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Short communication

Multiresidue method for the rapid determination – in grape, must and wine – of fungicides frequently used on vineyards

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Abstract

A rapid multiresidue gas chromatographic method for determining 17 fungicides in grapes, must and wine, widely used on vineyards, is described. A simple on-line microextraction method for isolation of fungicides was used. Nitrogen–phosphorus and electron-capture detection were used for the identification and quantitation of pesticides. For confirmation, mass spectrometic detection was used. Because of the high selectivity of both detection methods, no clean-up was necessary. The regression coefficients relating to linearity were at least 0.994. Recoveries from spiked grapes, must and wine samples ranged from 78 to 107% and relative standard deviations were not higher than 14%. Individual detection limits were in the range 0.02–0.1 ng. Limits of quantification varied from 0.01 to 0.05 mg/kg, smaller in all cases than the maximum residue limits set down by the legislations of Spain, France and Italy, the main wine-producing countries of the European Union. Only for fludioxonil and hexaconazole do the limits of quantification coincide with the maximum residue limits (0.05 mg/kg) established by the Spanish legislation.

Keywords: Grapes; Must; Wine; Food analysis; Pesticides

1. Introduction

Climate influences the presence and development of a great number of pests in such a decisive way that mathematical models have been developed relating the development of some of them with the values of the main climatic factors [1,2]. On the other hand, soil has a great influence because it is decisive in the nutritional diseases (deficiencies, excesses, etc.) and in the level of development in the nematodes and diseases of the root, and because according to its nature it influences the general state of the plant, which can determine higher resistance and sensibility to certain pests. Finally variety also has an important role in the resistance or sensibility to the different pests and especially to those of cryptogamic origin.

The negative influence of pests and diseases on vineyards is obvious in symptoms like blighting, distortion, shriveling, decay and tissue destruction. More subtle are effects on vine vigor, berry size and fruit ripening. Sequelae such as reduced root growth, poor grafting success, reduced photosynthesis or increased incidence of bird damage on weak vines [3] can be easily overlooked.

All pests and disease agents disrupt vine physiology and, thereby, can influence fruit yield and quality to some degree. However, agents that attack berries directly have the greatest impact on fruit quality. These include three of the major fungal grapevine pathogens, namely, *Botrytis cinerea*, *Plasmopara viticola* and *Uncinula necator* [4].

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For this reason, the vinegrower uses different pesticides, mainly fungicides, to control the pests that affect the vine, but the possibility exists that residues of these products can pass from grape to must and, later, to wine [5–9] with the resulting risk to the consumer's health. Therefore, it is necessary to control the grape production and wine so if residues exist, they do not surpass the established maximum limits in the different countries. Because the European Union has not yet established maximum residue limits (MRLs) for wine, those established for viniferous grapes must be used.

Numerous analytical methods for determining pesticide residues in different fruits and vegetables and also in must and wine have been published. The most frequently used are gas chromatography (GC) with nitrogen–phosphorus (NPD), electron-capture (ECD) or mass spectrometric (MS) detection and liquid chromatography (LC) with ultraviolet (UV) and diode-array detection (DAD). These methods are mainly based on solvent partitioning, supercritical fluid extraction (SFE), solid-phase extraction (SPE) or microextraction (SPME) and on-line micro- or macroextraction [10–23].

In this paper, we report the validation, following the criteria of GLP (Good Laboratory Practice), of a rapid multiresidue method using on-line microextraction and GC with ECD, NPD and MS that provides the determination of residues of 17 fungicides, frequently used on vineyards, in grape, must and wine samples.

2. Experimental

2.1. Chemicals and reagents

Pesticide analytical standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Standards were certified and at least >98% pure. Acetone, dichloromethane, isooctane and toluene were for pesticide residues (Scharlau, Barcelona, Spain). Sodium chloride was analytical grade (Panreac). Two standard solutions containing different fungicides (ca. 200 μg/ml) were prepared in isooctane–toluene (1:1, v/v) (captan, chlozolinate, dichlofuanid, fenarimol, folpet, hexaconazole, myclobutanil, nuarimol, penconazole, procymidone, triadimefon and vinclozolin for GC–ECD and benalaxyl, cyprodinil, fludioxonil, metalaxyl and pyrimethanil for GC–NPD). In both cases, different working standard solutions (0.01, 0.05, 0.1, 0.5 and 2 μg/ml) were prepared by dilution in the same solvent.

2.2. Apparatus and chromatography

2.2.1. GC–ECD

A Perkin-Elmer Autosystem gas chromatograph was used for determination of captan, chlozolinate, dichlofuanid, fenarimol, folpet, hexaconazole, myclobutanil, nuarimol, penconazole, procymidone, triadimefon and vinclozolin. It was fitted with an ECD system, an autosampler (Perkin-Elmer) and a split–splitless injector, connected to a Nelson 1020 (Perkin-Elmer) reporting integrator. A SPB-608 (Supelco) fused-silica column (30 m×0.25 mm I.D., film thickness 0.25 μm) was employed. The injector and detector were operated at 250 and 320°C, respectively. The sample (2 μl) was injected in the splitless mode (30 s), and the oven temperature was programmed as follows: 90°C for 1 min, raised to 150°C (10°C/min) for 4 min, to 290°C (6°C/min) and held for 7.7 min.

2.2.2. GC–NPD

A Hewlett-Packard 6890 equipped with an NPD system, an autosampler 6890 (Hewlett-Packard) and a split–splitless injector and connected to a HP ChemStation (Hewlett-Packard) was used for determination of benalaxyl, cyprodinil, fludioxonil, metalaxyl and pyrimethanil. The capillary column was a HP-5 (30 m×0.32 mm I.D.) with 5% diphenyl–95% dimethylsiloxane (film thickness 0.25 μm) (Hewlett-Packard). The injector and detector were operated at 250°C and 300°C, respectively. The sample (2 μl) was injected in the splitless mode (0.75 min) and the oven temperature was programmed as follows: 90°C for 1 min, raised to 180°C (10°C/min) for 1 min, to 205 (1°C/min), to 250 (30°C/min). Nitrogen was the carrier and make-up gas at 1 ml/min and 9 ml/min, respectively. Hydrogen and air were used as detector gases at 3 ml/min and 60 ml/min, respectively.

2.2.3. GC–MS

A Hewlett-Packard 6890 gas chromatograph was

employed to confirm the identity of all fungicides. It was fitted with a HP 5971 mass-selective detector (Hewlett-Packard), a split–splitless injector, connected to a HP Vectra 500 integrator (Hewlett-Packard). A HP-5MS fused-silica column (30 m×0.25 mm I.D.) was used, with 5% diphenyl–95% dimethylsiloxane liquid phase (film thickness 0.25 μm) (Hewlett-Packard). The injector and interface were operated at 250 and 280°C, respectively. The operation conditions were: acquisition mode scan (mass range 50–450), voltage 1650 V, ionization foil temperature 230°C, quadrupole temperature 150°C. The sample (2 μl) was injected in the splitless mode (60 s), and the oven temperature was programmed as follows: 90°C for 1 min, raised to 210°C (10°C/min), to 240°C (5°C/min), to 270°C (30°C/min), and held for 3 min. Table 1 shows the spectral characterization by GC–electron impact ionization (EI) MS of the fungicides studied.

2.3. Extraction procedure

For the extraction of fungicide residues in grapes, must and wine, a micro on-line extraction method was used. The vegetable material is extracted with an acetone–dichloromethane mixture, followed by filtering and concentrating the obtained extract.

(a) Extraction in grapes. Grapes (5 g) were homogenized at 8000 rpm for 3 min in a high-speed electric mixer (Polytron-Aggregate, Kinematica, Germany) with 30 ml of acetone–dichloromethane (1:1, v/v) and 2 g of anhydrous NaCl. The mixture was filtered through a porous plate funnel (pore size No. 4) and the filtrate was passed through Phase Separator Paper (Whatman 2100150 1 PS) into a washing flask with 10 ml of the solvent mixture. All the fractions were collected in a concentration flask and concentrated to dryness by rotary vacuum evaporation. The dry extract was dissolved in 5 ml of isooctane–toluene (1:1, v/v).

(b) Extraction in must and wine. Must or wine samples were placed in a 50-ml glass flask with hermetic closing, with 20 ml of acetone–dichloromethane (1:1, v/v) and 2 g of anhydrous NaCl. The flasks were introduced into an ultrasonic bath (Ultrasons 613, Selecta) with distilled water for 10 min and the liquid was passed through Phase Separator Paper (Whatman 2100150 1 PS), into a washing flask with 10 ml of the solvent mixture. All organic fractions were evaporated by rotary vacuum evaporation and the residue dissolved in 5 ml of isooctane–toluene (1:1, v/v).

Table 1
Spectral characterization by GC–EI-MS of the fungicides studied

Fungicide	*m/z* (100%)	Other fragments
Benalaxyl	148	206, 91
Captan	79	149, 117
Chlozolinate	259	331, 188
Cyprodinil	224	210, 77
Dichlofuanid	123	224, 167
Fenarimol	139	251, 219
Fludioxonil	248	154, 127
Folpet	260	295, 104
Hexaconazole	83	214, 175
Metalaxyl	206	249, 160
Myclobutanil	179	150, 82
Nuarimol	107	314, 107
Penconazole	248	159, 213
Procymidone	96	283, 67
Pyrimethanil	198	184, 99
Triadimefon	57	208, 85
Vinclozolin	212	198, 124

2.4. Recovery assays

Untreated grape, must and wine samples, once crushed and homogenized, were spiked with fungicides. Recovery assays were performed at 0.01–0.5 ppm. The samples were allowed to equilibrate for 60 min prior to extraction, and were processed according to the above procedure. At each fortification level, five replicates were analyzed.

3. Results and discussion

The fungicides determined by GC–ECD were eluted between 25 and 40 min according to the following sequence: vinclozolin, triadimefon, dichlofuanid, chlozolinate, penconazole, procymidone, hexaconazole, captan, folpet, myclobutanil, nuarimol and fenarimol. For the fungicides analyzed by GC–NPD, the elution order was pyrimethanil, metalaxyl, cyprodinil, fludioxonil and benalaxyl with retention times between 15 and 37 min. In both cases, the chromatograms were very clean without interfering peaks in the areas of interest. Therefore, no clean-up

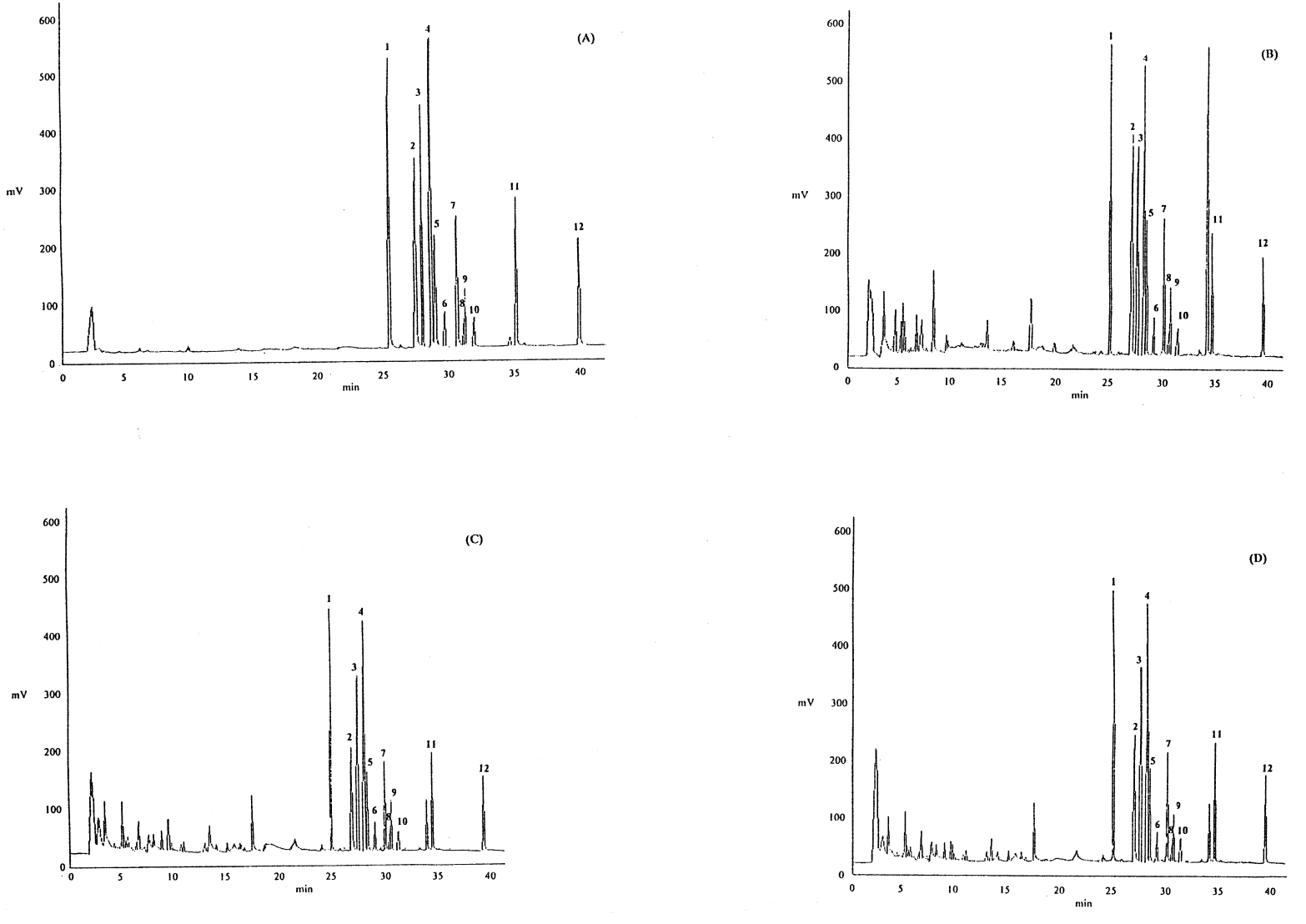

Fig. 1. GC–ECD chromatograms of standard solutions (0.1–0.5 ng/μl) of fungicides (A), and spiked extracts of untreated grapes (B), must (C) and wine (D) samples at 0.1–0.5 mg/kg. 1: Vinclozolin; 2: triadimefon; 3: dichlofuanid; 4: chlozolinate; 5: penconazole; 6: procymidone; 7: hexaconazole; 8: captan; 9: folpet; 10: myclobutanil; 11: nuarimol; 12: fenarimol.

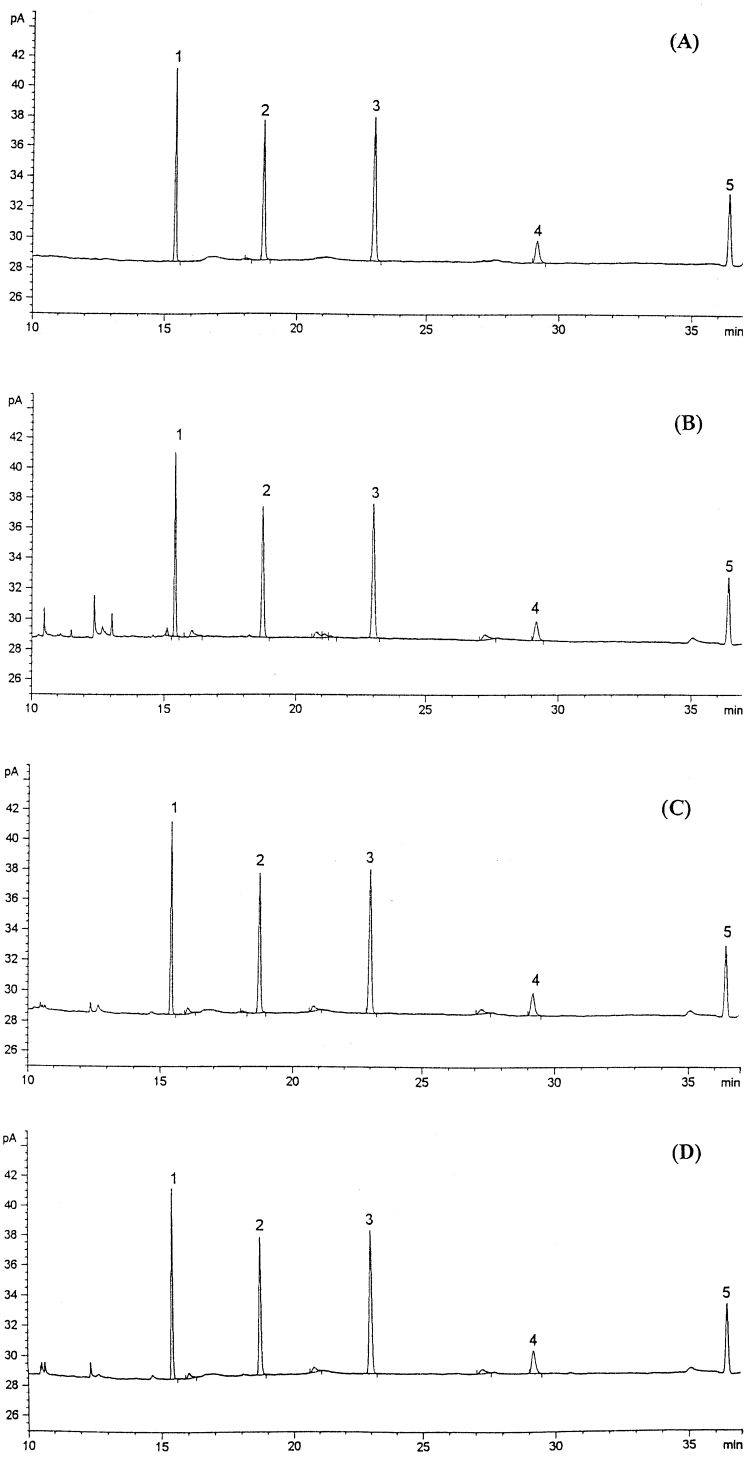

Fig. 2. GC–NPD chromatograms of standard solutions (0.1–0.5 ng/μl) of fungicides (A), and spiked extracts of untreated grapes (B), must (C) and wine (D) samples at 0.1–0.5 mg/kg. 1: Pyrimethanil; 2: metalaxyl; 3: cyprodinil; 4: fludioxonil; 5: benalaxyl.

was necessary. Figs. 1 and 2 show chromatograms of standard solutions of fungicides and spiked untreated grapes, must and wine samples for both GC–ECD and GC–NPD systems.

Calibration curves for the fungicides were prepared by plotting peak areas vs. concentrations for both, ECD and NPD. Good linearity was achieved in the 0.01–2 μg/ml range with correlation coefficients ranging between 0.994 for vinclozolin and 1 for penconazole. The repeatability of peak areas were also good with relative standard deviations (RSDs) ranging between 3.9% for folpet and 8.4% for vinclozolin in the case of ECD and 0.9% for pyrimethanil and 8.7% for fludioxonil for NPD. Table 2 summarizes the statistical parameters obtained when carrying out the linear regression and repeatabilities of peak area for each one of the active ingredients. The values in Table 2 show a great correlation between concentration–area for the 17 compounds studied. The detection limits obtained (signal-to-bottom noise ratio=3) ranged from 0.02 to 0.1 ng.

Table 3 shows the recoveries of 17 fungicides at two concentration levels. In the case of grapes, recoveries ranged from 79 to 104% with RSDs of 6 and 5% for fludioxonil and vinclozolin, respectively. For must and wine, the lowest recoveries were for dichlofuanid (78%) and folpet (81%) and repeatability was acceptable (RSDs were not higher than 14% in the most unfavorable case).

According to the detection limits obtained, the corresponding limits of quantification (LOQs) for each fungicide, keeping in mind the detection limit for each compound, mass of sample, volume of extract and volume injected, are shown in Table 4. In this table, the real LOQ (theoretical limit of quantification multiplied by the mean recovery of the extraction method) is also shown. For its calculation, the mean recovery at the lowest fortification level in grapes, must and wine for each fungicide was used. As can be seen, the values calculated are in all cases lower than the MRLs established by the Spanish, French and Italian legislations (the main wine-producing countries of the European Union) for viniferous grapes because they have not yet established MRLs for wine [24], except for fludioxonil

Table 2
Linearity (peak area=b·ng±a) and repeatability (RSD %, n=7) of peak areas for both NPD and ECD

Fungicide	Linearity				Repeatability
	r	S.E.E.[a]	a±(95%) CI[b]	b±(95%) CI	
Benalaxyl[d]	0.998	0.759	−0.01±1.54	15.03±1.49***	2.9
Captan[c]	0.999	0.056	0.03±0.11	1.23±0.006***	4.6
Chlozolinate[c]	0.995	2.682	2.83±5.43	14.73±2.68***	6.2
Cyprodinil[d]	0.999	0.863	−1.09±1.74	6.60±1.71***	1.1
Dichlofuanid[c]	0.999	0.558	0.31±1.13	13.70±0.55***	8.1
Fenarimol[c]	0.999	0.418	0.37±0.84	10.73±0.41***	7.4
Fludioxonil[d]	0.999	0.708	−0.95±1.50	9.11±0.72***	8.6
Folpet[c]	0.999	0.220	0.15±0.45	3.24±0.22***	3.9
Hexaconazole[c]	0.995	1.467	1.47±2.97	7.98±1.44***	7.7
Metalaxyl[d]	0.999	0.532	−0.86±1.85	25.62±1.61***	1.4
Myclobutanil[c]	0.996	0.298	0.27±0.60	1.92±0.20***	4.4
Nuarimol[c]	0.999	0.710	0.39±1.44	10.25±0.70***	6.0
Penconazole[c]	1.000	0.130	−0.06±0.26	8.28±0.13***	4.0
Procymidone[c]	0.997	0.245	0.47±0.50	1.82±0.23***	7.2
Pyrimethanil[d]	0.999	1.294	−1.60±2.64	117.25±2.56***	0.8
Triadimefon[c]	0.999	8.421	3.72±17.06	136.09±8.31***	4.7
Vinclozolin[c]	0.994	3.255	3.20±6.59	16.11±3.21***	8.4

[a] Standard error of estimation.
[b] CI=Confidence interval.
[c] ECD.
[d] NPD.
***P<0.001.

Table 3
Recovery (%, ±RSD, $n=5$) of fungicides from grape, must and wine samples

Fungicide	Fortification level (mg/kg)	Mean recovery (%)±RSD (%)		
		Grapes	Must	Wine
Benalaxyl	0.05	91.3±7.9	102.2±3.2	100.6±3.5
	0.5	98.7±8.4	101.6±6.5	100.0±2.6
Captan	0.05	101.0±4.1	98.0±4.7	96.2±5.3
	0.5	98.3±3.1	85.6±10.2	86.0±11.6
Chlozolinate	0.01	101.6±5.0	97.2±7.4	104.2±7.2
	0.1	103.3±8.5	100.0±7.2	100.3±3.0
Cyprodinil	0.01	93.5±17.5	103.2±6.4	102.0±3.0
	0.1	94.7±8.7	101.7±6.7	95.0±6.4
Dichlofuanid	0.01	97.2±13.2	77.6±8.9	92.6±9.2
	0.1	87.7±0.6	91.0±7.9	82.3±2.5
Fenarimol	0.01	100.0±4.5	94.6±10.2	98.8±14.6
	0.1	93.7±11.4	92.0±8.5	81.6±3.7
Fludioxonil	0.05	98.6±17.2	100.8±3.2	100.0±5.1
	0.5	78.8±6.2	100.7±4.1	102.0±1.9
Folpet	0.05	99.2±2.4	87.6±6.3	93.6±5.3
	0.5	93.3±9.3	84.0±13.7	81.3±6.8
Hexaconazole	0.05	97.0±8.8	88.0±3.8	93.4±10.9
	0.5	87.3±9.6	97.6±10.3	87.3±3.5
Metalaxyl	0.05	89.0±6.2	97.2±11.0	82.0±6.8
	0.5	89.8±8.0	98.3±13.5	87.7±9.1
Myclobutanil	0.05	97.6±7.1	100.4±8.9	101.2±6.9
	0.5	99.0±5.0	101.0±8.8	88.3±9.6
Nuarimol	0.01	95.4±14.3	93.6±12.5	98.0±5.7
	0.1	97.3±7.9	93.3±9.3	86.6±2.9
Penconazole	0.01	101.0±4.1	86.8±2.9	96.6±8.9
	0.1	96.7±12.3	103.3±3.4	91.3±0.6
Procymidone	0.05	97.6±3.6	101.8±5.5	98.6±3.8
	0.5	97.0±4.1	100.7±0.6	98.0±5.7
Pyrimethanil	0.01	92.6±14.3	103.4±5.7	99.0±9.9
	0.1	89.3±7.0	101.0±1.0	96.7±6.2
Triadimefon	0.01	90.6±7.1	90.0±6.5	94.2±4.9
	0.1	91.7±9.3	91.7±3.8	92.7±2.7
Vinclozolin	0.01	100.8±3.9	103.2±7.5	102.0±12.8
	0.1	103.7±5.3	103.6±2.0	107.3±5.1

and hexaconazole whose LOQs correspond with the established limits in Spain; France and Italy do not have established limits for those compounds.

The validation of the method described has been carried out according to European norms EN-45000 [25,26], keeping in mind the following criteria: specificity (interferences), limit of detection (LOD) (minimum detectable concentration or mass), LOQ (minimum quantifiable concentration or mass), accuracy (recovery from 70 to 110%), precision (repeatability, RSD$<$20%), sensitivity (linearity, $r>$ 0.99) and practicality (cost, complexity, etc.).

Table 4
Theoretical (TLOQ) and real (RLOQ) limit of quantification (mg/kg) calculated and maximum residue limit (mg/kg) permitted in different countries of the European Union for each fungicide

Fungicide	TLOQ	RLOQ			MRL		
		Grapes	Must	Wine	Spain	France	Italy
Benalaxyl	$5\cdot10^{-2}$	$4.56\cdot10^{-2}$	$5.16\cdot10^{-2}$	$5.03\cdot10^{-2}$	0.20	0.20	0.20
Captan	$5\cdot10^{-2}$	$5.05\cdot10^{-2}$	$4.90\cdot10^{-2}$	$4.81\cdot10^{-2}$	3.00	3.00	3.00
Chlozolinate	$1\cdot10^{-2}$	$1.01\cdot10^{-2}$	$0.97\cdot10^{-2}$	$1.04\cdot10^{-2}$	3.00	5.00	5.00
Cyprodinil	$1\cdot10^{-2}$	$0.93\cdot10^{-2}$	$1.03\cdot10^{-2}$	$1.02\cdot10^{-2}$	0.05	NE	NE
Dichlofuanid	$1\cdot10^{-2}$	$0.87\cdot10^{-2}$	$0.77\cdot10^{-2}$	$0.92\cdot10^{-2}$	10.00	10.00	10.00
Fenarimol	$1\cdot10^{-2}$	$1.00\cdot10^{-2}$	$0.94\cdot10^{-2}$	$0.99\cdot10^{-2}$	0.30	0.30	0.30
Fludioxonil	$5\cdot10^{-2}$	$4.93\cdot10^{-2}$	$5.00\cdot10^{-2}$	$5.00\cdot10^{-2}$	0.05	NE	NE
Folpet	$5\cdot10^{-2}$	$4.96\cdot10^{-2}$	$4.38\cdot10^{-2}$	$4.78\cdot10^{-2}$	3.00	3.00	NE
Hexaconazole	$5\cdot10^{-2}$	$4.85\cdot10^{-2}$	$4.40\cdot10^{-2}$	$4.67\cdot10^{-2}$	0.05	NE	0.10
Metalaxyl	$5\cdot10^{-2}$	$4.45\cdot10^{-2}$	$4.86\cdot10^{-2}$	$4.10\cdot10^{-2}$	1.00	0.50	1.00
Myclobutanil	$5\cdot10^{-2}$	$4.88\cdot10^{-2}$	$5.02\cdot10^{-2}$	$5.06\cdot10^{-2}$	0.50	0.20	0.20
Nuarimol	$1\cdot10^{-2}$	$0.95\cdot10^{-2}$	$0.93\cdot10^{-2}$	$0.98\cdot10^{-2}$	0.20	0.20	0.20
Penconazole	$1\cdot10^{-2}$	$1.01\cdot10^{-2}$	$0.87\cdot10^{-2}$	$0.96\cdot10^{-2}$	0.20	0.05	0.10
Procymidone	$5\cdot10^{-2}$	$4.83\cdot10^{-2}$	$5.09\cdot10^{-2}$	$4.93\cdot10^{-2}$	5.00	5.00	5.00
Pyrimethanil	$1\cdot10^{-2}$	$0.93\cdot10^{-2}$	$1.03\cdot10^{-2}$	$0.99\cdot10^{-2}$	5.00	2.00	3.00
Triadimefon	$1\cdot10^{-2}$	$0.91\cdot10^{-2}$	$0.90\cdot10^{-2}$	$0.94\cdot10^{-2}$	1.00	1.00	0.50
Vinclozolin	$1\cdot10^{-2}$	$1.00\cdot10^{-2}$	$1.03\cdot10^{-2}$	$1.02\cdot10^{-2}$	5.00	5.00	5.00

NE: Not established.

According to the previous premise and taking into account the obtained results, we can affirm that the proposed method is appropriate for determining the residues of the studied fungicides in a rapid and reliable way and also at a low cost.

4. Conclusions

The proposed method allows a rapid determination of 17 fungicides, widely used on vineyards, and can be used for their determination in grapes, must and wine after a simple extraction of the sample, according to criteria of quality control and GLP. No clean-up is necessary, because chromatograms of untreated grape, must and wine samples are free from interfering peaks. The method provides good recoveries and repeatabilities. The LOQs are much lower than the MRLs limits set by the legislations of the main wine-producing countries of the European Union for fungicide residues in viniferous grapes.

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