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Application of porous carbon for solid-phase extraction of dicarboxyimide fungicide residues from wines in combination with high-resolution capillary gas chromatography and gas chromatography–mass spectrometry

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Abstract

Solid-phase extraction with a novel porous carbon sorbent CARB GR was used for the clean-up step of dicarboxyimide fungicides residues from variety of Slovak grape wines with subsequent capillary gas chromatography–flame ionization detection, –electron-capture detection (ECD) and –mass spectrometry–ion-trap detection (MS-ITD) analysis. Recovery was tested at various concentration levels of vinclozolin and iprodione in standard solutions (R=80–97%, R.S.D.≤5). The value of recovery in spiked wines is dependent on concentration level (studied in the range of 5.9 μg/l–1.96 mg/l) and on the variety of wine (R=80–96%; R.S.D.=3–5%). Limits of quantitation (for sample volume 50 ml) were determined to be with GC–ECD for both fungicides in ppt range and with GC–MS-ITD in the multiple ion detection mode monitoring in ptt range for vinclozolin and ppb range for iprodione. Concentration levels of vinclozolin residues were determined in treated wines (with 0.1% Ronilan 50 WP) as well as iprodione residues (with 0.15% Rovral 50 WP) and a strong dependence on the protective term before the harvest is shown.

Keywords: Wine; Food analysis; Sample preparation; Pesticides; Dicarboxyimides

1. Introduction

The development of new types of sorbent for solid-phase extraction (SPE) is growing rapidly. Carbonaceous sorbents, the matrix of which mainly consists of carbon, belong to the group of materials which attracted attention because of their potential for the optimum solution of the separation problems. From review article on carbon sorbents and their utilisation for the preconcentration of semivolatile and nonvolatile organic pollutants from water matrices it follows their superior performance over "traditional" sorbents such as C_{18} silica bonded phase adsorbent [1]. The advantages of carbon sorbents are their thermal stability, chemical resistance and stability over a wide pH range. It is supposed that non-volatile organics require the use of a homogeneous surface that is met by graphitized carbon blacks (GCBs) [2–4] and porous graphitized

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carbon blacks (PGCBs) [5], that are non-polar, inert adsorbents with prevailing hydrophobic properties.

A novel porous carbon sorbent prepared by pyrolysis of succharose in a matrix of silica-gel was tested for the preconcentration of contact dicarboximide fungicides vinclozolin and iprodione, which have been developed for the protection of vine against *Botritis cinerea* Pers. et Fries. They have broad spectrum of effect against other diseases what allows their broad application in agrochemical praxis (fruit, vegetables). Vinclozolin and iprodione have been applied on vine in the final stage of vegetation, as fungi attack grapes shortly before the harvest. Therefore, residues can be carried through into the products [6]. They have been isolated from viticulture products and/or other commodities utilising liquid–liquid extraction with subsequent cleaning procedure with column liquid–solid chromatography [7–9]. In recent years several authors have applied SPE with C_{18} cartridges for the isolation of iprodione from vegetables [10] with recovery values $\leq$80%, fruits with recovery values $\leq$78% [11] and 75–107% [12].

Wine, an important in international trade, is subject to strict regulation in its quality in regard to truth-to-label (grape variety, region of origin) and freedom from additives [13]. Residues in wines are generally regulated through the various national standards set for foods as maximum residue limits (MRLs) on the viniferous grapes, which is in the low ppm range and there is a trend for separate, lower MRLs to be set for wine [14]. The range of pesticides registered for use on grapes and the MRLs set for grapes or wine vary widely among countries. Holland et al. [14] published the method for screening wine for many pesticide residues. Extraction was performed with propylene extraction columns packed with 500 mg C_{18}-silica bonded phase adsorbent at two concentration levels, 0.2 and 0.02 mg/l in white and red wine. With iprodione recovery at 0.2 mg/l was determined to be 91%, vinclozolin 89%; at 0.02 mg/l iprodione 160% in white wine and 100% in red wine, vinclozolin 120% in white wine and 85% in red wine; minimum detectable quantities for both were indicated to be 0.01 mg/l [for electron-capture detection (ECD), nitrogen–phosphorus detection (NPD) $S/N \geq 5$].

The aim of this paper was to develop sufficiently rapid, rather simple and at the same time reliable and sensitive method for the determination of vinclozolin and iprodione in the variety of grape wines utilising SPE with a novel porous carbon sorbent with subsequent high-resolution capillary GC and GC–MS analysis.

2. Experimental

2.1. Chemicals

The used solvents acetone, chloroform, *n*-hexane, toluene, methyl and ethyl alcohol (Labos, Bratislava, Slovakia) were of UV grade; all other chemicals (HCl, NaOH) were of analytical grade. The used standard of vinclozolin, 3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidin-2,4-dione, was certified to be 99.5% pure (Rhône Poulene Agrochemie, Lyon, France) and iprodione, 3-(3,5-dichlorophenyl)-imidazolidin-2,4-dione-1-(N-isopropyl)carboxamide, 99.4% (BASF, Ludwigshafen, Germany). Standard stock solutions were prepared in toluene (10 mg/100 ml) and stored at 5°C in glass vials and were stable for 5 weeks. The solutions with lower concentrations were prepared by dilution.

2.2. Wines

The samples of wines (locality Bratislava) used in the experiment were white wines Veltlínske zelené (VZ), Silvánske zelené (SZ), Bouvierovo hrozno (BH), Rizling vlašský (RV), Rizling rýnsky (RR), Muškát ottonel (MO) and red wine Frankovka modrá (FM). Spiked wines were prepared adding 1 ml of standard solution of fungicides to 50 ml of wine (0.005–2 mg/l). Treated wines were prepared from grapes treated in vivo experiments with Ronilan 50 WP (0.1%) with active compound vinclozolin (50%) and Rovral 50 WP (0.15%) with active compound iprodione (50%) in 1993 in protective terms: 14, 28 and 35 days; fungicides analysis in wines was performed after the first racking.

2.3. SPE

The tested porous carbon sorbent with particle size 50–125 μm of irregular shape and specific surface

area 1200 m^2/g was prepared by controlled pyrolysis of saccharose in a matrix of silica gel [15]. In the next stage silica gel was removed by dissolving in NaOH. The product was prepared in the Institute of Polymers of the Slovak Academy of Sciences, Bratislava. Glass cartridges (SPE glass Carb GR, 6 cm×0.9 cm) were filled with the mass of sorbent 250; 500 mg. Sorbent bed was placed between two glass frits. Carbon cartridges were pretreated before SPE by washing with 5 ml 0.1 *M* HCl, 5 ml 0.1 *M* NaOH, distilled water to neutral reaction (pH=7). After drying in the stream of N_2 (5 min) cartridges were washed with 5 ml of acetone, 5 ml methyl alcohol and again dried in N_2 (5 min).

Before the use the cartridge is washed with 3 ml toluene, 3 ml 15% ethanol and 5 ml water. Liquid samples-standard solutions (1 ml) were allowed to suck into sorbent, or-wines (25, 50 ml) were forced to pass through the cartridge by vacuum with a flow-rate 2.5 ml/min. After passage of a sample the cartridge was washed with 15 ml redistilled water. Residues of water were removed, sorbent was shortly dried (5 min) by vacuum (water pump). Vinclozolin and iprodione were eluted by toluene. The volume of toluene was dependent according to the mass of sorbent (for 250 mg–25 ml; 500–50 ml). Extracts were dried in a water bath at 50°C under vacuum (oil pump). Residues were reconstituted with known volumes of toluene (1 ml or smaller) and suitable aliquots were injected into GC and GS apparatus.

2.4. GC apparatus and operation

Chromatographic measurements were performed on a HP-5890 Series II (Hewlett-Packard, USA) gas chromatograph equipped with a flame ionisation detection (FID) system, ECD system, a splitless injector, an on-column injector with electronic pressure control, an HP 3396 integrator; FID gases: hydrogen, air and make up gas nitrogen; ECD, with nitrogen (5.0) as make up gas; 1 μl sample was injected with a 10-μl Hamilton syringe by fast injection.

On-column: fused-silica capillary column CP-SIL-5 CB (25 m×0.32 mm, 0.12 μm) with chemically bonded dimethylsiloxane stationary phase (Chrompack) connected via a press-fit connector with a 1.5 m retention gap (uncoated fused-silica tubing 0.53 mm I.D.) was used under temperature program conditions-initial temperature 50°C, temperature gradient 10°C/min, final temperature 250°C; the carrier gas was hydrogen (4.0) with linear velocity 45.2 cm/s under isothermal conditions (100°C); pressure program: initial 10 kPa for 0.1 min, gradient 680 kPa/min, final pressure 47 kPa until the end of analysis; detectors temperature 280°C. The ballistic pressure program was used to avoid potential losses of compounds in on-column injection;

Splitless: purge off time 1.0 min; fused-silica capillary column HP-1 (50 m×0.2 mm, 0.5 μm) with chemically bonded dimethylsiloxane phase was used under temperature program conditions: vinclozolin-initial temperature 106°C 3 min temperature gradient 10°C/min, final temperature 300°C 10 min; injector temperature 250°C; iprodione-initial temperature 225°C 10 min, temperature gradient 10°C/min, final temperature 300°C 10 min, injector temperature 290°C; the carrier gas was nitrogen (5.0) with linear velocity 13 cm/s under isothermal conditions (180°C); ECD temperature was 300°C.

2.5. GC–MS apparatus and operation

Measurements were performed on a Varian 3400 gas chromatograph equipped with a splitless injection system (250°C; purge time 0.5 min) in a direct connection with a mass spectrometer ITD 800 (Finnigan, USA); fused-silica capillary column DB-5 (30 m×0.25 mm, 0.25 μm) with chemically bonded phenylmethylsiloxane phase under temperature program conditions-initial temperature 60°C 1 min temperature gradient 10°C/min, final temperature 250°C, 20 min; carrier gas helium (4.0) with a flow-rate 1 ml/min; scan speed 1 scan/s in full scan mode and MID monitoring; detector temperature 220°C with electron impact ionisation (70 eV ionisation energy).

3. Results and discussion

3.1. SPE recovery tests

In recent years SPE has been the method of choice for the preconcentration of non-volatile trace organic components from various environmental matrices, as

Table 1
Reproducibility of recovery ($\bar{R}$) determination of vinclozolin (in standard solutions) on cartridges SPE glass Carb GR (50–125 μm; 500 mg) at various concentration levels; $n^*=3$

Standard concentration (mg/ml)	Recovery			$L_{1,2}$ (%)
	$\bar{R}$ (%)	S.D.	R.S.D. (%)	
0.0005	80.0	3.2	4.0	80.0±3.6
0.0007	85.7	3.3	3.9	85.7±3.7
0.0030	90.0	3.8	4.2	90.0±4.3
0.0050	94.0	4.5	4.8	94.0±5.1
0.0100	96.0	4.8	5.0	96.0±5.4
0.0700	97.6	4.9	5.0	97.6±5.5
0.1000	97.1	4.6	4.8	97.1±5.2

$n^*=3$ cartridges, every cartridge 5 GC determinations.

it offers a number of well known advantages compared to liquid extraction [1,16]. We have developed reliable and rapid analytical method for the determination of residues of fungicides in wines. The preconcentration of vinclozolin and iprodione from standard solutions was preliminary tested utilising various sorbents (silica gel, chemically modified silica gel C_1, C_8, CN, NH_2, porous carbon sorbent). Insufficient sorption of fungicides and consequently the low recovery values observed with the tested modified silica gels (Anapron, Slovakia) could be explained with the non-optimal physicochemical characteristics of the tested sorbents [17]. Very good results were 'obtained with porous carbon sorbent

Table 2
Reproducibility of recovery ($\bar{R}$) determination of iprodione (in standard solutions) on cartridges SPE glass Carb GR (50–125 μm; 500 mg) at various concentration levels; $n^*=3$

Standard concentration (mg/ml)	Recovery $\bar{R}$ (%)	S.D.	R.S.D. (%)	$L_{1,2}$ (%)
0.0005	80.0	3.4	4.3	80.0±3.9
0.0007	85.7	3.4	4.0	85.7±3.9
0.0030	86.3	4.1	5.0	86.3±4.7
0.0050	88.0	4.3	5.0	88.0±4.9
0.0100	92.0	4.6	5.0	92.0±5.2
0.0700	94.0	4.7	5.0	94.0±5.3
0.1000	96.7	3.6	4.1	96.7±4.0

$n^*=3$ cartridges, every cartridge 5 GC.

Table 3
Recovery of vinclozolin and iprodione after SPE from spiked wine Veltlínske zelené at various concentration levels on cartridges SPE glass Carb GR 500 mg; $n^*=3$

Pesticide concentration in spiked wine (mg/l)	Vinclozolin			Iprodione		
	$\bar{R}$ (%)	R.S.D. (%)	$L_{1,2}$ (%)	$\bar{R}$ (%)	R.S.D. (%)	$L_{1,2}$ (%)
0.0059	85.9	3.3	85.9±3.2	83.3	4.2	83.3±4.0
0.0098	87.6	3.7	87.6±3.7	87.4	4.4	87.4±4.3
0.0137	90.6	3.0	90.6±3.0	89.3	4.9	89.3±4.9
0.0196	91.2	4.2	91.2±4.4	89.9	4.0	89.9±4.0
0.0588	91.4	4.9	91.4±5.0	90.2	3.9	90.2±3.9
0.0980	92.2	4.0	92.2±4.2	92.1	4.9	92.1±5.2
0.1372	92.3	5.0	92.3±5.2	92.9	5.1	92.9±5.3
0.1961	94.7	5.0	94.7±5.3	93.1	4.3	93.1±4.5
0.9804	94.9	5.0	94.9±5.4	93.9	4.8	93.9±5.1
1.9609	95.7	4.8	95.7±5.2	93.0	4.6	93.0±4.8

$n^*=3$ cartridges, every cartridge 5 GC determinations.

CARB GR in glass cartridges. Polar components from wines were eluted with redestilled water. Various solvents differing in polarity (acetone, chloroform, hexane, toluene) were tested to elute vinclozolin and iprodione from carbon sorbent. Elution with acetone results in strong interferences from wine; hexane brought not sufficiently high recovery values; chloroform with ECD is not recommended. The best results were obtained with toluene, whereby the mass of sorbent influences the final solvent volume to achieve the pesticide elution.

The recovery tests were performed with the standard solution of fungicides in concentration range of 0.0005–0.1 mg/ml (1 ml was loaded). The overall capacity of cartridges was also tested. The reproducibility of recovery determination in the dependence on vinclozolin and iprodione standard concentration are given in Tables 1 and 2. In both fungicides the recovery values are concentration and/or loaded amount dependent and the mean recovery value at all concentration levels was found to be in the range of 80–97% with the relative standard

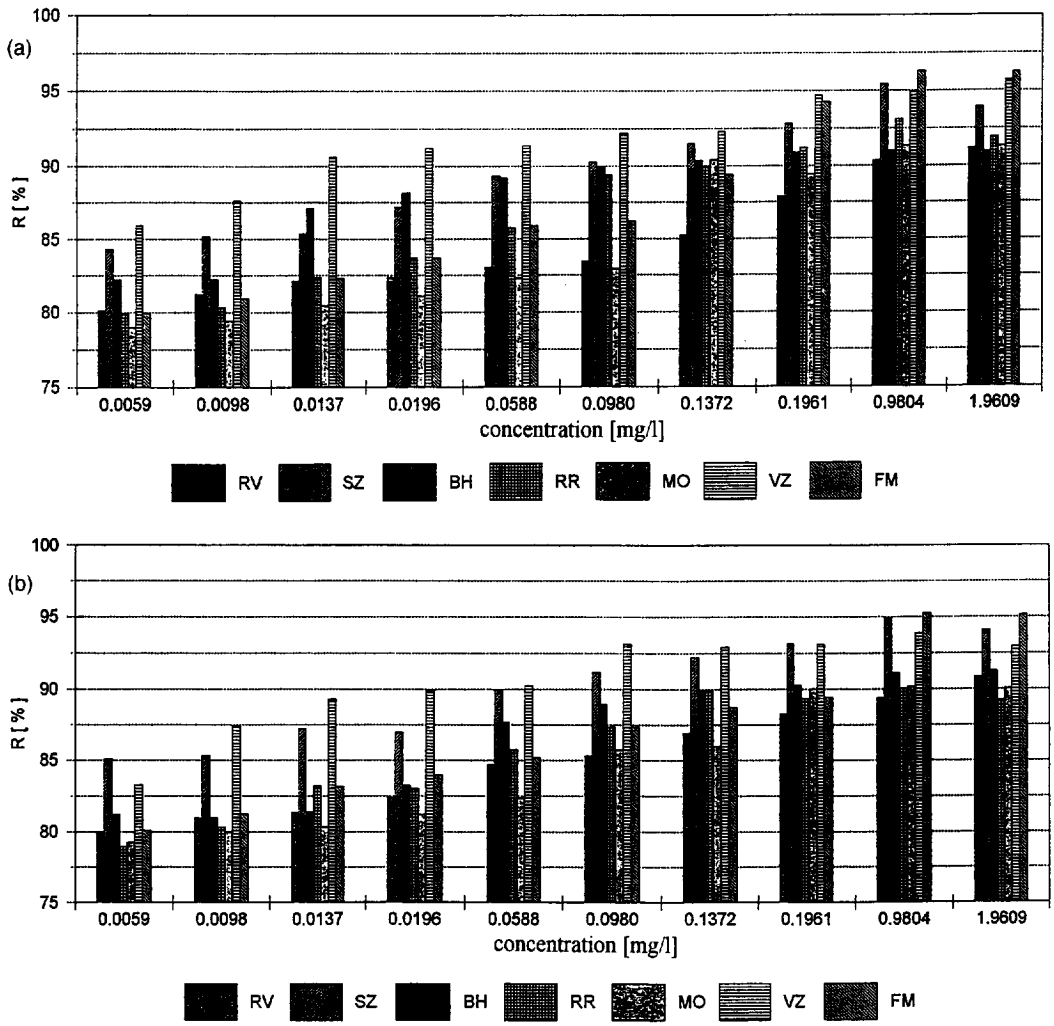

Fig. 1. Recoveries of dicarboxyimide fungicides in spiked variety grape wines at various concentration levels after SPE on porous carbon sorbent Carb GR; white wines: RV=Rizling vlašský; SZ=Silván zelený; BH=Bouvierovo hrozno; RR=Rizling rýnsky; MO=Muškát ottonel; VZ=Veltlínske zelené; red wine: FM=Frankovka modrá; (a): Recoveries of vinclozolin; (b): Recoveries of iprodione.

deviation R.S.D.≤5%. The reliability of results is characterised within the mean confidence interval $L_{1,2}$=91.5±4.7 for vinclozolin and 89.0±4.5 for iprodione at a significance level of 95% (α=0.05).

With wines the minimal sample volume depends on the concentration of residues. Capacity of columns with porous carbon is relatively high and is influenced besides properties of analytes (fungicides) also with properties of wine sample matrix, which usually contains sugars, esters, compounds of proteins nature, acids, pigments etc.). Breakthrough volume of viclozolin and iprodione in all tested wines was ≥25 ml for the mass of sorbent 250 mg in a cartridge, and ≥50 ml for the mass of sorbent 500 mg in a cartridge. The recovery of studied pesticides was tested in the spiked Slovak white wine Veltlínske zelený at various concentration levels (5.9 μg/l–1.96 mg/l), the results are presented in Table 3. In all tested concentration levels R≥83%. The reliability of results is characterised within the mean confidence interval $L_{1,2}$=91.5±4.7 for vinclozolin and $L_{1,2}$=90.6±4.6 for iprodione at a significance level of 95% (α=0.05). Recoveries of vinclozolin and iprodione were tested in the spiked variety of Slovak white and red wines. The results are shown in Fig. 1a and b. The spiked wines were prepared from wine produced from grapes without the treatment of the investigated fungicides. The obtained recoveries (R=80–96%, R.S.D.=3–5%) were found to be dependent on the concentration level of vinclozolin and iprodione in wines and on the variety of grape wine, where the sample matrix influences the adsorption-desorption process.

3.2. SPE column performance

Using the same column to process 5 aliquots (50 ml) of wine gave the same recovery values; no significant differences were observed with the number of column washes (equivalent to confidence interval for the studied concentration level and given variety of wine).

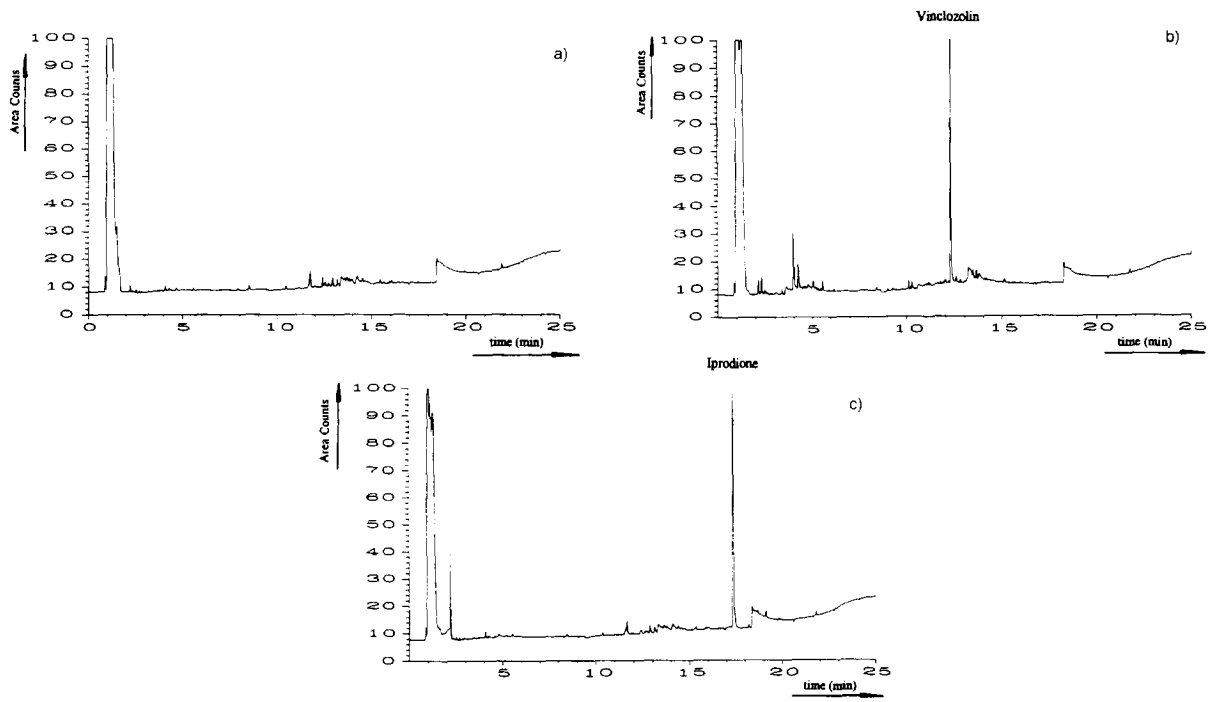

Fig. 2. Gas chromatogram of extract of white treated wine Veltlínske zelené after SPE on Carb Gr (500 mg) with on-column injection (1 μl) on a column CP-SIL-5 CB (25 m×0.32 mm, 0.12 μm) under temperature-programmed conditions, carrier gas hydrogen, ECD; (a): wine produced of grapes not treated with fungicides; (b): wine produced of grapes treated with 0.1% Ronilan 50 WP; determined vinclozoline concentration 0.074 mg/l; (c): wine produced of grapes treated with 0.15% Rovral 50 WP; determined iprodione concentration 0.130 mg/l.

3.3. GC and GC–MS measurements

All GC and GC–MS measurements were performed with fused-silica capillary columns under optimised experimental conditions. In the present time the determination of vinclozolin and iprodione has been performed and prevails on nonpolar methyl silicones [18–20] or slightly-medium polar methylphenyl silicones [14].

In our GC measurements dimethylsiloxane stationary phase columns were utilised. All analyses were performed under temperature-programmed conditions and ECD and FID; the sensitivity of ECD compared to FID was found to be about 200 times higher for vinclozolin and 600 times higher for iprodione. The linearity range of ECD response was checked in the range of 5 pg–100 ng for vinclozolin and 10 pg–100 ng for iprodione. Repeatability of peak area measurements with on-column and splitless injection was dependent on injected amount, R.S.D. varied in the range of 0.5–2.7% for $n=5$.

Chromatograms of determination of fungicides in treated wine (variety Veltlínske zelené) is presented in Fig. 2a and b. For the illustration in Fig. 3a and b the dependence of studied fungicide residues in treated wines (1993) on the protective term (days)

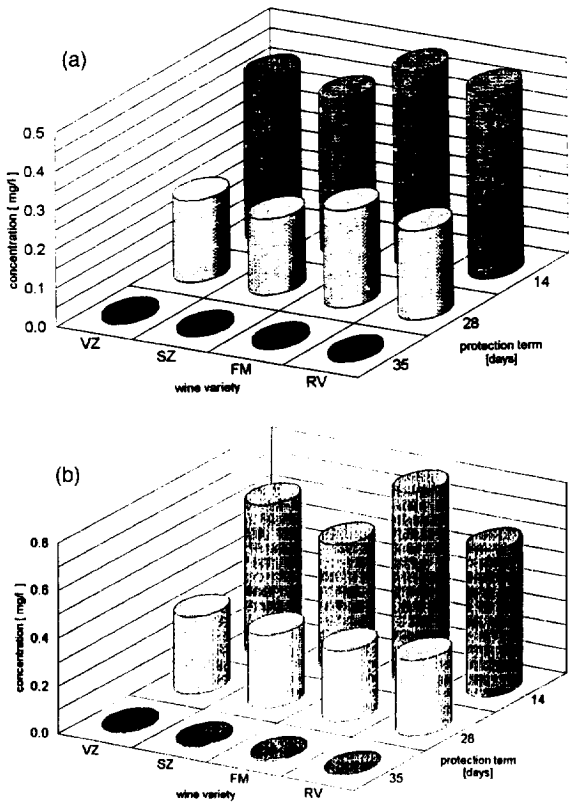

Fig. 3. The dependence of concentration of residues of dicarboxyimide fungicides in treated wines on the protective term (days) before the harvest; for wine variety abbreviations see Fig. 1. (a): vinclozolin-grapes treated with 0.1% Ronilan 50 WP; (b): iprodione-grapes treated with 0.15% Rovral 50 WP.

Table 4
Limit of quantitation of vinclozolin and iprodione by capillary GC with injection system splitless, on-column and FID, ECD

Injection system	Limit of quantitation	
	Vinclozolin (ng) (μg/ml)	Iprodion (ng) (μg/ml)
	FID	
On-column		
$S/N=3$	$3.492\cdot10^{-2}$	$6.984\cdot10^{-1}$
$S/N=10$	$1.164\cdot10^{-1}$	2.328
	ECD	
Splitless		
$S/N=3$	$4.599\cdot10^{-4}$	$4.882\cdot10^{-3}$
$S/N=10$	$1.533\cdot10^{-3}$	$1.627\cdot10^{-2}$
On-column		
$S/N=3$	$1.790\cdot10^{-4}$	$1.150\cdot10^{-3}$
$S/N=10$	$5.967\cdot10^{-4}$	$3.833\cdot10^{-3}$

1 μl injected.

before the harvest is given. From the graphs it is clearly illustrated that the concentration of vinclozolin and iprodione residues is strongly dependent on the protective term, so the main way how to protect consumers is to pay attention to the long protective terms of the final application of pesticide before the harvest.

The limits of quantitation [signal (S) to noise (N) ratio equals to 3 and 10 respectively] with ECD, FID are presented in Table 4. The limit of GC quantitation combined with SPE is dependent on wine sample volume, recovery value, the final volume of solvent used for reconstitution of residues and the volume injected into GC; for 50 ml sample and 0.2 ml toluene as residue solvent and 1 μl injected, the limit of quantitation was determined to be for

Table 5
Limit of quantitation of vinclozolin and iprodione determined by GC–MS-ITD

Compound	Limit of quantitation ($S/N=3$)			
	Full scan		MID	
	(ng)	(mg/ml)	(ng)	(mg/ml)
Vinclozolin	1.0	0.001	0.01	0.00001
Iprodione	100.0	0.100	10.00	0.01

1 μl injected.

splitless injection: vinclozolin 7.66 ng/l, iprodione 81.35 ng/l; for on-column injection: vinclozolin 2.98 ng/l and iprodione 19.16 ng/l ($S/N=10$ and 80% recovery after SPE).

With GC–MS equipped with ion-trap detection (ITD) in MID (multiple ion detection) scan mode the characteristic ions [9,21] were selected and experimentally verified to achieve the lowest limit of quantitation. The data for full and MID scan mode are presented in Table 5 ($S/N=3$). That correspond for wines with MID (under the same SPE conditions given in GC–ECD) 50 ng/l for vinclozolin and 50 μg/l for iprodione. For vinclozolin the comparison of chromatograms in full scan and MID scan monitoring is presented in Fig. 4A. Whereas at concentration of vinclozolin standard solution 0.0001 mg/ml (injected amount 0.1 ng) in full scan mode the obtained spectrum is represented by detector background only, in MID monitoring even with 10 times lower concentration (0.00001 mg/ml) the identification by selected ions is unambiguous (Fig. 4B). Full and MID chromatograms of treated wine with active compound vinclozolin are shown in Fig. 5, where in full mode the identification according to the record of spectrum is not sufficiently convincing (the high background peaks).

The sensitivity of ITD for iprodione is significantly lower compared to vinclozolin (Table 5). In Fig. 6 chromatograms of treated wine with active compound iprodione is presented, where again it was shown that the identification in MID mode is unambiguous compared to full scan mode.

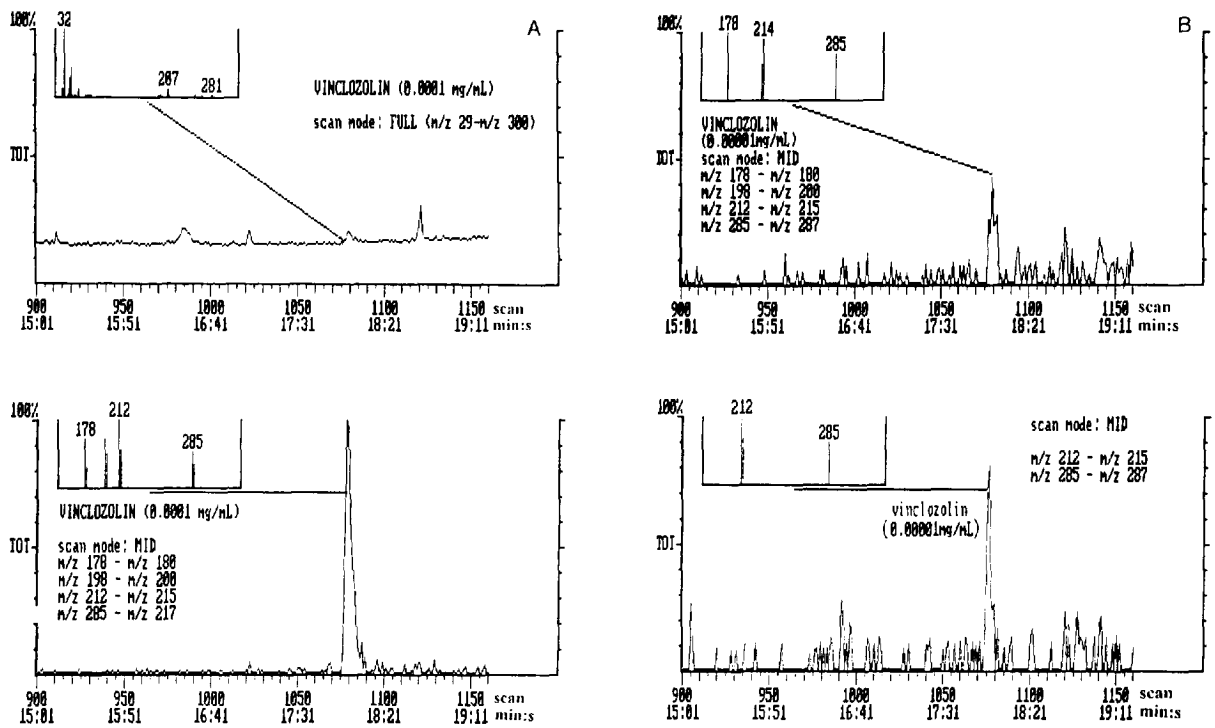

Fig. 4. (A): Full scan and MID scan mode chromatograms of standard vinclozolin (0.0001 mg/ml); conditions see Section 2. (B): MID scan mode chromatograms of standard vinclozolin (0.00001 mg/ml); for conditions see Section 2.

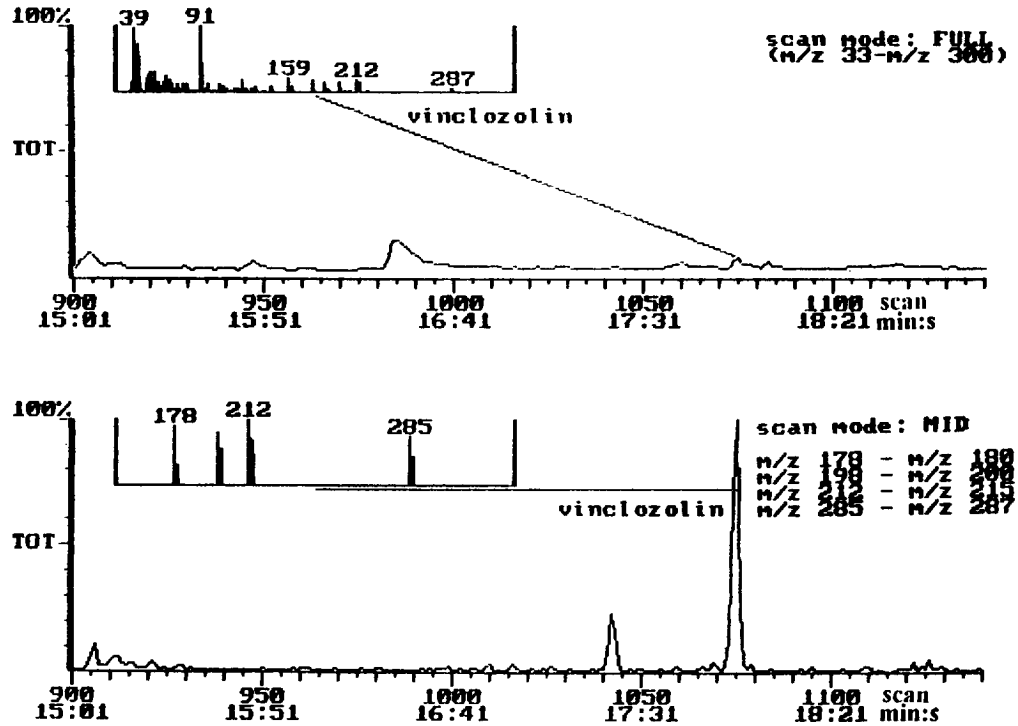

Fig. 5. Full scan and MID scan chromatograms of treated white wine variety Rizling vlašský (with 0.1% Ronilan 50 WP).

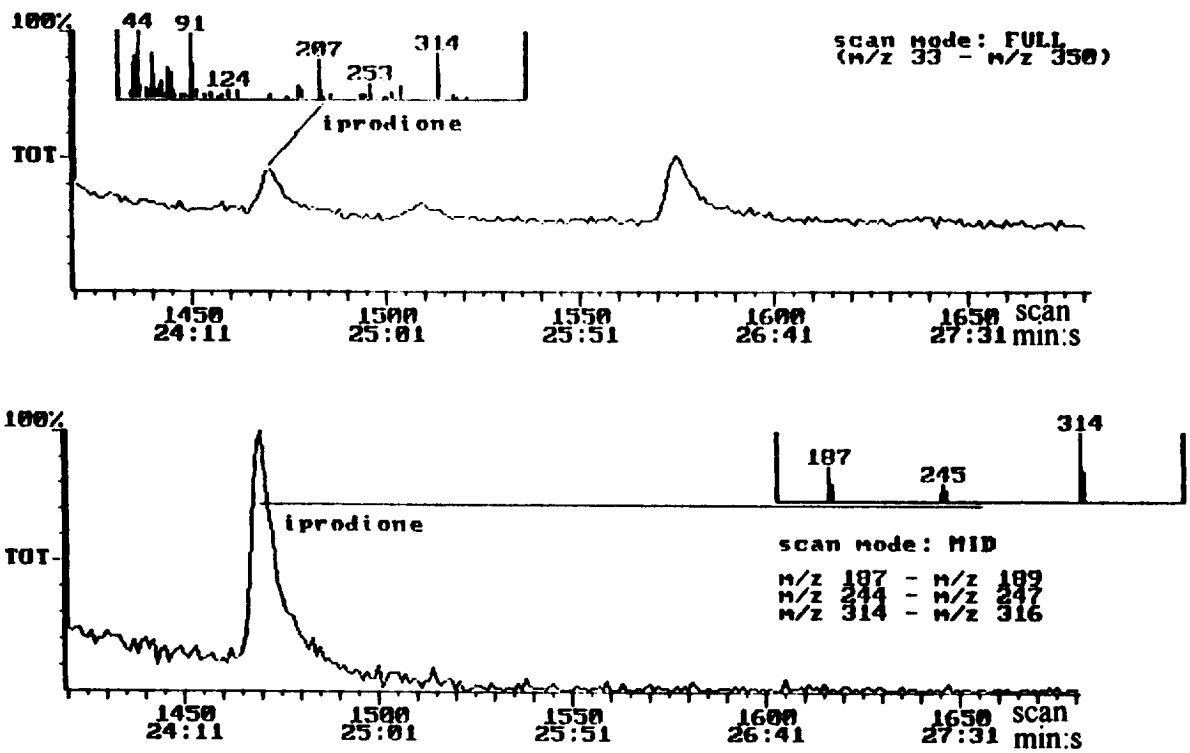

Fig. 6. Full scan and MID scan chromatograms of treated white wine variety Rizling vlašský (with 0.15% Rovral 50 WP).

4. Conclusion

It was shown that a novel porous carbon prepared by controlled pyrolysis of succharose in a matrix of silica-gel is convenient sorbent for the preconcentration of non-volatile carboxyimide fungicides-vinclozolin and iprodione. Reliable recovery data were measured at various concentration of fungicides in standard solutions (0.0005–0.1 mg/ml) and spiked wines 5.90 μg–1.96 mg/l). SPE analysis was performed in combination with high-resolution capillary GC and GC–MS-ITD under optimised experimental conditions. Excellent limits of quantitation were determined.

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