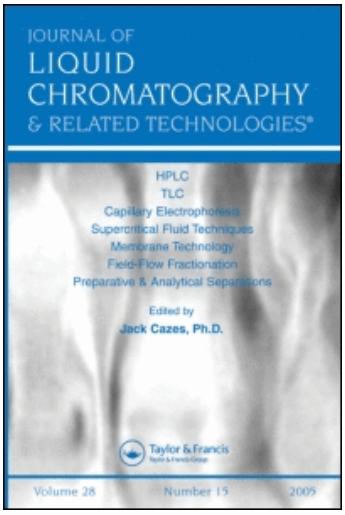

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PESTICIDE RESIDUES IN RASPBERRIES AND LETTUCE: EXTRACTION AND COMPARISON OF THREE CHROMATOGRAPHIC METHODS: HPLC, HPTLC AND GC

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ABSTRACT

The determination of iprodione, vinclozolin, and cymoxanil fungicide residues in raspberries and lettuce has been carried out by HPLC with an UV detector, by HPTLC with an densitometric detection, and by GC with an electron capture detector (ECD). In all cases, fungicide residues were extracted with acetone and liquid-liquid partitioning process and finally purified on silica gel. Recoveries are always higher than 70%. For iprodione, vinclozolin, and cymoxanil, respectively, the limits of detection were 0.01 ppm, 0.013 ppm, and 0.08 ppm for the HPLC method, 0.2 ppm, 0.43 ppm, and 0.5 ppm for the HPTLC method, and 0.025 ppm, 0.004 ppm, and 0.03 ppm for the GC method.

INTRODUCTION

Dicarboximidic fungicides are widely used to control *Botrytis, Monilia,* and *Sclerotinia* on fruits and vegetables. A number of articles have been writ-

ten referring to the gas chromatographic (GC) analysis of dicarboximide fungicides in fruits and vegetables,[12,18,26,27,29-31] but not in raspberries. Other methods have been developed. Iprodione and vinclozolin have been analysed by reversed phase HPLC in grapes and wine,[4-6,9] in tomatoes,[8] and carrots.[13] Some studies have been realized by HPTLC on silica gel plates.[10,16,24]

In France, in the west part of Rhône-Alpes Region named Coteaux du Lyonnais, iprodione and vinclozolin are currently employed to treat raspberries and lettuce. Cymoxanil is highly effective against mildew on lettuces. This fungicide is a derivative of urea and it is used in association with many fungicides on lettuces, but it is not employed on raspberries. The aim of this work is to develop a multi-residue method for simultaneous determination of fungicides that may be used on raspberries and lettuces. Thus, liquid and gas chromatographic analysis procedures were developed and compared.

EXPERIMENTAL

Fungicides

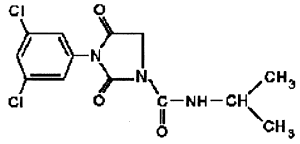
Three fungicides were selected by the Institut Supérieur d'Agriculture Rhône-Alpes (ISARA) in collaboration with the Société Coopérative Agricole des Coteaux du Lyonnais (SICOLY) and with the Station d'Expérimentation et d'Information Rhône-Alpes Légumes (SERAIL). Their structure is presented in Figure 1. The maximum residue levels tolerated in France are 5 mg/kg and 10 mg/kg for iprodione in raspberries and lettuces, respectively. It is the opposite for vinclozolin, 10mg/kg in raspberries and 5 mg/kg in lettuces. The tolerance for cymoxanil in lettuces is as low as 2 mg/kg. Also the chemicals should not be sprayed on the vegetables within at least three weeks before crop.

Apparatus

Liquid chromatography was carried out on a Merck system consisting of a model L-6200 pump, a UV L-4000 detector, and a Rheodyne injector with a 20 µL loop. The liquid chromatographic column was a Lichrospher 100 RP-18, 5 µm, 250 x 4.0 mm I.D. (Merck). The mobile phase was CH_3CN/0.01% NH_4Cl 55:45 (v/v) at a flow-rate of 1 mL/min.

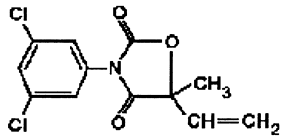
For the HPTLC analysis, the CAMAG Automatic TLC Sampler III (ATS 3) was employed. This system is composed of the application module, interface, software and an IBM-compatible PC. The CAMAG TLC Scanner II with CAMAG Labdata System and "CATS" software has been designed for the densitometric evaluation of objects up to 20 x 20 cm. Scanning was performed in reflectance or transmittance mode, by absorbance or by fluorescence. The use-

Iprodione (Rovral, Kidan or Verisan) : PM = 330 g.mol^{-1}



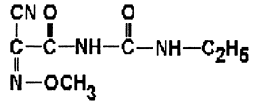
3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioxoimidazolidine-1-carboxamide

- Vinclozolin (Ronilan, Drive or Ornalin) : PM = 286 g.mol^{-1}



(RS)-3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione

- Cymoxanil (Curzate) : PM = 198 g.mol^{-1}



1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea

Figure 1. Structures of the fungicides used in this study.

ful spectral range was 190-800 nm. The HPTLC plates were silica gel 60 F_{254}layers (support material : glass, size : 10 x 20 cm) (Merck).

A Perkin Elmer 9000 gas chromatograph, equipped with a 15 mCi ^{63}Ni electron-capture detector and with a split/splitless injector, was employed for

the analysis. The gas chromatographic column was a DB-17 (J.W.), 30 m x 0.25 mm (I.D.), 0.25 μm film thickness. The carrier gas was helium 55 and the makeup gas was nitrogen 50.

Materials and Reagents

Ultra-Turrax T25 (Fisher).; Rotary evaporator (Büchi). All solvents used were of ultrapure for pesticides analysis grades (Merck). Acetonitrile was of HPLC grade (Merck) and water was distilled in the laboratory. The fungicides iprodione, vinclozolin, and cymoxanil were obtained from Cluzeau Laboratories. Internal standard : fluoranthene. Sodium sulfate was reagent grade (anhydrous). Silica gel 60 with 0.063 - 0.2 mm of particle size distribution (70-230 mesh ASTM) (Merck). Ammonium chloride (Merck).

Analytical Procedure

Sample Preparation and Extraction

Raspberries and lettuce were obtained from SICOLY and SERAIL, respectively, and were stocked at -20°C since analysis. Before storage, raspberries and lettuces were chopped up in a mixer. For analysis, 50 g samples were homogenized with 100 mL of acetone for 2 min in an ultra-turrax blender. The solution was filtrated under vacuum through Whatman filter paper using a Buchner funnel. The extraction was repeated using 100 mL acetone and the ultra-turrax was rinsed with 50 mL of acetone. The combined extracts were transferred to a 500 mL graduated cylinder and adjusted to 300 mL with acetone.

The extract (60 mL) was transferred to a separating funnel (500 mL). Distilled water (250 mL), 50 mL of distilled water saturated with chloride sodium and 50 mL of dichloromethane were added. The separating funnel was shaken vigorously and the filtrate was allowed to separate into two phases. The organic phase (inferior) was collected and filtrated through anhydrous Na_2SO_4 into a 250 mL round-bottom flask. The aqueous layer was extracted twice with 50 mL of dichloromethane.

The combined extract was concentrated by evaporation to dryness under reduced pressure in a rotary evaporator using a 35-40°C water-bath. The residue was recovered with 15 mL of dichloromethane for cleanup.

Silica Gel Column Cleanup

A 10 x 400 mm chromatographic column was prepared by filling the column with 8 g of silica gel 60 retained by a plug of glass wool. The column was

rinsed with 50 mL of dichloromethane that was discarded. A 15 mL volume of extract was deposed on the top of the column. The eluate was discarded. When the last of the rinses reached the top, the column was eluted with 50 mL of dichloromethane/ethyl acetate 75:25 (v/v).

The eluate was completely evaporated under reduced pressure in rotary evaporator using a 35-40°C water-bath and the residue was redissolved in a minimum amount of acetonitrile for analysis.

HPLC Analysis

Table 1 lists the UV spectral characteristics of the studied pesticides. 210 nm was chosen for the simultaneous determination of iprodione and vinclozolin and 240 nm was chosen for the determination of cymoxanil.

For routine analyses, the chromatographic conditions were as follows. The 25 cm, 4 mm i.d. column packed with Lichrospher C18 5 µm was the core of the HPLC chain. The buffer was an ammonium chloride 0.01% w/w aqueous solution adjusted to pH 7.9 by drops of ammonium hydroxide. The mobile phase (CH_3CN 55, buffer 45 %v/v) flow rate was 0.5 or 1 mL/min. The Merck L-4000 UV detector was set at 240 nm for cymoxanil detection and 210 nm for the two other pesticides.

HPTLC Analysis

This method was compared to the HPLC method. The chromatographic parameters tested on raspberries and lettuces are summarized in Table 2. Scanning is carried out in reflectance mode by absorbency. The UV spectrum of each fungicide was obtained and the maximal wavelength was determined. Thus, the densitometric evaluation of the chromatogram is performed at 210 nm for iprodione and vinclozolin, and at 268 nm for cymoxanil.

Table 1

UV Spectra of Fungicides in Acetonitrile Solution

Fungicide	c(mol.l^{-1})	λ_{max} (nm)	DO	ε_{mxx} (l.mol^{-1}.cm^{-1})
Cymoxanil	5.05 x 10^{-4}	243	3.1884	6314
Iprodione	9.1 x 10^{-5}	214	2.5264	27763
Vinclozolin	1.05 x 10^{-4}	207	2.2772	21688

Table 2

Chromatographic Parameters for HPTLC Analysis*

Raspberries

Fungicide	Solvents	R_F
Iprodione	Hexane/acetone 70:30 (v/v)[a]	0.44
Vinclozolin	Hexane/acetone 80:20 (v/v)[a]	0.55
	Cyclohexane/ethyl acetate/acetic acid 90:10:10 (v/v/v)	0.61

Lettuce

Fungicide	Solvents	R_F
Cymoxanil	Ethyl/ acetate cyclohexane 90:10 (v/v)	0.73
Iprodione	Hexane/acetone 70:30 (v/v)[a]	0.41
	Hexane/acetone 60:40 (v/v)	0.7
Vinclozolin	Hexane/acetone 70:30 (v/v)[a]	0.69
	Cyclohexane/ethyl acetate/acetic acid (v/v/v)	0.61
	Cyclohexane/ethyl acetate/acetic acid 80:20:10 (v/v/v)	0.8

*HPTLC plates: silica gel 60 F_{254}, 10 x 20 cm (Merck). [a] Solvent mixtures chosen for the study.

GC Analysis

The following conditions were used for gas chromatographic analysis with the PE 9000 apparatus: temperatures: injector 250°C; detector 300°C; gases: nitrogen (makeup) 40 mL/min; helium (carrier), 1 mL/min, capillary column 30 m, 250 µm i.d. DB-17 stationary phase, 0.25 µm film thickness. The 30 min program of the oven temperature was 120°C for 2 min followed by a step gradient at 16°C/min for 5 min and the temperature was maintained at 200°C for 6 min. Next, a second gradient at 20°/min was applied for 4 min and the temperature was maintained at 280°C for 12 min.

A 1 µL aliquot from a total volume of 1 mL was injected with a 5/1 split ratio. For the quantitative analysis we used fluoranthene, $C_{16}H_{10}$ (PM = 202.26 $g.mol^{-1}$) as an internal standard. This molecule does not exist in the vegetables and fruits, and no interference is observed with co-extracted substances.

RESULTS AND DISCUSSION

HPLC Analysis

This methodology was chosen for multiresidue determination of fungicides. Very good separation of the three fungicides is obtained and no interference was observed in raspberries (Figure 2) and lettuce samples with the chromatographic parameters exposed in the experimental section.

The recovery data for raspberry materials spiked with iprodione and vinclozolin is presented in Table 3. The mean recoveries were 75.6-84.4% for ipro-

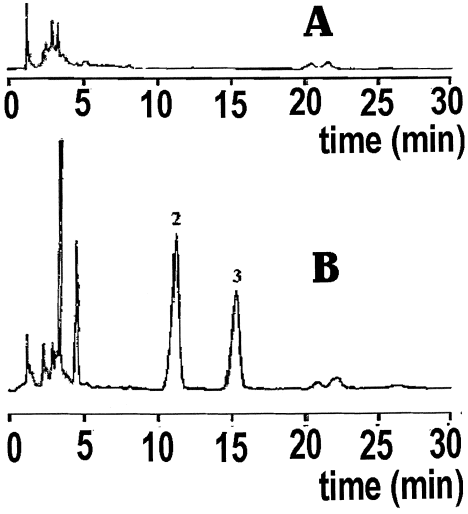


Figure 2. Chromatogram of (**A**) a blank extract of raspberries and (**B**) Chromatogram of raspberries spiked with 2 ppm of Iprodione (2) and Vinclozolin (3) at 210 nm. Experimental conditions, CH_3CN-buffer 55-45% v/v, 1 mL/min, UV@210 nm, 0.02 aufs, colonne Lichrospher 100 RP18 22 x 0.4 cm, injected mass: 40 ng of each pesticide.

Table 3

HPLC Analysis: Recoveries Obtained for Iprodione and Vinclozolin in Raspberries at Various Fortification Levels with Three Repetitions for Each Sample*

Iprodione	**2 ppm**	**5 ppm**	**10 ppm**
Sample 1	70.5 ± 2 R.S.D. = 2.8%	83.4 ± 8.8 R. S. D. = 10.5%	80.6 ± 7.3 R.S.D. = 9.1 %
Sample 2	75.6 ± 2.6 R.S.D.= 3.4%	84.1 ± 2.9 R.S.D. = 3.5%	86 ± 1.8 R.S.D. = 2.1%
Sample 3	80.7 ± 4.7 R.S.D. = 5.8%	85.6 ± 2.2 R.S.D. = 2.6%	81.3 ± 8.7 R.S.D. = 10.7%
Mean Recovery (%) ± standard deviation	75.6 ± 5.1	84.4 ± 1.1	82.6 ± 2.9
R.S.D. (%)	6.7	1.3	3.5
Vinclozolin	**2 ppm**	**5 ppm**	**10 ppm**
Sample 1	75.2 ± 0.5 R.S.D. = 0.6%	87.7 ± 8.6 R.S.D. = 9.8%	84.9 ± 7.1 R.S.D. = 8.4%
Sample 2	81.6 ± 2.5 R.S.D. = 3.1%	89.9 ± 2.5 R.S.D. = 2.8%	91.2 ± 1.8 R.S.D. = 1.9%
Sample 3	85.2 ± 3.4 R.S.D. = 4%	90.5 ± 2.2 R.S.D. = 2.5%	86.8 ± 9.3 R.S.D. = 10.7%
Mean Recovery (%) ± standard deviation	80.6 ± 5.1	89.4 ± 1.5	87.6 ± 3.2
R.S.D. (%)	6.3%	1.6%	3.7%

* n = 3.

dione and 80.6-89.4% for vinclozolin over the spiked range (2-10 mg/kg or ppm) with excellent reproducibility, even at low levels (mean R.S.D. 3.8% for iprodione and 3.9% for vinclozolin). For lettuce the results are summarized in Table 4. The mean recoveries were 76.4-102.7%, 76.1-98.3% and 73.9-86.4% for iprodione, vinclozolin, and cymoxanil, respectively

The limit of detection (LOD) was 0.01 ppm, 0.013 ppm, and 0.08 ppm for iprodione, vinclozolin, and cymoxanil,respectively.

The HPLC method is adequate for measurement of the residues in two matrices and the multiresidue determination was obtained. The results showed

Table 4

HPLC Analysis: Recoveries Obtained for Fungicides in Lettuces at Various Fortification Levels with n Repetitions for Each Sample

Cymoxanil	**2 ppm**	**3 ppm**	**10 ppm**
Sample 1	76.9 ± 10.4 R.S.D. = 13.6% n = 3	77.6 ± 2.4 R.S.D. = 3.1% n = 3	87.4 ± 9.7 R.S.D. = 11.1% n = 3
Sample 2	82.2 ± 15.6 R.S.D. = 18.9 % n = 3		88.1 ± 1.42 R.S.D. 4.7 % n = 2
Sample 3	62.6 ± 6.1 R.S.D. = 9.8% n = 3		83.7 ± 8.5 R.S.D. = 10.2% n = 3
Mean recovery (%) ± standard deviation	73.9 ± 10.1		86.4 ± 2.4
R.S.D. (%)	13.7		2.7
Iprodione	**2 ppm**	**3 ppm**	**10 ppm**
Sample 1	92.8 ± 4.2 R.S.D. = 4.5% n = 3	82.9 ± 9.6 R.S.D. = 11.6% n = 3	85 .1 ±7.7 R.S.D. = 9.1% n = 3
Sample 2	115.4 ± 19.9 R.S.D. = 17.2% n = 3		75.5 ± 4.7 R.S.D. = 6.2% n = 2
Sample 3	99.8 ± 12.2 R.S.D. = 12.2% n = 3		68.7 ± 2.5 R.S.D. = 3.6% n = 2
Mean recovery (%) ± standard deviation	102.7 ± 11.5		76.4 ± 8.2
R.S.D. (%)	11.3%		10.8%
Vinclozolin	**2 ppm**	**3 ppm**	**10 ppm**
Sample 1	84.8 ± 5.6 R.S.D. = 6.6% n = 3	76.1 ± 2.4 R.S.D. = 3.1% n = 3	93 ± 5.9 R.S.D. = 6.4% n = 3
Sample 2	106.5 ± 10.8 R.S.D. = 10 n = 3		84.2 ± 1.2 R.S.D. = 1.4% n = 2
Sample 3	102.6 ± 11.9 R.S.D. = 11.6% n = 3		83.1 ± 2.7 R.S.D. = 3.2% n = 2
Mean recovery (%) ± standard deviation	98.3 ± 11.9		86.8 ± 5.4
R.S.D. (%)	12.1%		6.2 %

that the method can be used to control the quality of samples (amount spiked< residues tolerances).

HPTLC Analysis

Cymoxanil was analyzed alone in lettuce at 268 nm without difficulty. The solvent mixture ethyl acetate/cyclohexane 90:10 (v/v) was employed. Chromatographic separation of dicarboximidic fungicides was obtained with satisfactory resolution in raspberries at 210 nm. The solvent mixtures used are hexane/acetone 70:30 (v/v) for iprodione and hexane/acetone 80:20 (v/v) for vinclozolin.

On the other hand, we obtained a multiresidue determination in lettuces with hexane/acetone 70:30 (v/v) mixture (Figure 3). In this study lettuces were analyzed with HPLC and HPTLC methods and the results are similar. This methodology is very interesting because it's a simple and rapid method. Twenty samples can be analyzed in one hour when only two were analyzed in HPLC. So, HPTLC was complementary to HPLC analysis and permitted to obtain a rapid information about residue pesticides content.

The LODs were 0.2 ppm for iprodione and 0.43 ppm for vinclozolin in the two matrices. For cymoxanil in lettuces, the LOD was 0.5 ppm. These LODs are one order of magnitude lower than the maximum tolerated levels.

GC Analysis

This methodology is widely employed to detect pesticides. With chromatographic conditions described in the GC Analysis paragraph. Vinclozolin eluted in approximately 14.7 min, iprodione in 21.8 min and cymoxanil in 6.6 min (Figure 4). But, we observed a degradation at high temperature for cymoxanil, so, it is difficult to have a quantitative analysis.

The LODs are better than in HPLC except for iprodione: 0.025, 0.004 ppm and 0.03 ppm for iprodione, vinclozolin, and cymoxanil respectively. These LODs values are almost two orders of magnitude lower than the tolerated levels showing that GC may be the first method to use to obtain a rapid estimation of the pesticide concentration in the extracted sample under investigation

CONCLUSION

An HPLC multiresidue method has been developed for determination of the fungicides iprodione, vinclozolin, and cymoxanil in raspberries and lettuces

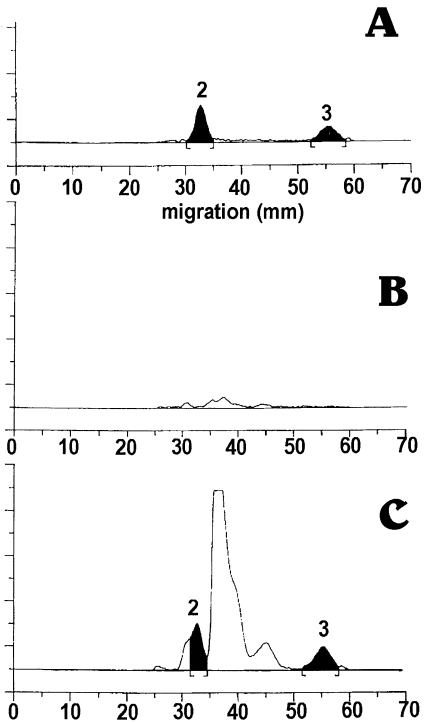


Figure 3. HPTLC chromatograms of (**A**) iprodione (2) and vinclozolin (3) (10 mg/L) in acetonitrile (application: 100 ng); (**B**) unspiked lettuce extract and (**C**) lettuce spiked with 5 ppm of iprodione (2) and vinclozolin (3). The wavelength was 210 nm and the solvent mixture was hexane/acetone 70:30 (v/v).

using reversed-phase chromatography with UV detection at 210 and 240 nm. This method is very rapid and highly sensitive. For sample extraction, the method described in this study was applied to vegetable samples (raspberries and lettuces) with satisfactory recoveries.

This method, combined with HPLC, permits the determination of iprodione, vinclozolin, and cymoxanil residues at levels lower than residue tolerances. Further, the HPTLC technique has been demonstrated to be adequate for screening samples. HPTLC could be a complementary method for HPLC analysis.

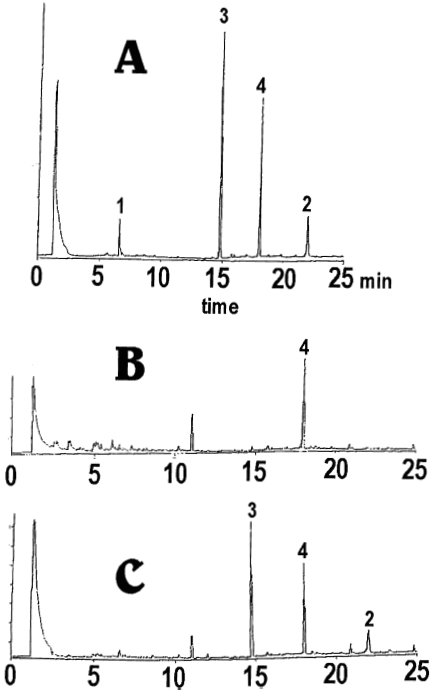


Figure 4. Gas Chromatographic Separation of a Standard Mixture of (**A**), cymoxanil (1), iprodione (2), Vinclozoline (3) at 1 ng/µL and fluoranthene (4) (internal standard); (**B**) a blank extract of raspberries and (**C**) raspberries spiked with 0.2 ppm of iprodione (2) and vinclozolin (3).

With the GC method, the fungicides studied can also be analyzed rapidly, all together, without derivatization and with very low LODs. For iprodione and vinclozolin, GC is the method to be selected, but the determination of cymoxanil that is temperature sensitive, is more difficult than with HPLC.

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