was: amidosulfuron , detected in 9 samples of the 13 detected pesticide residue, residue concentrations ranging from 0.01-0.04 mg / kg, propioconazol, detected in a sample of 13 containing 0.03 mg / kg tebuconazole detected in 4 samples of 13 residue concentration ranging from 0.11-0.19 mg / kg. Did not detect deltamethrin and thiacloprid.

Regarding the variation on pesticide content, applying the test ANOVA found significant correlations between pesticide residues detected in the three years of study

Keywords: cereals, pesticides, extraction, acetonitril, content, detected.

1. Introduction

Cereals are by far the most important sources of food in the world, directly for human consumption and indirectly as a factor in livestock production. What happens in the grain sector is therefore crucial for the world's food supply. The need to feed a growing population is a constant pressure on the crop production, that faces with increasingly degraded environment. [1].

The increased food needs due to world population growth led to an increased use of chemicals, particularly fertilizers and pesticides. In addition to the beneficial role of increased production, some pesticides have been shown to have negative effects on human health through bioaccumulation due to persistent residues in food. [2]

The QuEChERS (quick, easy, cheap, effective, rugged, and safe) sample preparation method accommodate various cereal grain matrices (corn, oat, rice, and wheat) and provide good analytical results (recoveries in the range of 70-120% and RSDs <20%) for the majority of the target pesticides (about 180 analytes). [3]

2. Materials and Methods

The purpose of this study was to determine of pesticides in cereal species studied by modern methods of investigation. To achieve the objective have been studied two species of grain (wheat, triticale variety-variety Turda 2000 Titan) from SCDA Turda, popular cereals grown in Transilvania.

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The Turda 2000 wheat variety was created to SCDA Turda in 2000 and was achieved by repeated individual selection in combination the hybrid varieties Arieşan and Apulum. This variety has been certified its baking quality. [4] The Titan triticale variety was created in 1998 at INCDA Fundulea and is a synthesis species of man-made hybrid by amfiploidization between wheat (Tritium sp.) and rye (Sacale cereal). It is a variety with high productive potential and adaptability, superior to other cereals. The setting of interest compounds: Have been identified the active substances of commercial products that were used for the treatment of the samples subjected to the experience. The treatments applied to the grain varieties under study aimed to combat pests, plant diseases and fungi that cause destruction of weed in crops. These pesticides were applied according to the prospectus in different stages of vegetation. It was pursued 5 active residue(amidosulfuron,propioconazl, deltamethrin, thiacloprid and tebuconazole), which has been identified as AML or MRL Reg. (EU) No. 600/2010. [5]

The extraction method chosen is QuEChERS method, adapted to wheat- matrix according to the literature and based on solid phase extraction with the advantage of retaining substances co-extracted, letting the pesticide to pass. [6]

3. Results and Discussion

Samples were coded according to experimental design and the analyzes by the methodology described.

The Protocol requires the extraction of pesticides using acetonitrile extraction and purification using the solid phase extract (D-SPE) using C18 as sorbent material (octadecil), followed by gas chromatographic determination coupled with mass spectrometry (GC-MS).

According to existing regulations in determining pesticide residues in food matrix, it is required the determining of performance parameters of the method (linearity, repeatability and reproducibility, accuracy (recovery coefficient) for standard methods as well as for those that bring slight changes to improve the method.

For the purposes of the foregoing, the following step were taken:

Standard solutions were injected individually resulting in a chromatogram for each compound using SCAN mode. Following the standards injection the retention time of each compound of interest was identified.

For a qualitative determination there were injected all 48 samples in SCAN and extraction method, then was made a quantitative determination the card by making a calibration curve for the three compounds analyzed. Identifying the spectrum scan using NIST libraries 127şi NIST 147

To set the concentration levels for which there is linearity of achieving a 5-point calibration curve, determining the correlation coefficient R2, the following standard concentrations: 0.02 ppm, 0. 05 ppm, 0.2 ppm, 0.5 ppm, 1.25. Because the concentration area is a fairly wide, two types of calibration curves were chosen:

Low concentration calibration curve (0.02 ppm, 0. 05 ppm, 0.2 ppm)

High concentration calibration curve (0.2 ppm, 0.5 ppm, 1.25)

To highlight the method's accuracy, repeatability and reproducibility, the determination of pesticide residues was performed simultaneously on six samples, determining the average standard deviation. (RSD%) (RSD%)

In order to verify the method's accuracy, we determined the recovery coefficient (± CV) for three compounds(amidosulfuron, propioconazol,tebuconazole,realizig in this way, an enrichment of the sample with standard solution concentrations.

The identified compounds are: amidosulfuron, detected in 9 samples of the 13 detected pesticide residue, residue concentrations ranging from 0.01-0.04 mg / kg, propioconazol, detected in a sample of 13 containing 0.03 mg / kg tebuconazole detected in 4 samples of 13 residue concentration ranging from 0.11-0.19 mg / kg. Did not detect deltamethrin and thiacloprid.

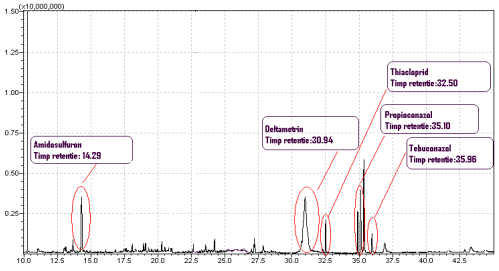

Figure 1. Chromatogram of standard mix

Regarding the variation on pesticide content, applying the test <One- Way ANOVA>, found significant correlations between pesticide residues detected in the three years of study, based on the following results:

$$F=10.8;\ R^2=0.4279;\ P<0.001;\ S^{***}$$

Variations in pesticide content and comparison with legislation MRLs (maximum residue limit), and the report of the analyzed samples are presented in the following figures

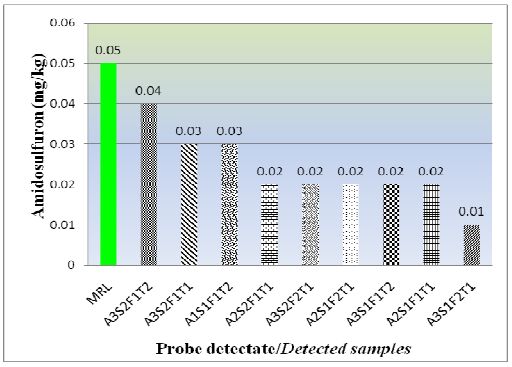

Figure 2. The amidosulfuron content variation in correlation with MRL

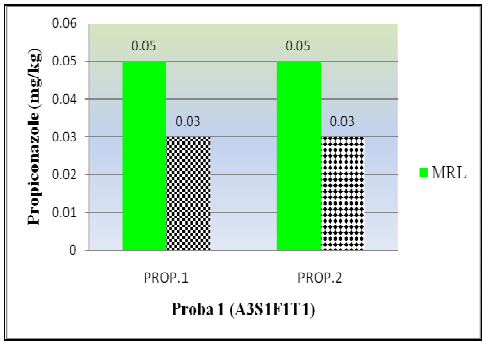

Figure 3. The propiconazol content variation in correlation with MRL

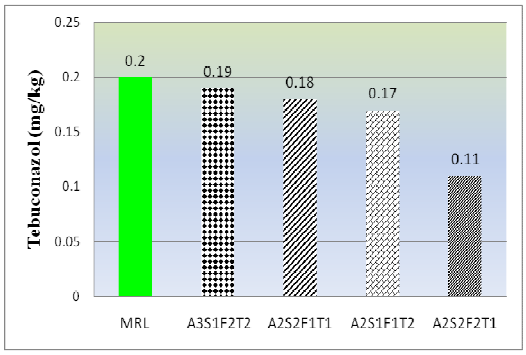

Figure 4. The tebuconazol content variation in correlation with MRL

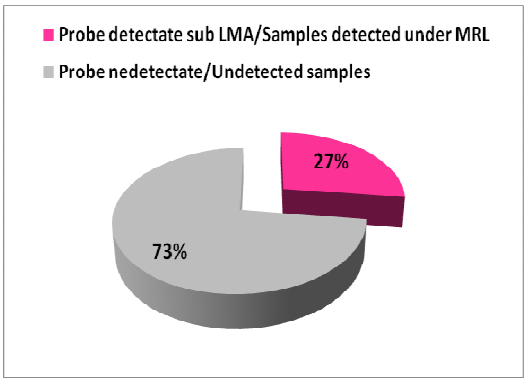

Figure 5. The report analyzed samples

Of the 48 samples analyzed for the determination of pesticide residues in 13 samples, representing 27% of all samples analyzed, pesticide residues have been identified as under maximal limit admitted, in the remaining 35 samples, meaning 73% of all samples analyzed, were no pesticide residues detected.

4. Conclusion

The amidosulfuron compound was detected below the maximum limit allowed in a number of 9 samples of 13.

The propioconazol compound was detected below the maximum limit allowed in one sample of 13.

The tebuconazole compound was detected in four samples of 13.

The extraction of pesticide residues was done by QuEChERS modified method, based on the following considerations: reducing working time, smaller volumes of solvents in analytical terms of repeatability and reproducibility, the possibility of three samples simultaneously.

Quantitative determination of pesticide residue in samples taken in the study was performed with GC-MS technique, mass spectrometer operating in SIM mode (single ion monitoring)

Compliance with Ethics Requirements:

Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human and/or animal subjects (if exists) respect the specific regulations and standards.

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