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High temperature liquid chromatography of triazole fungicides on polybutadiene-coated zirconia stationary phase

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Abstract

High temperature liquid chromatography using water-rich and superheated water eluent is evaluated as a new approach for the separation of selected triazole fungicides, hexaconazole, tebuconazole, propiconazole, and difenoconazole. Using a polybutadiene-coated zirconia column at temperatures of 100–150 °C, clear separations were achieved when 100% purified water was utilized as organic-free eluent. Excellent limits of detection down to pg level were obtained for the separation of the triazole fungicides under optimum conditions. Van't Hoff plots for the separations were linear suggesting that no changes occurred in the retention mechanism over the temperature range studied.

Keywords: High temperature HPLC; Triazole fungicides; Zirconia–PBD stationary phase; Superheated water

1. Introduction

Control of column temperature has become increasingly accepted as a separation parameter in reversed-phase high performance liquid chromatography (RP-HPLC). High temperature operation in RP-HPLC provides the opportunity to reduce the quantity of organic solvent used in mixed organic–water mobile phase, increases analyte mass transfer rates and decreases column back pressure and total analysis time significantly [1]. Elevated column temperature operation in RP-HPLC can be used as a tool to overcome the flow rate problem associated with high back pressure, allowing the use of higher flow rates that otherwise could not be applied [2]. According to the Stokes–Einstein relationship, the diffusion coefficient is directly proportional to the absolute temperature and inversely proportional to the viscosity. High temperature separation has been shown to improve analyte resolution by decreasing mobile phase viscosity and by increasing the diffusion rate of the sample species, thus increasing mass transfer of the analyte to the stationary phase and thereby decreasing the peak width [3].

High temperature as an optimization parameter in the separation process of the RP-HPLC system has been widely studied due to the recent findings of the alternative stationary phase, which has high thermal stability at a high temperature. Sanagi and See [4], in their paper, described a comprehensive study on PS-DVB column using water-rich and superheated water eluent at high column temperatures of up to 200 °C.

Zirconia based stationary phase can be regarded as one of the latest high thermal stability stationary phases introduced and is able to withstand extended exposure to column temperature as high as 150 °C. Zirconia by itself has very rich surface chemistry and able to operate at a wider pH range of 1–14. In contrast, for conventional alkyl silane bonded phases, high temperature will directly accelerate the dissolution of silica in aqueous solution [5]. The advantages of zirconia as a stationary phase were more apparent with the development of polybutadiene-coated zirconia [6–8] and carbon-clad zirconia stationary phase [9–11]. Zirconia columns coated with polybutadiene (PBD) have been widely

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used as a reversed-phase HPLC stationary phase because it is a more durable substrate compared with silica, while not imparting the high retentive characteristics of the aromatic polymer-based column. In another work, Sun and Carr [7] established a reversed-phase/cation-exchange mixed-mode chromatographic system on PBD phases. The existence of hydroxyl groups on the surface of zirconia control the surface chemistry and reflected in its cation and anion exchange properties [8].

Fungicides have been developed since the discovery of the antifungal activity of N1-substituted azoles in the late 1960s [12]. Triazole fungicides are well known as curative fungicides, usually applied to the plant after initial infection before it produces visible symptoms. Triazole fungicides provide excellent protective and a relatively low resistance risk compared with other fungicides such as benzimidazoles and dicarboximides. The common structural moiety for triazole fungicides is the 1,2,4-triazole ring, which is connected to the hydrophobic backbone through position 1 [13]. Currently, triazoles comprise about 25 commercial agrochemicals and represent the latest group of modern agricultural fungicides. Most of the triazole fungicides are used against rusts, powdery mildews, and scabs [12].

The analysis of fungicides have been carried out largely by capillary gas chromatography (GC) [14,15], liquid chromatography [16,17], and capillary electrophoresis [18,19] in conjunction with a variety of detectors. Recently, the separation of 14 triazole fungicides was demonstrated by Li and coworkers [13] using capillary electrophoresis but the sensitivity and efficiency of the separation were not fully described. In order to establish a high sensitivity and efficiency separation technique of triazole fungicides, it is thus of interest to find out if high temperature can be utilized in the separation and detection of these compounds using PBD-coated zirconia as stationary phase.

The present study was set out to develop a high-sensitivity high temperature high performance liquid chromatography (HT-HPLC) separation method on selected triazole fungicides (hexaconazole, tebuconazole, propiconazole, and difenoconazole) (Table 1) using water-rich and 100% pure water as eluent. The performance of polybutadiene-coated zirconia column (ZirChrom-PBD) for the separation of triazole fungicides was also investigated.

2. Experimental

2.1. Reagents

HPLC grade acetonitrile was obtained from Caledon Laboratories Ltd. (Canada). Double distilled deionised water of at least 18 MΩ was purified by Nano ultra pure water system (Barnstead, USA). Triazole fungicides (hexaconazole, tebuconazole, propiconazole, and difenoconazole) were obtained from Dr. Ehrenstorfer (Augsburg, Germany).

2.2. Chromatographic conditions

The instrumental set-up is shown in Fig. 1. The high temperature HPLC system consisted of a conventional HPLC system coupled with a column oven of a Perkin-Elmer Autosystem Gas Chromatography (USA). HPLC separations were carried out using a Waters 515 HPLC pump (Milford, USA) for mobile phase delivery. A Rheodyne 7125 injection valve (Cotati, USA) fitted with a 20 μL loop was used for sample introduction. Samples were loaded into the valve using a partially filled injection technique with a 25 μL syringe (Hamilton, Australia). Injection reproducibility was maintained with a R.S.D. <1% based on retention time and area of solvent peak on triplicate injection. Analyte peaks were detected using a Shimadzu SPD-6A variable wavelength UV detector (Kyoto, Japan) and were recorded on a Hewlett-Packard HP 3396 Series II integrator (USA). A 30 cm × 0.5 mm i.d. stainless-steel tubing that served as a pre-heating coil was placed in the oven between the injection valve and column. Separations were carried out on a column (100 mm × 2.1 mm i.d.) packed with 3 μm ZirChrom-PBD 300 Å (ZirChrom Separations, Anoka, MN, USA). The column and the pre-heating coil were placed together in the oven. A Jasco 880-81 (Japan) backpressure regulator was connected to the outlet of the detector to maintain a constant backpressure (∼20 bar) in the detector cell.

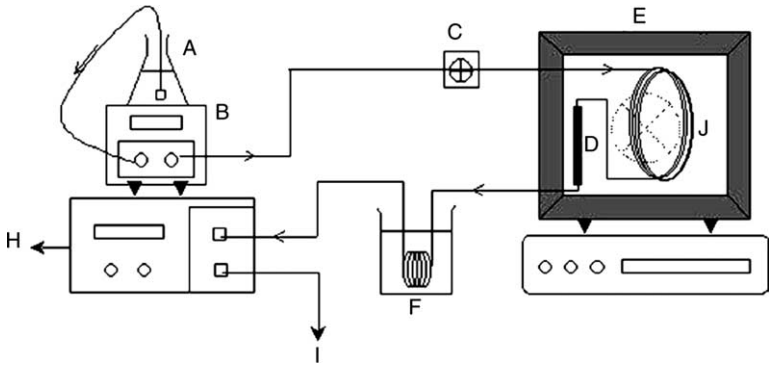
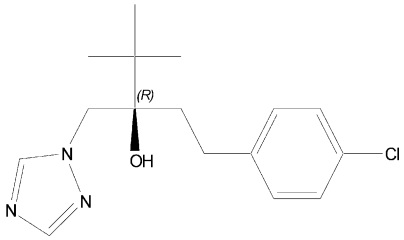
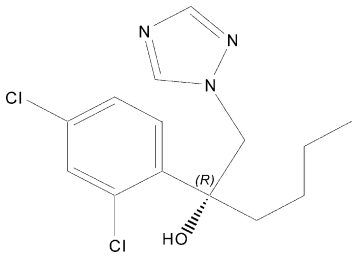
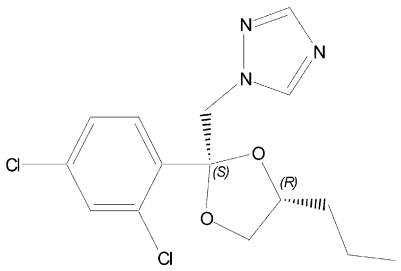
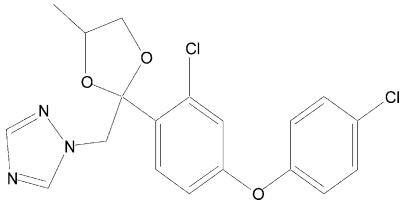


Fig. 1. Experimental set-up: (A) mobile phase reservoir; (B) HPLC pump; (C) injection valve; (D) column; (E) oven; (F) cooling system (ice water); (G) UV detector; (H) integrator; (I) backpressure regulator; (J) mobile phase pre-heating coils.

Table 1
Properties of four triazole fungicides

Fungicides	Structure	Molecular weight	log P[a]	pK_a
Tebuconazole, (*RS*)-1-*p*-chlorophenyl-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol, $C_{16}H_{22}ClN_3O$		307.82	4.01	–
Hexaconazole, (*RS*)-2-(2,4-dichlorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)hexan-2-ol, $C_{14}H_{17}Cl_2N_3O$		314.21	3.77	2.30[b]
Propiconazole, *cis-trans*-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazole, $C_{15}H_{17}Cl_2N_3O_2$		342.22	4.16	1.09[c]
Difenoconazole, *cis-trans*-3-chloro-4-[4-methyl-2-(1*H*-1,2,4-triazol-1-ylmethyl)-1,3-dioxolan-2-yl]phenyl 4-chlorophenyl ether, $C_{19}H_{17}Cl_2N_3O_3$		406.26	4.79	–

[a] Prediction of logarithm of partition coefficient (*n*-octanol/water) (log P) according to mechanic molecular modeling methods by using CS ChemOffice Chem3D Pro version 5.0 and CS ChemDraw Ultra version 6.0 computer software.
[b] pK_a value obtained from Ref. [20].
[c] pK_a value obtained from Ref. [21].

2.3. Procedure

The mobile phase used was prepared by mixing double distilled deionised water with acetonitrile and the mixture was subsequently degassed using vacuum-ultrasonic method. Samples of triazoles fungicides dissolved in acetonitrile were injected in triplicate onto the column. Separations of analytes on the ZirChrom-PBD column were carried out using acetonitrile–water: 10:90, 5:95, and 0:100 (v/v) at high temperatures (100–150 °C). The eluent flow rate was 0.5 mL/min and sample injection volume was 1 μL. Solute concentrations were 0.1 mg/mL. Sample solvent (acetonitrile) peak was used to determine the void volume of the system. UV detection of analytes for the comparison study was at 220 nm. The limit of detection was determined based on each solute that gave a peak with a height three times the background noise level using 100% pure water eluent on PBD-coated zirconia column at UV wavelength of 195 nm.

3. Results and discussion

3.1. Influence of temperature on retention factor, resolution, and column efficiency

RP-HPLC separations of four triazole fungicides as a function of temperature with different mobile phase compositions at an elevated flow rate of 0.5 mL/min on PBD–zirconia column are investigated. From the results obtained, it was apparent that the elution order for the triazole fungicides was directly proportional to the molecular weight of the solute (Table 1). Tebuconazole with the lowest molecular weight

Table 2
Retention factor of four triazole fungicides as a function of temperature using different proportion of organic modifier on PBD-coated zirconia column

Compounds	Mobile phase, MeCN:water (v/v)	Retention factor, k (R.S.D., %)[a]					
		Column temperature (°C)					
		100	110	120	130	140	150
Tebuconazole	10:90	6.92 (0.3)	5.37 (0.5)	3.95 (0.3)	–	–	–
	5:95	–	–	7.10 (0.4)	5.31 (0.5)	3.84 (0.2)	–
	0:100	–	–	–	11.03 (1.6)	7.61 (0.9)	5.38 (0.7)
Hexaconazole	10:90	9.12 (0.3)	6.91 (0.4)	5.01 (0.3)	–	–	–
	5:95	–	–	9.49 (0.3)	6.94 (0.5)	4.93 (0.2)	–
	0:100	–	–	–	14.26 (1.5)	9.69 (0.9)	6.75 (0.7)
Propiconazole	10:90	NS	7.19 (0.4)	5.41 (0.3)	–	–	–
		9.52 (0.3)	7.43 (0.4)	NS	–	–	–
	5:95	–	–	9.67 (0.3)	7.33 (0.3)	5.44 (0.2)	–
		–	–	10.12 (0.3)	7.57 (0.3)	NS	–
	0:100	–	–	–	15.31 (1.5)	10.74 (0.4)	7.66 (0.7)
		–	–	–	16.18 (1.5)	11.17 (0.4)	7.84 (0.8)
Difenoconazole	10:90	27.86 (0.3)	20.27 (0.4)	14.05 (0.4)	–	–	–
		29.29 (0.3)	21.11 (0.4)	14.45 (0.3)	–	–	–
	5:95	–	–	28.24 (0.4)	19.86 (0.3)	13.82 (0.2)	–
		–	–	29.63 (0.4)	20.51 (0.5)	NS	–
	0:100	–	–	–	48.15 (1.5)	30.95 (0.9)	20.41 (0.8)
		–	–	–	50.72 (1.5)	32.28 (0.9)	21.02 (0.8)

NS, not separated; (–) not studied.
[a] R.S.D. (%) was based on triplicate injection.

was first eluted across the column followed by hexaconazole, propiconazole, and difenoconazole in all cases studied. Li and Carr [22], in their report, demonstrated that although PBD phase possess polymeric nature, the partition effect is the dominant retention process of non-polar solutes on PBD-coated zirconia stationary phase.

For each compound studied, there was a markedly decrease in retention factors with increasing temperature from 100 °C to 150 °C with 10 °C increments using different proportions of acetonitrile (Table 2). It was observed that a 1% increase in acetonitrile concentration has the same effect as a 4 °C increase in column temperature in controlling solute retention. Several studies have directly compared the effects of changing the solvent composition and column temperature. Bowermaster and McNair [23] observed that a 1% increase in methanol concentration had approximately the same effect as a temperature increase of 4 °C. Chen and Horvath [24] found a similar relationship after examining a series of homologous *n*-alkylbenzenes in acetonitrile/water (1%, 5 °C). As shown in Table 2, equivalent separations were obtained at 110 °C with 10% acetonitrile, at 130 °C with 5% acetonitrile, and at 150 °C with 0% acetonitrile. This indicates that retention can be controlled either by the amount of organic solvent in the mobile phase or by column temperature.

Based on the experimental data gathered, it was observed that the separation resolution for each pair of solutes by using 10% and 5% of acetonitrile as eluent were generally unsatisfactory, with a resolution value <0.70 especially for hexaconazole, propiconazole and difenoconazole (result not shown). This phenomenon is probably due to the water-rich eluent that is unable to wet the PBD-coated zirconia particles and leads to insufficient mass transfer and hence poor analyte resolution and selectivity on the stationary phase [22]. However, a very surprising result was observed when greater resolution for the separation of the four triazole fungicides were obtained by using 100% pure water eluent on PBD-coated zirconia column at high column temperatures (Table 3). Clear separation was observed for the diastereoisomers (propiconazole and difenoconazole) as well as the two enantiomers (tebuconazole and hexaconazole) (Fig. 2). Solutes are more favorably retained on the stationary phase when fully aqueous mobile phase was used and this leads to higher selectivity as well as greater resolution. The PBD-coated phases, in general, have slightly greater hydrophobic selectivities, especially in highly aqueous mobile phases, than do either conventional monomeric or polymeric ODS phases. This suggests that separation based on hydrophobic selectivities could be easily performed on the PBD-coated zirconia stationary phase [22] (Fig. 3).

Based on the variation of column efficiency with temperature for tebuconazole (Fig. 4), it can be seen that the column efficiency (N/m) markedly decreased when the column temperature was increased. This trend was observed for all compounds studied (Table 3). Carr and Li [25] reported that

Table 3
Resolution (R_s) and column efficiency (N/m) of four triazole fungicides as a function of temperature using 100% pure water as eluent on PBD-coated zirconia column

Triazole fungicides	Column temperature (°C)					
	130		140		150	
	N/m	R_s	N/m	R_s	N/m	R_s
Tebuconazole	16000 (2.2)	2.30 (1.0)	14000 (3.6)	1.98 (2.0)	12000 (1.8)	1.65 (1.3)
Hexaconazole	15000 (3.6)	1.73 (2.1)	14000 (3.9)	1.20 (5.0)	12000 (1.4)	1.05 (0.8)
Propiconazole (1)	35000 (3.6)	0.85 (0.1)	33000 (7.0)	0.70 (2.1)	37000 (3.5)	0.45 (5.5)
Propiconazole (2)	31000 (1.6)	14.45 (1.6)	25000 (4.5)	11.38 (2.1)	25000 (5.0)	11.08 (0.9)
Difenoconazole (1)	38000 (4.0)	1.01 (0.7)	26000 (5.5)	0.80 (3.6)	30000 (0.9)	0.62 (1.5)
Difenoconazole (2)	44000 (4.0)		35000 (4.7)		28000 (2.1)	
Total run time (min)	43		27		18	

low column efficiency at high temperature could probably be due to the longitudinal molecular diffusion that is more pronounced at high temperature. However, by using high linear velocity region, the longitudinal molecular diffusion is no longer significant. On the other hand, the use of bigger i.d. temperature equilibration coil in this study might have lead to significant extra-column broadening that resulted in poorer column efficiency. It is, therefore, of interest to utilize smaller i.d. temperature equilibration coil in the future study to achieve more acceptable separation efficiency.

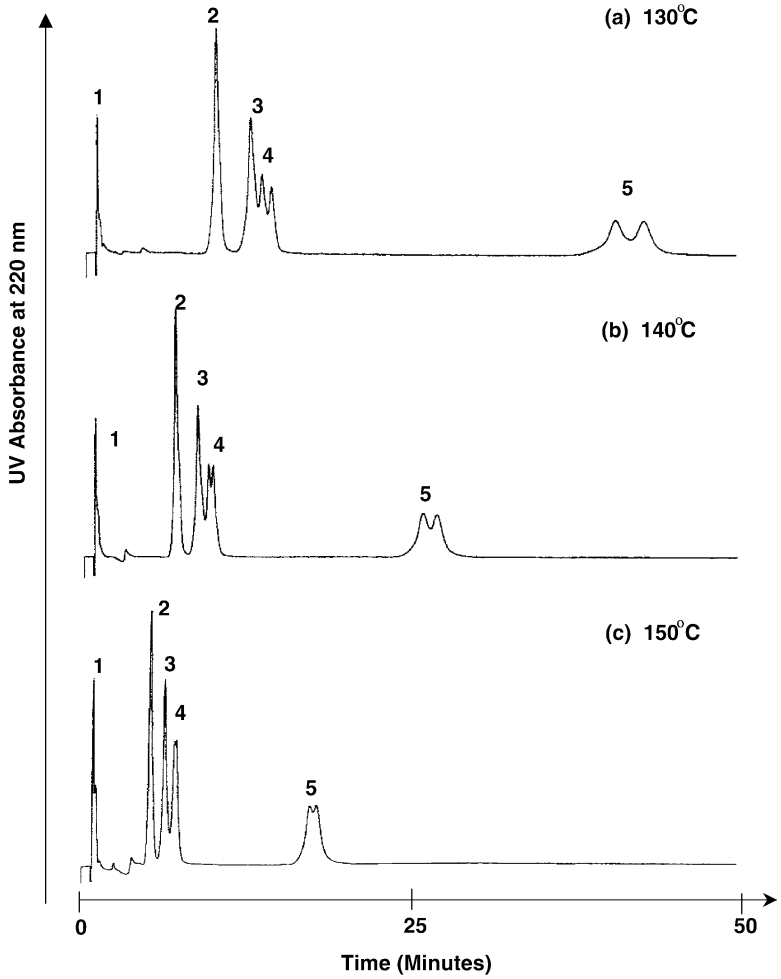


Fig. 2. Separation of four triazole fungicides on ZirChrom-PBD column (100 mm × 2.1 mm i.d.). Chromatographic conditions: mobile phase, 100% pure water; flow rate, 0.5 mL/min; temperature, 130–150 °C; detection, UV absorbance at 220 nm; injection volume, 1 μL; solute concentration, 0.1 mg/mL. Peaks: (1) solvent; (2) tebuconazole; (3) hexaconazole; (4) propiconazole; (5) difenoconazole.

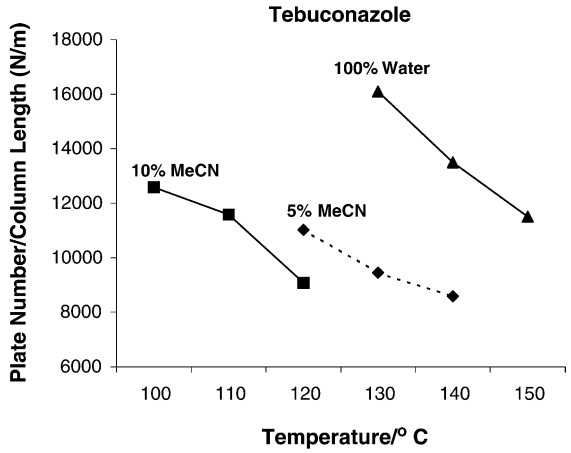


Fig. 3. Variation of column efficiency as a function of temperature using low proportion of organic modifier on PBD-coated zirconia column (solute: tebuconazole).

3.2. Influence of temperature on PBD-coated zirconia column separation mechanism

The influence of temperature on column separation mechanism can be calculated from retention data by evaluation of the Van't Hoff plots. As a theoretical basis for the Van't Hoff plots, the retention factor is expressed in terms of standard enthalpies and entropies of transfer from mobile to stationary phase. The relation between the logarithm of the retention factor ($\ln k$) and enthalpies and entropies equals [26]:

$$\ln k = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} + \ln \Phi \quad (1)$$

where k is the measured retention value; ΔH°, the enthalpy; ΔS°, the entropy; T, the absolute temperature; R, the gas constant and Φ, the phase ratio of the column. ΔH° and ΔS° are the standard enthalpy and standard entropy of transfer of a solute from the mobile phase to the stationary phase. A rectilinear plot indicates that the same separation mechanism prevails across the entire temperature range of interest [27].

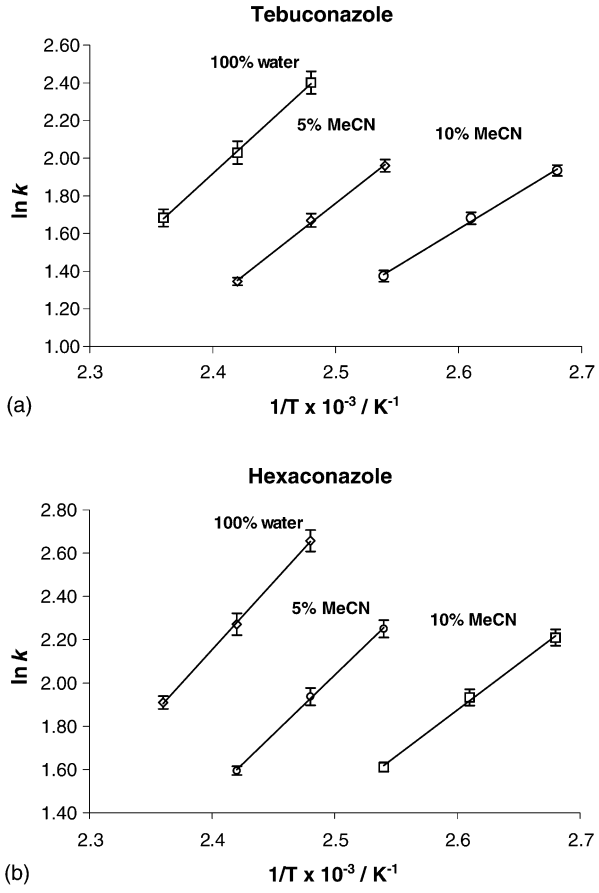


Fig. 4. Van't Hoff plots for tebuconazole (a) and hexaconazole (b) using different proportions of acetonitrile on PBD-coated zirconia column.

Table 4
Enthalpy data for tebuconazole and hexaconazole at high column temperatures on PBD-coated zirconia column

Compound	Enthapy ΔH° (kJ/mol)			Correlation, r		
	10:90[a]	5:95[a]	0:100[a]	10:90[a]	5:95[a]	0:100[a]
Tebuconazole	−34.13	−41.45	−50.88	0.9951	0.9979	0.9999
Hexaconazole	−36.47	−44.16	−53.01	0.9967	0.9984	0.9999

Temperature range: 100–150 °C.
[a] Mobile phase composition, MeCN:water.

From the Van't Hoff plots for the tebuconazole and hexaconazole (Fig. 4), it was obvious that there was no significant deviation from linearity. It was, therefore, concluded that over the temperature range, there was no changes in the retention mechanism for triazole fungicides. In all cases, the ΔH° values were negative under the experimental conditions, demonstrating that retention of compounds studied is an exothermic process (Table 4). It is energetically more favorable for the compounds to remain in the stationary phase than in the mobile phase. As expected, the value of ΔH° became more negative with decreasing acetonitrile content in the eluent. This showed that a strong retention interaction between mobile and stationary phase occurred when the percentage of organic modifier in the eluent is decreased.

3.3. Limit of detection

In order to examine the sensitivity of the high-temperature high performance liquid chromatography system, the limit of detection for all four triazole fungicides was investigated. From the overall column separation efficiency and all the data gathered in this work, separation of triazole fungicides using 100% pure water as eluent at 140 °C was chosen as the optimum separation condition in our further studies on limit of detection. The limit of detection was determined based on each solute that gave a peak with a height three times the background noise level. The detection wavelength was optimized and it was observed that the maximum absorbance for four triazole fungicides was obtained at 195 nm. Excellent detection limits for the separation of the four triazole fungicides were obtained by using 100% pure water eluent on PBD-coated zirconia column at 140 °C. From the results

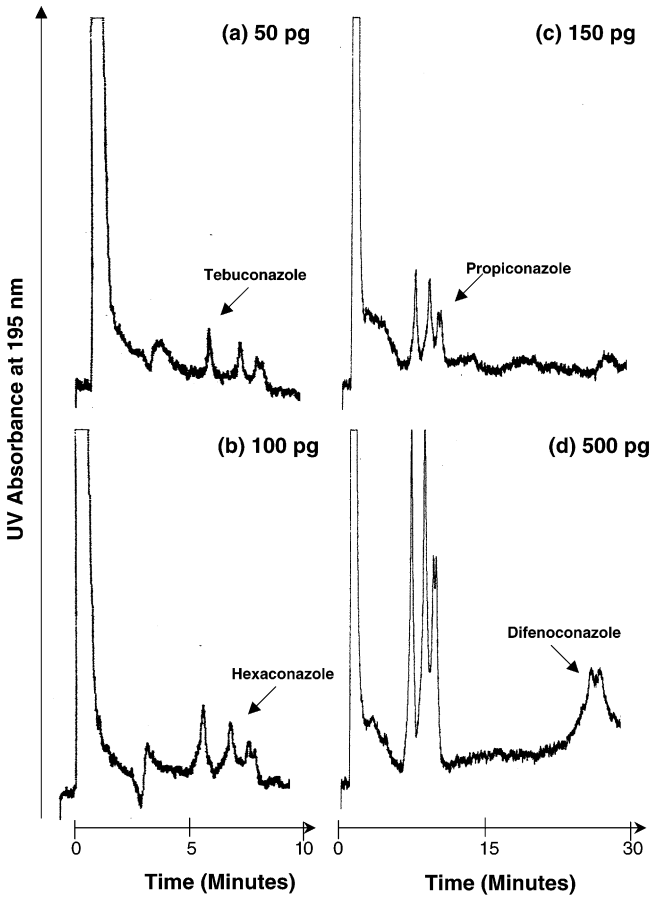


Fig. 5. Detection limits of four triazole fungicides separation on ZirChrom-PBD column (100 mm × 2.1 mm i.d.). Chromatographic condition: mobile phase, 100% pure water; flow rate, 0.5 mL/min; temperature, 140 °C; detection, UV absorbance at 195 nm; injection volume, 1 μL.

(Fig. 5), tebuconazole could be detected down to 50 pg followed by hexaconazole (100 pg), propiconazole (150 pg), and difenoconazole (500 pg).

The results were outstandingly low when compared with most conventional HPLC. Smith and Burgess, in their paper [28], pointed out the spectrometric advantages of pure superheated water eluent. Solutes that possess only weak chromophores that can be easily detected by UV detection system, thanks to the development of superheated water as eluent that is transparent even down to 190 nm. It is important to note that the detection limits reported are calculated in purified double distilled deionized water as the eluent. The use of normal clean tap water will probably decrease the detection limit as it is not so transparent. This phenomenon should be considered in the future study in order to explore the flexibility of the developed system.

4. Conclusions

A novel approach to separate triazole fungicides using superheated water as organic-free eluent is presented for the first time. The method developed justified that purified water can be utilized as eluent to completely separate triazole fungicides with excellent detection limit down to ppb level at high column temperatures (100–150 °C) on PBD-coated zirconia column. Current work provides a great interest to further investigate on the applicability of the developed method to the analysis of different sample matrices, performance study of other alternative high thermal stability columns, and also the reliability and reproducibility of the excellent detection limit using non-purified water samples.

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