Monitoring of pesticide residues in processed and unprocessed cereals from different regions of Macaronesia

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Introduction

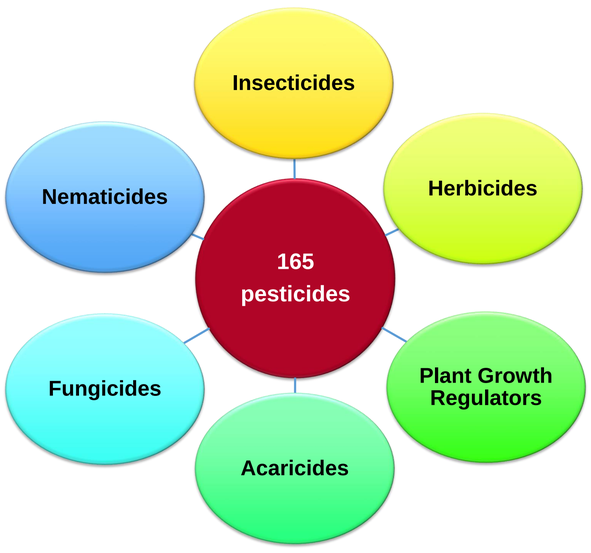
Cereals and their derivatives are staple foods in balanced diets mainly because of their contribution of carbohydrates, which constitute an important source of energy, as well as their high content of vitamins, minerals, and fiber. They are one of the most consumed foods in the Canary Islands due to the popular tradition, as well as their great nutritional values. The high demand of the Canarian population added to the considerable decrease in its own production have led to a massive import. In the case of Cape Verde, statistical data published by The World Bank [1] in 2016 estimates that the cereal production was 5642 tons. These facts demonstrate the high consumption of cereals in the Macaronesia Region.

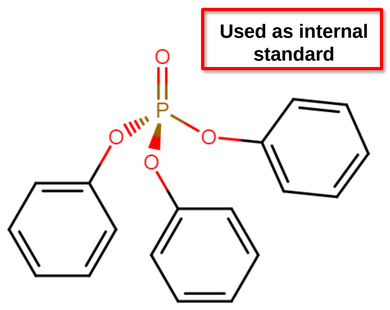
Nowadays, it is of great importance to develop methodologies for the evaluation and monitoring of pesticide residues, that are intensively used as phytosanitary products to prevent, mitigate or even eliminate pests during harvesting and storage of cereals, with the aim of assuring the quality of these products.

In this study, an analytical method has been applied for the determination of 165 pesticide residues in processed and unprocessed cereals from the Macaronesia Region, using both gas (GC) and liquid chromatography (LC) coupled to mass spectrometry in combination with the QuEChERS method [2] as extraction and clean-up procedure. In order to ensure the reliability of sample analysis results, the methodology was validated following the European guidelines of SANTE/12682/2019 guidance [3] obtaining good recovery values and sensitivity.

Experimental

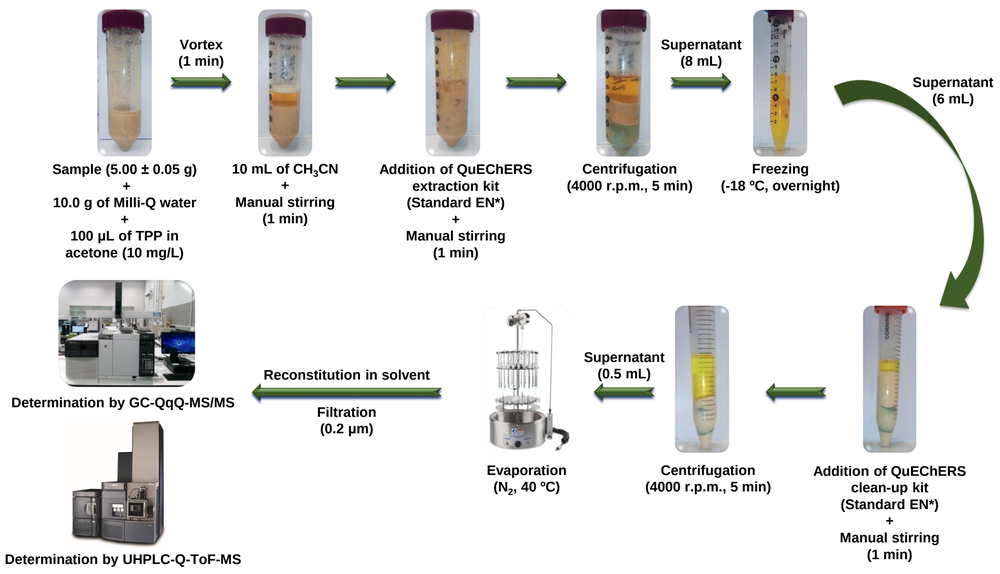
SELECTED PESTICIDES





Triphenyl phosphate (TPP)

QuEChERS-GC/LC-MS PROCEDURE



*Standard EN 15662:2008. Food of plant origin. Determination of pesticide residues using GC–MS and/or LC–MS/MS following acetonitrile extraction/partitioning and clean-up by dSPE. QuEChERS Method [4].

Results and discussion

SAMPLES ANALYZED

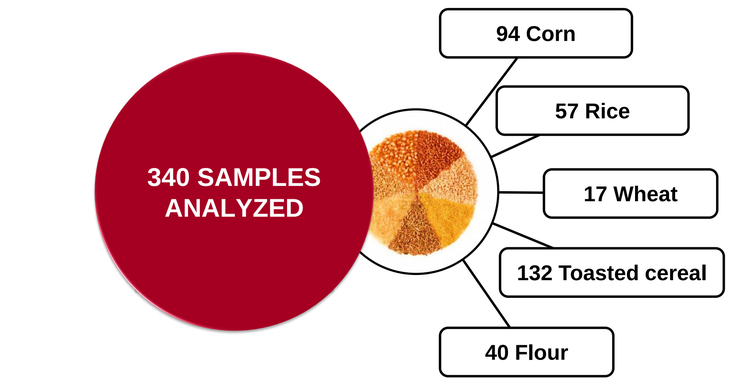


Figure 1.- Processed and unprocessed cereals analyzed in the period 2017-2019.

POSITIVE SAMPLES

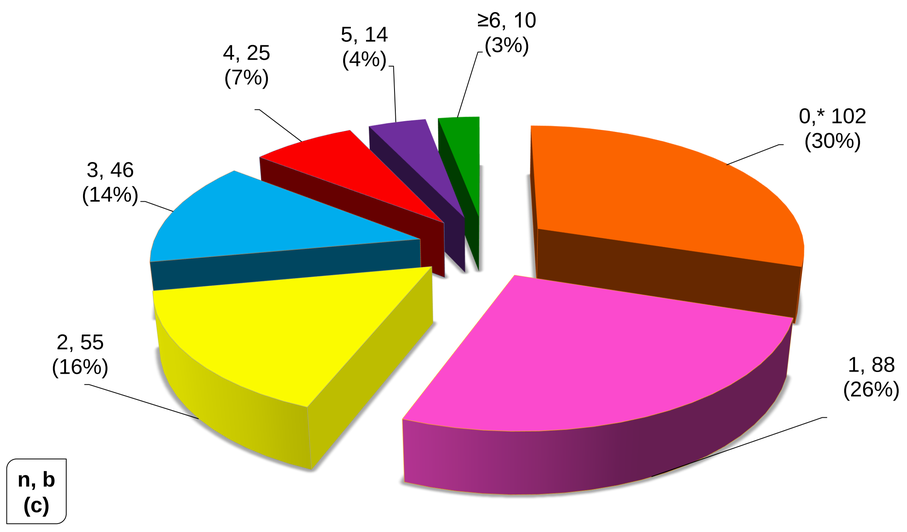


Figure 2.- Graphical representation of the statistical results obtained. (n) Number of pesticides detected and/or quantified in the samples analyzed. (b) Number of samples containing any of the n detected and/or quantified pesticides. (c) Percentage of positive samples with respect to the total samples analyzed. (*) Number of samples in which pesticide residues have not been detected.

METHOD VALIDATION OF QuEChERS-GC/LC-MS PROCEDURE

Table 1.- Method validation data related to the quantified pesticide residues.

Analytical methodology	GC-QqQ-MS/MS	UHPLC-Q-ToF-MS
R^2 in Matrix-matched calibration (n = 7)	0.9992	0.9962
Recovery study[a] (n = 5) (RSD, %)	66 – 96 (18)	68 – 107 (9)
LOQ_{method}[b] (mg/kg)	0.01 – 0.02	0.002 – 0.03

R^2: Determination coefficient. a) Average of 5 extractions at two different concentrations (10 and 100 µg/L for GC method and 75 µg/L for LC method). b) Defined as the concentration which provides a signal-to-noise ratio higher than 10.

ANALYSIS OF SAMPLES RECEIVED FROM 2017 TO 2019

Table 2.- Summary of the results obtained from the analysis of different samples using the QuEChERS-GC/LC-MS method.

Pesticide	Number of samples[a]	Range of analyte concentration[b] (mg/kg)
Acetamiprid	3	0.02 – 0.17
Carbendazim	2	0.01
Chlorpyrifos	11	0.01 – 0.04
Chlorpyrifos-methyl	19	0.01 – 0.34
Cyfluthrin	1	0.02
Cypermethrin	33	0.01 – 0.56
Deltamethrin	86	0.01 – 0.74
Dichlorvos	4	0.12 – 0.16
Fenitrothion	3	0.03 – 0.10
Hexaconazole	3	0.03 – 0.04
Imidacloprid	2	0.05
Lambda-Cyhalothrin	5	0.01 – 0.03
Nitenpyram	1	0.02
Permethrin	2	0.01
Pirimiphos-methyl	111	0.01 – 7.83
Propiconazole	18	0.01 – 0.02
Tebuconazole	15	0.01 – 0.02

a) Number of samples with detected and/or quantified pesticides residues . b) Range of analyte concentrations found for the quantified pesticide residues.

Conclusions

- In this work, the QuEChERS method combined with both GC and LC coupled to mass spectrometry has been applied for the analysis of 165 pesticide residues in processed and unprocessed cereals from the Macaronesia Region received in the period 2017-2019.
- A percentage of 70% of the samples showed one or more pesticide residues, while 30% did not contain any of them.
- Pirimiphos-methyl, deltamethrin and cypermethrin were the most frequently found pesticides in the cereal samples analyzed in the present study.
- Seven, nine and fifteen violations of the established MRLs were found in corn, wheat and rice samples, respectively. Twenty of them from approved pesticides and eleven from non approved pesticides.

Acknowledgments

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1. The World Bank (http://www.worldbank.org/).
2. Anastassiades M, Lehotay SJ, Štajnbaher D, Schenck FJ. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. J AOAC Int. 2003;86:412-31.
3. Analytical quality control and method validation procedures for pesticide residues analysis in food and feed. Document Nº SANTE/12682/2019.
4. Standard EN 15662:2008. Food of plant origin. Determination of pesticide residues using GC–MS and/or LC–MS/MS following acetonitrile extraction/partitioning and clean-up by dSPE. QuEChERS Method.

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