EVALUATION OF PESTICIDES IN WHITE WINES FROM DIFFERENT ORIGINS USING GAS CHROMATOGRAPHY MASS SPECTROMETRY. PRELIMINARY RESULTS

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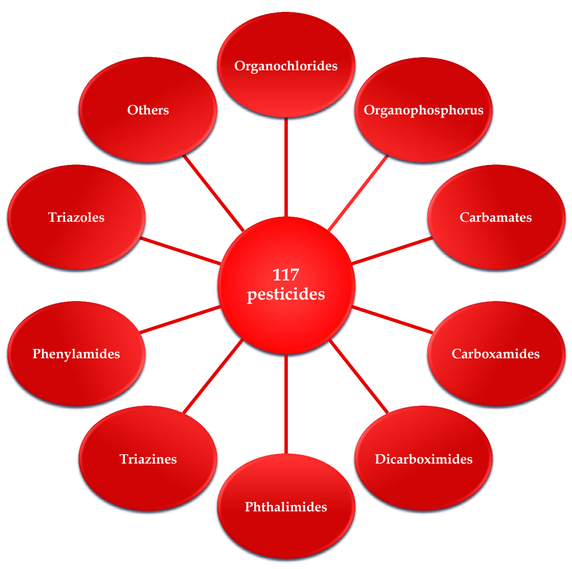
INTRODUCTION

Wine is one of the most consumed alcoholic beverages in the world, being part of human culture for more than 6000 years and playing, in many cases, an important role in the ceremonial life of different cultures. Wine production represents one of the most important within the agrifood sector of the Macaronesia. That is why, control and monitor the pesticides present in them is of great importance in order to ensure the safety of their consumption, especially in those wines that have not been subject to strict controls. The analytical techniques for its determination include both gas chromatography (GC) and liquid chromatography (LC) with mass spectrometry (MS) detection systems combined with extraction techniques. Among them, solid phase extraction and the QuEChERS method (*quick, easy, cheap, effective , rugged, safe*) are the most commonly applied [1], always using good practice criteria in their determination as it is indicated by the SANTE/11813/2017 guide [2].

In this work a method based on QuEChERS sample preparation method and GC-MS analysis was developed for simultaneous determination of 117 pesticide residues in white wine, using Triphenyl phospate (TPP) as internal standard . The methodology was validated obtaining limits of quantitation between 0.010 mg/kg and 0.025 µg/kg and recovery values in the range 70 and 120% for most analytes (with relative standard deviations lower than 19%). This leds to the identification and quantitation of a wide group of pesticides commonly used in Canary wines and from other regions allowing establishing a comparison between the results obtained.

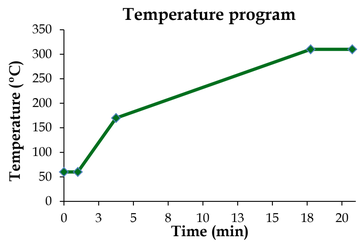
EXPERIMENTAL

SELECTED PESTICIDES



GC CONDITIONS

TEMPERATURE PROGRAM	Temperature (ºC)	Rate (ºC/min)	Hold time (min)	Run time (min)
Initial	60	-	1	1.00
Ramp 1	170	40	-	3.75
Ramp 2	310	10	3	20.75

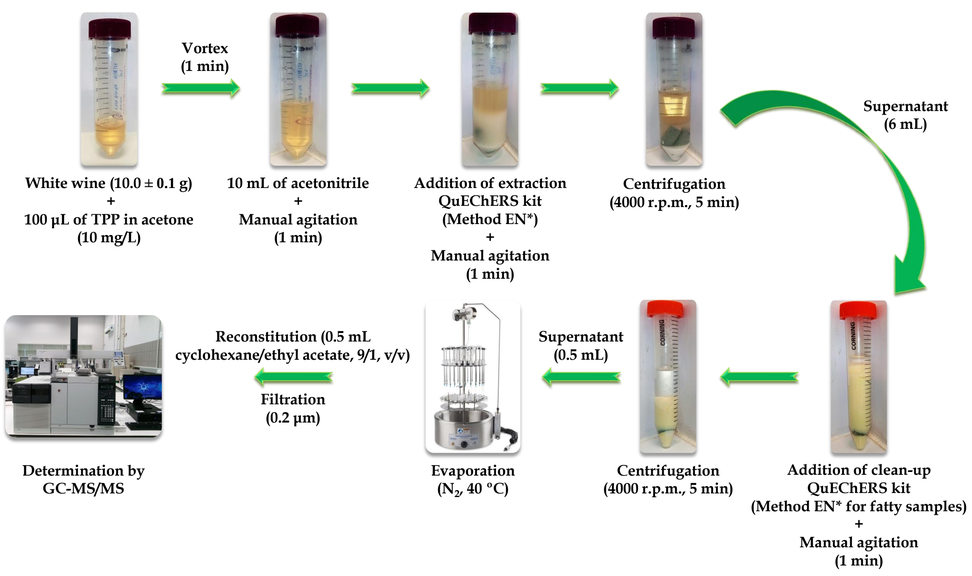


- **Injection volume:** 2 µL.
- **Injection mode:** Splitless.
- **Injector temperature:** 280 ºC.
- **Columns:** Two identical (5% phenyl)-methylpolysiloxane-bonded fused silica capillary columns (HP-5ms; 15 m × 0.25 mm, 0.25 µm film thickness).
- **Carrier gas flow(He):** 1.0 and 1.2 mL/min (*backflush* system).

MS CONDITIONS

- **Ionisation mode:** Electron impact (EI)
- **Mass analyser:** Triple quadrupole (QqQ)
- **Electron ionisation energy:** -70 eV
- **Transfer line temperature:** 280 ºC
- **Ion source temperature:** 280 ºC
- **Quadrupoles temperature:** 180 ºC

QuEChERS-GC-MS/MS PROCEDURE



*QuEChERS method considered by the European Committee for Standardization (CEN) as a standardized method. Standard EN 15662 [3].

RESULTS AND DISCUSSION

MATRIX-MATCHED CALIBRATION

Table 1.- Matrix-matched calibration data for some of the most relevant pesticides evaluated. R^2: Determination coefficient; b: Slope; S_b: Slope standard deviation; a: Intercept; S_a: Intercept standard deviation.

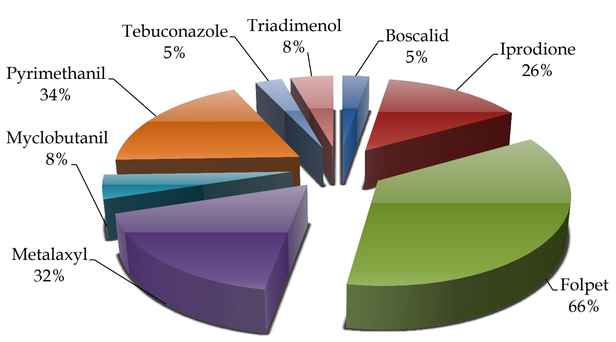
Pesticide	Range of concentration studied (µg/L)	Calibration data (n = 7) $b \pm S_b \cdot t_{(0.05;5)}$	$a \pm S_a \cdot t_{(0.05;5)}$	R^2	Pesticide	Range of concentration studied (µg/L)	Calibration data (n = 7) $b \pm S_b \cdot t_{(0.05;5)}$	$a \pm S_a \cdot t_{(0.05;5)}$	R^2
Benalaxyl	10-200	$8.59 \cdot 10^{-3} \pm 1.26 \cdot 10^{-4}$	$-1.76 \cdot 10^{-2} \pm 1.36 \cdot 10^{-2}$	0.9998	Metalaxyl	10-200	$4.74 \cdot 10^{-3} \pm 8.07 \cdot 10^{-5}$	$7.51 \cdot 10^{-4} \pm 8.99 \cdot 10^{-3}$	0.9998
Boscalid	10-200	$1.92 \cdot 10^{-2} \pm 5.07 \cdot 10^{-4}$	$-1.02 \cdot 10^{-1} \pm 5.65 \cdot 10^{-2}$	0.9995	Myclobutanil	10-200	$1.51 \cdot 10^{-2} \pm 1.94 \cdot 10^{-4}$	$-4.49 \cdot 10^{-2} \pm 2.09 \cdot 10^{-2}$	0.9999
Chlorpyrifos	10-200	$1.34 \cdot 10^{-2} \pm 1.39 \cdot 10^{-4}$	$-2.73 \cdot 10^{-2} \pm 1.55 \cdot 10^{-2}$	0.9999	Penconazole	10-200	$2.20 \cdot 10^{-2} \pm 3.07 \cdot 10^{-4}$	$-6.48 \cdot 10^{-2} \pm 3.42 \cdot 10^{-2}$	0.9999
Cyprodinil	10-200	$6.06 \cdot 10^{-3} \pm 9.57 \cdot 10^{-4}$	$-9.86 \cdot 10^{-3} \pm 1.03 \cdot 10^{-2}$	0.9998	Propoxur	10-200	$6.77 \cdot 10^{-3} \pm 1.94 \cdot 10^{-4}$	$-1.29 \cdot 10^{-2} \pm 2.00 \cdot 10^{-2}$	0.9994
Fludioxonil	10-200	$2.78 \cdot 10^{-2} \pm 3.30 \cdot 10^{-4}$	$-1.18 \cdot 10^{-1} \pm 3.68 \cdot 10^{-2}$	0.9999	Pyrimethanil	10-200	$1.25 \cdot 10^{-2} \pm 1.61 \cdot 10^{-4}$	$5.03 \cdot 10^{-3} \pm 1.84 \cdot 10^{-2}$	0.9999
Folpet	10-200	$4.67 \cdot 10^{-3} \pm 1.90 \cdot 10^{-4}$	$-1.68 \cdot 10^{-3} \pm 2.11 \cdot 10^{-2}$	0.9988	Simazine	10-200	$6.21 \cdot 10^{-3} \pm 1.33 \cdot 10^{-4}$	$-1.62 \cdot 10^{-3} \pm 1.52 \cdot 10^{-2}$	0.9997
Iprodione	10-200	$2.80 \cdot 10^{-3} \pm 1.08 \cdot 10^{-4}$	$-1.71 \cdot 10^{-2} \pm 1.24 \cdot 10^{-2}$	0.9989	Tebuconazole	10-200	$9.81 \cdot 10^{-3} \pm 1.24 \cdot 10^{-4}$	$-4.43 \cdot 10^{-2} \pm 1.38 \cdot 10^{-2}$	0.9999
Lindane	10-200	$1.38 \cdot 10^{-2} \pm 4.74 \cdot 10^{-4}$	$-1.85 \cdot 10^{-2} \pm 5.42 \cdot 10^{-2}$	0.9991	Triadimenol	10-200	$2.27 \cdot 10^{-2} \pm 2.55 \cdot 10^{-4}$	$-8.00 \cdot 10^{-2} \pm 2.75 \cdot 10^{-2}$	0.9999

RECOVERY STUDY

Table 2.- Recovery and LOQ data for some of the most relevant pesticides evaluated. a) Average of the results obtained from the recovery study (n = 5) for the analytes selected in the white wine samples at two concentration levels: 0.025 mg/kg and 0.100 mg/kg. b) Defined as the lowest matrix-matched calibration concentration which provides a signal-to-noise ratio higher than 10 for the quantification transition and at least 3 for the confirmation transition, taking into account the dilution factor and recovery.

Pesticide	Recovery (%)[a]	LOQ_{method}[b] (mg/kg)	Pesticide	Recovery (%)[a]	LOQ_{method}[b] (mg/kg)
Benalaxyl	79 (9)	0.013	Metalaxyl	74 (6)	0.014
Boscalid	120 (7)	0.008	Myclobutanil	84 (10)	0.011
Chlorpyrifos	69 (10)	0.014	Penconazole	80 (11)	0.012
Cyprodinil	75 (8)	0.013	Propoxur	91 (8)	0.010
Fludioxonil	106 (10)	0.009	Pyrimethanil	75 (6)	0.013
Folpet	71 (12)	0.014	Simazine	76 (8)	0.010
Iprodione	115 (6)	0.009	Tebuconazole	108 (16)	0.009
Lindane	65 (3)	0.015	Triadimenol	79 (10)	0.012

Percentage of samples with analytes at concentrations above the Maximum Residue Level (MRL)



- **Total samples analysed:** 38
- **Origin of the samples:** Canary Islands (23) and Mainland (15)
- **Samples that present pesticides at concentrations higher than the MRL:** 28 (74%)
- **Samples with pesticides at concentrations below the MRL:** 5 (13%)
- **Samples in which no residues were detected:** 5 (13%)

SAMPLES ANALYSIS

Table 3.- Summary of the results obtained from the analysis of different white wines (n = 2) by the QuEChERS-GC-MS/MS method. a) Number of samples containing the analytes present in the table at concentrations higher than their respective MRLs.

Pesticide	Number of samples[a]	Concentration range (mg/kg)
Boscalid	2	0.017 - 0.020
Iprodione	10	0.025 - 0.438
Folpet	25	0.022 - 1.133
Metalaxyl	12	0.017 - 0.746
Myclobutanil	3	0.014 - 0.016
Pyrimethanil	13	0.028 - 1.463
Tebuconazole	2	0.014
Triadimenol	3	0.013 - 0.022

CONCLUSIONS

- In the present work, the QuEChERS method combined with GC-MS/MS was validated for the determination of 117 pesticides in white wine samples (38 samples).
- 24 of the evaluated samples (74%) presented one or more pesticide residues, while 8 of them (21 %) contained 4 or more analytes at concentrations above the corresponding MRL.
- Folpet, iprodione, metalaxyl and pyrimethanil were the pesticides most frequently found in the wine samples analysed in this study.
- A total of seventy violations of the established MRLs were found.
- Pyrimethanil was found at concentrations 140 times the MRL, folpet 110 times, metalaxyl 75 times and iprodione 44 times the MRL.
- The analytes presented in this communication correspond to those representative of the most important pesticide families analyzed in this work.

REFERENCES

[1] M. Pelajić, G. Peček, D. Mutavdži, P. Dubravk,V. Čepod, Food Chemistry 200 (2016) 98-106.

[2] Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed. SANTE/11813/2017

[3] Standard EN 15662:2008. Food of plant origin-Determination of pesticide residues using GC–MS and/or LC–MS/MS following ACN extraction/partitioning and clean-up by dSPE-QuEChERS Method 2008 (www.cen.eu).

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