Enantioseparation of polar pesticides on chiral capillary columns based on permethyl-β-cyclodextrin in matrices of different polarities

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ABSTRACT

This work describes the influence of different achiral polymers used to dissolve permethyl-β-cyclodextrin (PM-β-CD) on the gas chromatographic enantioresolution of racemic mixtures of polar pesticides (mecoprop, dichlorprop, fenoprop and hydroprop esters, fenoxaprop ethyl, metalaxyl, and haloxyfop esters). One main objective was to introduce a single column for robust and sensitive enantioseparations of several and different polar pesticides, which have to be chromatographed at relatively high temperature (unfavorable condition for enantiodiscrimination). In particular, the ability of capillary columns coated with PM-β-CD dissolved in either (14%-cyanopropylphenyl)(1%-vinyl)-86%-methylpolysiloxane (OV-1701-vi), (5%-phenyl)(1%-vinyl)-95%-methylpolysiloxane (SE-54) or in polyethyleneglycol (Carbowax 20 M), to resolve the racemates of the aforementioned pesticides was evaluated. An analogous commercial column, Hydrodex β-PM, was taken as reference. In addition, the influence of the achiral polymer in the availability of selector for enantioselective interactions with those pesticides was studied. Enantioseparations achieved with the phase based on the less polar polysiloxane SE-54 were higher for most chiral pesticides as compared with those obtained with PM-β-CD mixed in more polar polymers. The results furthermore indicate that a single column based on PM-β-CD/SE-54 exhibited great potential for application in the separation of a wide variety of polar pesticides and their derivatives.

1. Introduction

Pesticides widely used in agriculture are of diverse chemical nature. Because of their persistence, polar nature, and water solubility, many of these pesticides are mobile in the environment, and their residues are often found in a variety of matrices. In 2005, an estimate showed that about 25% of the pesticides used were chiral and it was predicted that this proportion would increase as more complex chemical compounds are regularly introduced [1]. For economic reasons, most chiral pesticides are primarily used as racemates [1]. It is well known that even though the enantiomers of a given compound possess identical physicochemical properties, individually they can exhibit different biological activities such as potency, action mode and/or toxicity [1,2]. In addition, their biodegradation and environmental fate can also differ [3–5].

Analytical techniques applied to enantiomeric determinations in environmental matrices include liquid chromatography (LC), capillary electrophoresis and gas chromatography (GC). The GC methods with chiral stationary phases are primarily chosen for the direct separation of volatile and thermally stable enantiomers because of its high sensitivity, efficiency and precision. The enantioseparation of polar (and less volatile) compounds, however, is difficult since usually it is necessary to decrease the column temperature in order to enhance the enantioselectivity factors, with the consequent increase in the analyte retention [6]. One way to keep reasonable analysis times at a relatively low elution temperature for the separation of those enantiomers by GC consists in the use of shorter columns coated with a reduced thickness of stationary phase film. Another possibility for the analysis of polar compounds by gas chromatography involves their conversion to volatile derivatives that can be eluted at relatively low temperatures.

Chiral stationary phases (CSP) based on cyclodextrins (CD), especially those involving β-CD, are the most widely used in enantioselective GC [7] since the enantioseparation ability of CD derivatives is not limited to certain class of compounds; their chiral recognition abilities are observed toward an extremely wide variety of chemical families. Common chiral stationary phases are usually designed by dissolving modified CDs in polysiloxanes [8]. The use of diluted chiral selectors has practical advantages such as reducing the column temperatures to values well below the generally high melting points of various pure chiral CD derivatives and, simultaneously, achieving improved column efficiencies owing to the usually superior coating properties of those polymers. With only a few exceptions, OV-1701 is the most common polysiloxane used for preparation of diluted CD chiral stationary phases [7].

The enantioselectivity features of these CD derivatives, however, can be influenced by the polymeric liquid used as solvent. Dietrich et al. [9] compared the performance of columns coated with heptakis(2,3-di-O-methyl-6-O-tert-butyldimethylsilyl)-β-CD (diMe-TBDMS-β-CD) diluted with SE-30, SE-52, and with OV-1701-vi in the analysis of trifluoroethanol and alkyl-branched free fatty acid racemates and they found that SE-52 led to an enhanced enantioselectivity. Bicchi et al. [10] compared the separation of volatile compounds in columns coated with heptakis(2,6-di-O-methyl-3-O-pentyl)-β-cyclodextrin diluted with OV-1701 with that of columns prepared with the same chiral selector diluted with phases of different polarities (i.e., PS-086, PS-347.5, and OV-225). In this instance, they found that no diluting phase investigated was unequivocally better than others, although PS-347.5, PS-086 and OV-1701 generally gave better results with the racemates studied than did OV 225. Subsequently, Dietrich et al. [11] investigated the influence of different polysiloxanes on the stereoselectivity and column efficiency of capillary columns coated with heptakis(2,3-di-O-acetyl-6-O-tert-butyldimethylsilyl)-β-cyclodextrin. The authors concluded that a certain CD- polysiloxane combination is superior to others only at a particular temperature. Osorio Grisales et al. [12] assayed different concentrations of PM-β-CD as chiral selector dissolved in SE-30, SE-54 and Carbowax 20 M and found examples of enantiomers of volatile compounds well resolved on one column but not on others.

Chiral separations depend on differences in the interactions between each enantiomer with the chiral selector. Those differences are usually quite subtle and decrease when temperature increases [6,7]. The challenge consists in separating enantiomers of polar herbicides at temperatures compatible with reasonable analysis times. In the present work, the influence of the polymeric solvent used to dilute PM-β-CD on the GC enantioseparation of polar pesticides widely used in agricultural practices was evaluated. Our aim was to improve the enantioresolution of these low volatile compounds using preferably a single column. In particular, the performance of columns coated with PM-β-CD mixed with OV-1701-vi, with SE-54 and with Carbowax 20 M was studied. In order to elucidate the magnitude of solute's achiral retention in the polymeric solvent, retention factors of the agrochemicals in columns of similar geometries but in absence of chiral selector were assessed. The pesticides comprised esters of the phenoxypropionic acids mecoprop, dichlorprop, and fenoprop, esters of the precursor hydroprop, esters of the aryloxyphenoxypropionic haloxyfop and fenoxaprop ethyl, and the acetamide metalaxyl. The chemical structures, vapor pressure data and agricultural uses of those pesticides are summarized in Table 1.

2. Experimental

2.1. Materials

Heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin was obtained from Cyclolab (Budapest, Hungary). (14%-cyanopropylphenyl)(1%-vinyl)-86%-methylpolysiloxane (OV-1701-vi) and (5%-phenyl)(1%-vinyl)-95%-methylpolysiloxane (SE-54) were obtained from Supelco (Bellefonte, PA, USA), and Carbowax 20 M (C20M) from Alltech (Deerfield, IL, USA). A commercial column containing heptakis-(2,3,6-tri-O-methyl)-β-CD (Hydrodex β-PM) column (25 m × 250 μm i.d.) was acquired from Macherey-Nagel (Macherey-Nagel GmbH & Co. KG, Düren, Germany). The herbicides 2-(4-chloro-2-methylphenoxy) propanoic acid (mecoprop), 2-(2,4-dichlorophenoxy)propanoic acid (dichlorprop) and 2-(2,4,5-trichlorophenoxy)propanoic acid (fenoprop) were obtained from Sigma-Aldrich (St. Louis, MO, USA), 2-

Table 1
Herbicides, structures and agricultural uses.

Solutes (CAS #)	Vapor pressure[a] (mm Hg	Structure	Uses[c]
1. Mecoprop(93-65-2)	2.2×10^{-5}		Herbicide. Control of broad-leaf weeds
2. Dichlorprop (120-36-5)	7.5×10^{-8}		Herbicide. Control of broad-leaf weeds
3. Fenoprop (93-72-1)	9.9×10^{-6}[b]		Herbicide. Plant- growth regulator
4. Metalaxyl (57837-19-1)	5.6×10^{-6}		Fungicide
5. Haloxyfop methyl (69806-40-2)	1.2×10^{-7}		Postemergence herbicide
6. Hydroprop (94050-90-5)	1.2×10^{-7}		Precursor
7. Fenoxaprop ethyl (66441-23-4)	3×10^{-8}		Postemergence herbicide

[a] At 25 °C. Taken from EPA Database (https://comptox.epa.gov/dashboard).
[b] At 25 °C. Taken from ChemIDplus, a Toxnet database. Toxicology Data Network. National Institutes of Health (NIH). U.S. NAtional Library of Medicine. (https://chem.nlm.nih.gov/chemidplus/rn/93-72-1).
[c] The R-enantiomer of all these pesticides exhibits biological activity.

(4-hydroxyphenoxy)propanoic acid (hydroprop acid), methyl 2-(N-(2-methoxyacetyl)-2,6-dimethylanilino)propanoate (metalaxyl), methyl 2-(4-{[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy}phenoxy) propanoate (haloxyfop methyl), and ethyl 2-{4-[(6-chloro-1,3-benzoxazol-2-yl)oxy]phenoxy}propanoate (fenoxaprop ethyl) were kindly provided by Agrofina (Buenos Aires, Argentina). Ethyl chloroformate and methyl chloroformate, methanol, ethanol, 2,2,2-trifluoroethanol (TFE) and pyridine were purchased from Sigma–Aldrich (St. Louis, MO), and chloroform and dichloromethane were obtained from Merck (Buenos Aires, Argentina). Trifluoroacetic anhydride (TFAA) was obtained from Fluka (Buchs, Switzerland). Deionized water was generated by a purification Milli-Q system (Simplicity, Millipore, MA).

2.2. Gas chromatography

An HP 6890 (Agilent, Palo Alto, CA) gas chromatograph equipped with flame-ionization detector and manual-injection port was used. The data were acquired by means of the software Clarity (DataApex, Czech Republic). The carrier gas was nitrogen, set at constant flow. Injections were made with a split ratio of 1/25, the injector and detector temperatures were set at 200 °C and 250 °C, respectively. Chromatographic separations were conducted with temperature programs. In the optimized program, the temperature was first held at 70 °C for 2 min, followed by heating at 2 °C/min to 200 °C.

2.3. Column coating

Fused-silica capillaries of 250 μm i.d. were purchased from Microquartz Electronics (Munich, Germany). No pretreatment of the inner surface was done. PM-β-CD was weighed with each achiral polymer, the mixture was then dissolved in dichloromethane and these solutions were introduced into the capillaries by pressure. The coating was made by a static method with controlled evaporation temperature [13,14]. Finally, the columns were conditioned with a slow flow of nitrogen at increasing temperatures. The geometrical characteristics of the columns are reported in Table 2. Their efficiencies (as theoretical plates by column length) were measured from n-dodecane eluted at 120 °C in the all capillary columns. The higher plate counts were obtained with the commercial column. The loss in efficiency observed for columns prepared with SE-54 and C20M can be attributed to the higher percentage of CD derivative contained in these phases [12,15,16]. Unfortunately, the information about the properties of the commercial column (e.g. film thickness, the achiral polymeric matrix and selector concentration) are not known.

2.4. Standard solutions.

2.3.1. Hydrolysis

As the pesticides metalaxyl and haloxyfop methyl are not available as free acids, they were prepared by alkaline hydrolysis. Each ester was dissolved in a 10% w/v aqueous solution of potassium hydroxide

(concentration of 1.8 mg/mL) and it was heated at 90 °C for 10 h. After cooling, the solution was acidified with 6 M hydrochloric acid up to neutral pH. The pesticide was then extracted with two portions of dichloromethane. The extracts were combined and the solvent was removed in a stream of dry nitrogen. The residue was next treated as described below.

2.3.2. Derivatization procedure

Methyl and ethyl esters were prepared by alkylation with alkyl chloroformates [17]. To 1 mg of each compound, 100 μL of alcohol/water/pyridine (60:32:8), and 6 μL of chloroformate (methyl or ethyl chloroformate) were added. The mixture was stirred for 5 s. Finally, the esters were extracted with 100 μL of chloroform containing 1% (v/v) of the corresponding chloroformate, and aliquots of the organic phases were injected.

For alkylation with trifluoroacetic anhydride and trifluoroethanol, the reaction mixture containing about 1 mg of each compound, 100 μL of TFAA and 50 μL TFE was heated at 110 °C in a closed vial for 20 min. After cooling, the solvent was removed in a stream of dry nitrogen. The residue was then dissolved in 200 μL of dichloromethane.

3. Results and discussion

Temperature programs were firstly optimized first after injecting a standard solution of the phenoxypropionic esters in each of the four columns under investigation. Fig. 1-A illustrates chromatograms of the methyl esters of the herbicides mecoprop (compound 1), dichlorprop (compound 2), and fenoprop (compound 3) obtained from the four columns under an optimized temperature program. Changing the diluting polymer did not affect significantly the choice of the operational temperatures. Fig. 1-B and -C depict the chromatograms obtained for the respective ethyl ester and TFAA/TFE derivatives of compounds 1, 2 and 3. The enantioseparation clearly depends on the enantiomer derivatives. With the methyl and ethyl esters of fenoprop (compound 3), for instance, baseline separation was not obtained, whereas with the more volatile fluorinated derivative a resolution >1 was achieved in two columns. A better resolution can be clearly noted for fluorinated derivatives (Fig. 1-C) in comparison to the methyl (Fig. 1-A) and ethyl esters (Fig. 1-B).

Jung et al. [18] demonstrated that the enantioselectivity factors increased upon increasing the concentration of the chiral selector, and each racemate reached a plateau at different amounts of selector. In general, however, the highest possible concentration of the chiral selector compatible with its solubility in the polymeric solvent would be expected to increase the enantioresolution factor for most solutes. Under these circumstances, the achiral (polymeric) solvent chosen to dissolve the selector would determine the amount of selector that can be solubilized at a given temperature. In this work, we prepared columns containing as high as possible PM-β-CD amount in the corresponding achiral matrix. The columns containing 30% PM-β-CD were constructed with a thinner film thickness in order to compensate for the higher

Table 2
Characteristics of the capillary columns.

Capillary columns	Dimensions: length (m), film thickness (μm)	Permethyl-β-cyclodextrin (CD) % (w/w)	Polymeric solvent	Polarity[a]	Maximum % (w/w) PM-β-CD at a given temperature[b]	Plate counts/m[c]
PM-β-CD/C20M	20 × 0.1	30	C20M	2208	<50% (60 −C)	1100
PM-β-CD/SE-54	20 × 0.1	30	SE-54	337	30% (>100 −C)	1750
PM-β-CD/OV-1701-vi	18.9 × 0.14	16	OV-1701	790	10–14% (25 −C)	1950
Hydrodex β-PM	25	_[d]	–	–		2500
SE-54	20 × 0.1	0	–	337	–	2300
C20M	20 × 0.1	0	–	2208	–	2700

[a] McReynolds indices of the polymeric matrix.
[b] Data taken from [12,29].
[c] Measured by injecting dodecane at 120 ⊐C and carrier flow-rate: 1 mL/min.
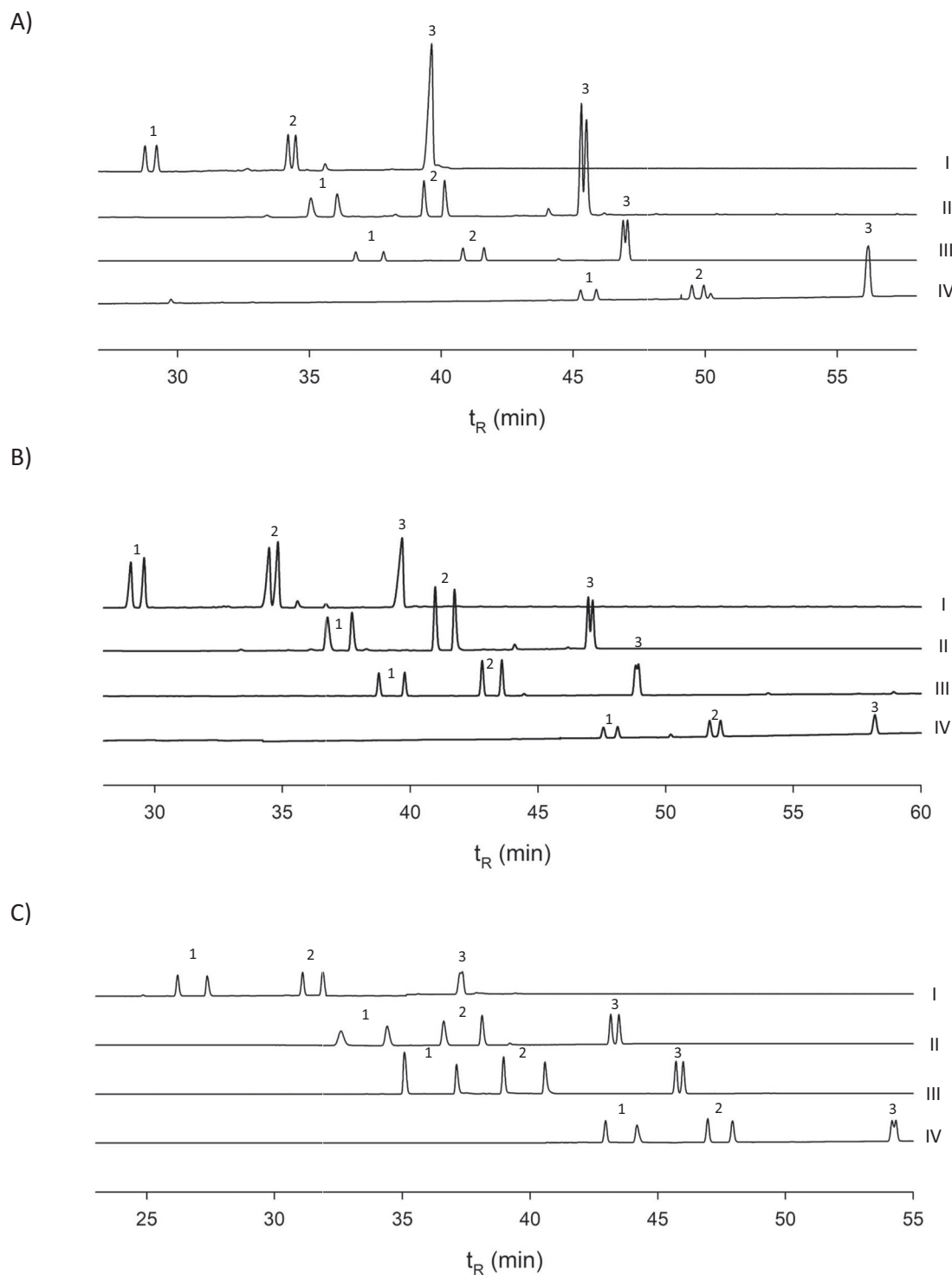[d] Data not available.

Fig. 1. Chromatograms of methyl esters (A), ethyl esters (B) and 2,2,2-trifluoroethyl esters of phenoxypropionic herbicides. Temperature program was initially held at 70 °C for 2 min, followed by heating at 2 °C/min to 200 °C. Column indications: I, PM-β-CD/C20M; II, PM-β-CD/SE-54; III, PM-β-CD/OV1701-vi; IV, Hydrodex. Flow-rate: 1 mL/min, solutes: 1) mecoprop; 2) dichlorprop; 3) fenoprop.

selector concentration and, thus, decrease somewhat the solute retention and analysis time.

Table 3 lists the retention factors for the first eluted enantiomer (k_1), the relative retention (k_2/k_1) and enantioresolution (R_s) factors measured for the pesticides and their derivatives with the same temperature program in the four columns. The highest values of relative retention for each analyte are indicated in boldface. The column PM-β-CD/OV-1701-vi produced the longest retention, even though the percentage of CD was lower than in the other columns. In principle, this can

be attributed to the 40% greater film thickness for this column than for the others (with the possible exception of the commercial column). The relative retention for the three derivatives (methyl, ethyl and 2,2,2-trifluoroethyl) esters of mecoprop and dichlorprop were barely greater in the column coated with the PM-β-CD/OV-1701, whereas for all others racemates the best separation factors were obtained with the column coated with PM-β-CD/SE-54.

A comparison of the PM-β-CD/SE-54 and PM-β-CD/C20M columns, both of which were made with the same amount of chiral selector and

Table 3
Retention factors (k1), relative retentions (k2/k1), and resolution (Rs) of esters of herbicides in the four columns.

Analyte	PM-β-CD/C20M			PM-β-CD/SE-54			PM-β-CD/OV-1701-vi			Hydrodex		
	k1	Rs	k2/k1	k1	Rs	k2/k1	k1	Rs	k2/k1	k1	Rs	k2/k1
Mecoprop-methyl	19.8	2.1	1.016	24.4	3.5	**1.030**	27.8	5.3	1.030	26.8	2.9	1.014
Mecoprop-ethyl	20.0	2.2	1.019	25.6	3.7	**1.027**	29.3	5.3	**1.027**	28.2	2.5	1.012
Mecoprop-trifluoroethyl	17.9	5.4	1.047	22.6	6.8	1.058	26.4	9.0	**1.060**	25.3	5.1	1.030
Dichlorprop-methyl	23.7	1.3	1.009	27.5	3.6	**1.021**	30.9	3.9	1.020	29.3	2.1	1.009
Dichlorprop-ethyl	23.9	1.3	1.010	28.7	3.4	1.019	32.5	4.3	**1.021**	30.7	1.9	1.009
Dichlorprop-trifluoroethyl	21.5	3.8	1.026	25.5	6.1	**1.043**	29.5	7.8	**1.043**	27.8	4.3	1.021
Fenoprop-methyl	27.6	–	1.000	31.8	<1	**1.004**	35.7	<1	**1.004**	33.4	–	1.000
Fenoprop-ethyl	27.7	–	1.000	33.0	<1	**1.004**	37.2	<1	1.002	34.7	–	1.000
Fenoprop-trifluoroethyl	25.9	<1	1.003	30.3	1.5	**1.008**	34.8	1.4	1.006	32.2	<1	1.003
Hydroprop-trifluoroethyl	37.1	–	1.000	37.0	2.2	**1.008**	38.5	1.1	1.005	34.0	–	1.000
Hydroprop-methyl	35.2	<1	1.003	36.9	2.5	**1.010**	40.2	1.0	1.005	36.1	1.1	1.004
Hydroprop-ethyl	36.8	<1	1.003	39.7	2.1	**1.007**	43.7	1.4	1.005	39.4	<1	1.002
Metalaxil	37.0	–	1.000	38.9	<1	**1.001**	43.3	–	1.000	39.7	–	1.000
Metalaxil-trifluoroethyl	32.7	<1	1.002	35.7	1.3	**1.006**	40.4	<1	1.004	37.1	–	1.000
Haloxifop-methyl	41.7	–	1.000	45.7	1.1	**1.004**	50.1	1.0	**1.004**	46.0	–	1.000
Haloxifop-trifluoroethyl	38.6	2.0	1.004	42.8	2.2	**1.008**	47.5	1.9	1.007	44.7	1.0	1.005
Fenoxaprop-ethyl	40.9	–	1.000	40.4	<1	**1.002**	41.6	–	1.000	37.1	–	1.000

the same film thickness, revealed that the retention, as well as the enantioseparations were systematically higher in the PM-β-CD/SE-54 column. These results indicate that the relative retentions increased with a decrease in the polarity of the polymeric solvent, independently of the structure (and polarity) of the racemic compound without exceptions.

The retention of a given enantiomer in a CSP is given by two contributions: specific interactions between the enantiomer with the selector (k_R or k_S), and other non-enantioselective (k_{ne}) interactions, equal for both enantiomers, with the achiral matrix. Thus, the experimental relative retention, r, will be.

$r = \frac{k_{2,\,exp}}{k_{1,\,exp}} = \frac{k_{ne}+k_R}{k_{ne}+k_S}$ where k_R and k_S were arbitrarily chosen, and $k_{i,exp}$ represents the experimental retention factor in the CSP. In principle, it is expected that stronger interaction between the solute with the achiral matrix should lead to larger retention factors, though lower apparent enantioseparations. Our results in PM-β-CD/SE-54 proved to be the opposite to that expectation. In order to explain the true role of the polymeric solvent, all the compounds were chromatographed in columns of C20M and SE-54 (without chiral selector) under the same temperature program. Retention factors for all compounds obtained in the column SE-54 were plotted against the corresponding values in the column C20M in Fig. 2-A. As expected, retention was systematically weaker in the less polar polymer, thus, the achiral contribution to the retention factor in the PM-β-CD/SE-54 column is smaller. However, more surprising results were that the chiral contribution to retention for each compound was not constant, *i.e.*, differences in compound retention in the chiral column respect to the corresponding achiral one are systematically larger in SE-54 (as shown in Fig. 2-B). Dietrich et al. [18] hypothesized that the interaction of a polar polymer and the CD derivative would either "block" active sites in the selector or lead to conformational changes in the selector that would favor the recognition of certain solutes but no others. Our results, however, would indicate that all the studied compounds were affected similarly in their interactions with the chiral selector in the column constructed with a solution of PM-β-CD in C20M. The ratio between the chiral contributions to retention (k_R) measured in PM-β-CD/SE-54 respect to those measured in PM-β-CD/C20M gave an average of 1.76 with a relative standard deviation of 13.8%. It can be inferred that PM-β-CD/C20M column behaves as if the selector were not totally accessible for enantiorecognition.

3.1. Comparison of results with previously reported enantioseparations of these herbicides

In the next paragraphs, we compared our findings with previously reported GC enantioseparation of those herbicides (see also the
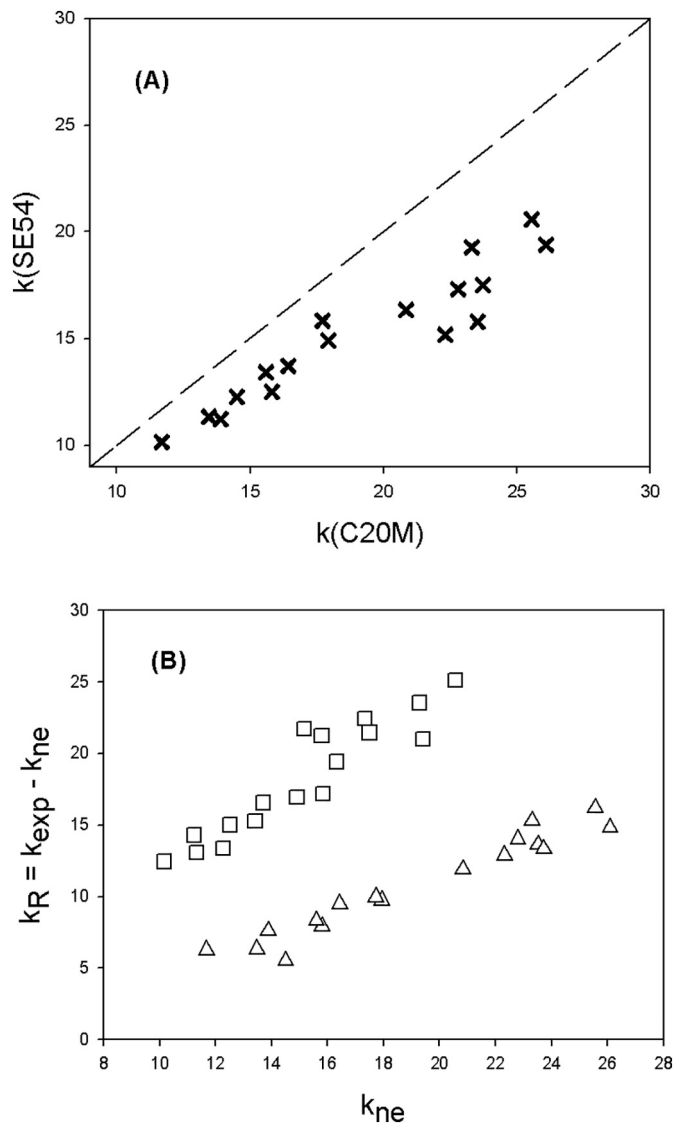

Fig. 2. A) Retention factors of the racemic pesticides in the column containing SE-54 against the values in the column coated with C20M; B) Chiral contribution to retention (k_R) as a function of retention in the achiral columns (k_{ne}). Symbols: (□): columns based on SE-54 polymer; (△): columns based on C20M polymer.

Table 4
Enantioresolution of the studied herbicides taken from the literature.

Compound	Chiral stationary phase	Resolution	Reference
Mecoprop methyl	PM-β-CD (Hydrodex column)	>1	[19,20]
Mecoprop methyl	Heptakis(2,3-dimethyl-6-O-*tert*-butyldimethylsilyl)-β-cyclodextrin/OV-1701	3	[21,22]
Mecoprop pentafluorobenzyl	Heptakis(2,3-dimethyl-6-O-*tert*-butyldimethylsilyl)-β-cyclodextrin/OV-1701	<1	[23,24]
Dichlorprop methyl	PM-β-CD (Hydrodex column)	>1	[19,20]
Dichlorprop methyl	Heptakis(2,3-dimethyl-6-O-*tert*-butyldimethylsilyl)-β-cyclodextrin/OV-1701	2.4	[21,22]
Fenoprop methyl	PM-β-CD (Hydrodex column)	0	[19]
Metalaxyl	35% heptakis(*tert*-butyldimethylsilyl)-β-CD/15% phenyl, 85% methylpolysiloxane	1.5	[25,26]
Metalaxyl (ethyl)	35% heptakis(*tert*-butyldimethylsilyl)-β-CD/15% phenyl, 85% methylpolysiloxane	1.3	[25,26]
Haloxyfop	15% PM-β-CD in OV1701	1.3	[27,28]
Haloxyfop (ethyl)	15% PM-β-CD in OV1701	1.3	[27,28]

summary in Table 4). Weber et al. [19] described the enantioselective separation of methyl esters of phenoxypropionic acids (compounds 1, 2 and 3) on a Hydrodex PM-β-CD column. They found a progressive decrease in enantioresolution from mecoprop and dichlorprop to the fenoprop methyl ester derivatives, with the latter eluting as a single peak. This result is consistent with our findings on the same column; whereas, in contrast, with the column containing 16% PM-β-CD in OV-1701, and using the same temperature program, a partial separation of enantiomers of fenoprop methyl esters was achieved (Fig. 1). A capillary column with the same chiral selector was used by Sánchez et al. [20] to determine the relative amounts of the *R* and *S* enantiomeric forms of mecoprop and dichlorprop in soil samples; the chromatograms show baseline resolutions for both racemates as methyl derivatives. Müller and Buser [21,22] studied the degradation of mecoprop and dichlorprop in soil under laboratory conditions. Enantioselective GC was carried out after methylation with diazomethane, using a column coated with 35% (diMe-TBDMS-β-CD) in OV-1701. Mecoprop and dichlorprop 2,3,4,5,6-pentafluorobenzyl esters were nearly baseline separated (Rs = 0.9) on a 15 m glass column (0.25 mm i.d.) with an OV1701 polysiloxane phase containing 35% of the same chiral selector [23,24].

Metalaxyl (compound 4) enantiomers were practically not separated in the columns here studied; only in the PM-β-CD/SE-54 column a separation factor of 1.001 was achieved. We also tested a slower temperature program with no better results. On the contrary, Fig. 3 shows the chromatograms of the enatiomers of TFE-metalaxyl derivatives run in the four columns. Baseline resolution was achieved on the PM-β-CD/SE-54 column. The S-enantiomers of both derivatives, metalaxyl and TFE-metalaxyl, were eluted before the R-enantiomers. In earlier work, Buser et al. had used a capillary column with 20% heptakis(6-O-*tert*-butyldimethylsilyl)-β-CD dissolved in 15%-phenyl-85%-methyl-polysiloxane for enantioseparation of this acetamide herbicide [25],

and Buerge et al. had studied the degradation and chiral stability of metalaxyl in soil with the same sylilated chiral selector [26].

Haloxyfop methyl (compound 5) is an herbicide that is rapidly hydrolyzed to haloxyfop acid, whose R-enantiomer possesses the herbicidal activity, although in soil the S-acid isomer enantiomerizes to the R-acid in less than one day [27,28]. A column coated with 15% PM-β-CD diluted in OV1701 was used for the separation of enantiomers of haloxyfop methyl and ethyl esters reacted with diazomethane and with diazoethane, respectively. Fig. 4 shows the chromatograms obtained for the methyl (A) and trifluoroethyl (B) ester derivatives, on each of the four columns. For these compounds, resolutions higher than 2 were obtained for the fluorinated derivatives with columns based on SE-54 and OV1701-vi along with acceptable enantioseparations with the other two columns. The S-enantiomer of both esters corresponds to the first peak.

Finally, Fig. 5 illustrates examples of the enantiomeric separations of derivatives of the precursor hydroprop (compound 6): trifluoroethyl (A), methyl (B) and ethyl (C) and of fenoxaprop-ethyl (compound 7) (D) on the column PM-β-CD/SE-54. Baseline resolutions were achieved, and the R-enantiomers of all the four compounds were eluted first. To the best of our knowledge, no information about the chiral GC separation of those compounds has been previously reported.

4. Conclusions

The chiral resolution of the polar mecoprop, dichlorprop, fenoprop, metalaxyl, hydroprop, haloxyfop, and fenoxaprop esters was investigated in capillary columns prepared with PM-β-CD dissolved in different polymers. Enatioseparations of these compounds were somewhat better in capillary columns prepared with 30% PM-β-CD in SE-54 than those achieved with other columns prepared by dissolution of PM-β-CD in more polar stationary phases for most racemates. One explanation
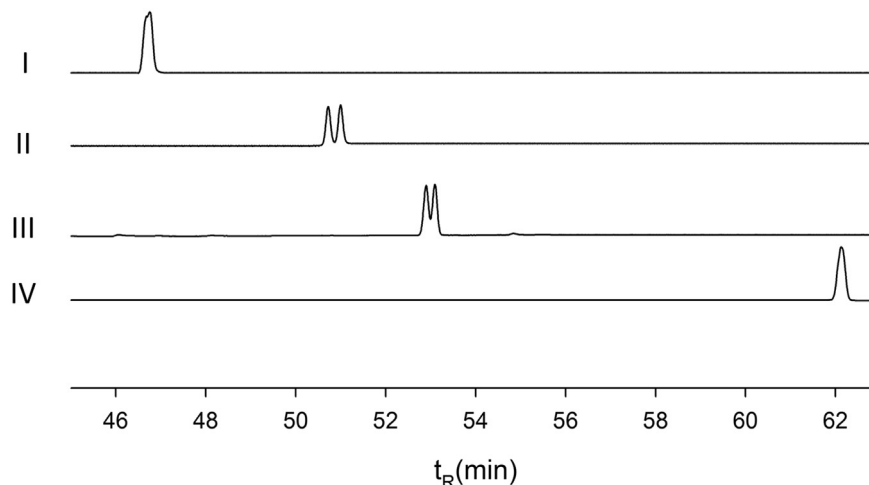

Fig. 3. Chromatograms of 2,2,2-trifluoroethyl ester of metalaxyl. First peak correspond to the R-enantiomer. All other details are as in Fig. 1.
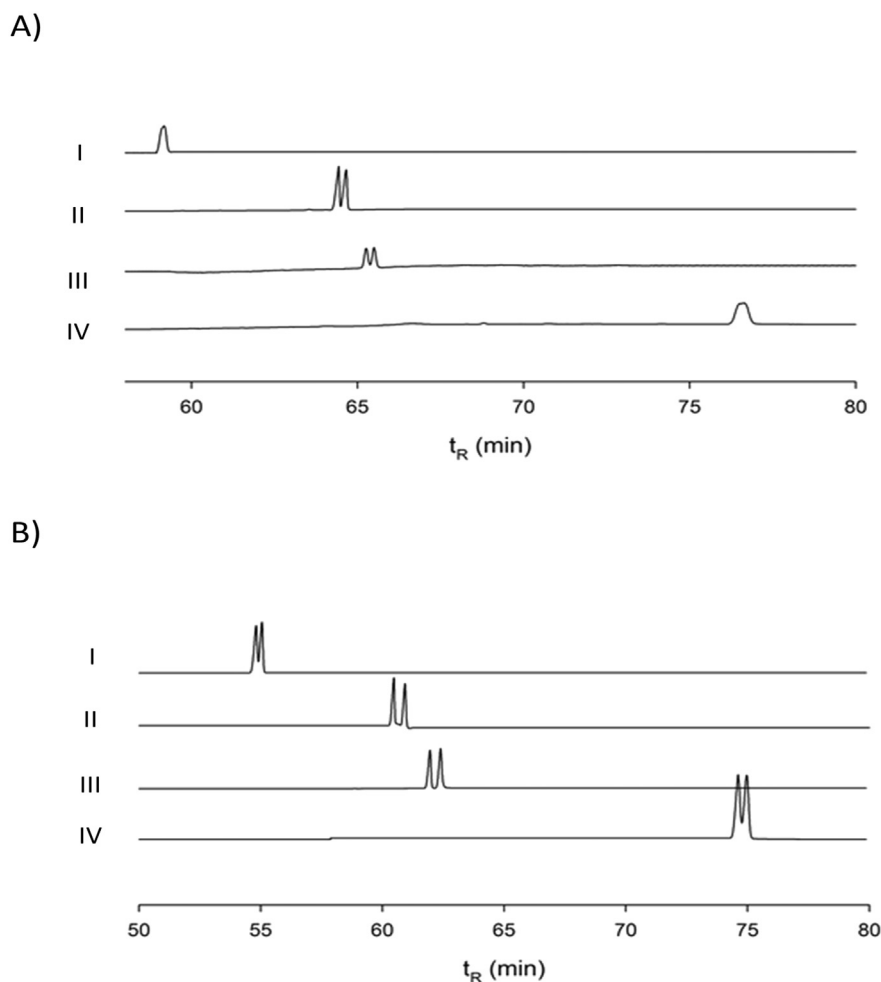
Fig. 4. A) Chromatograms of haloxifop methyl on the four columns (as indicated in Fig. 1). B) Chromatograms of haloxifop 2,2,2-trifluoroethyl in the four columns. The S-isomer of both esters eluted first. All other details are as in Fig. 1.

for the generally higher relative retention of these pesticides in this column can be the higher concentration of PM-β-CD in SE-54 than the one prepared with OV-1701. On the other hand, the comparison of enantiomeric separations of all compounds in the columns prepared with 30% PM-β-CD allowed to demonstrate that the interactions between enantiomer and chiral selector are strongly affected by the polymeric solvent nature. We conclude that the use of a less polar silicone results in columns with higher discrimination capacity toward polar (*i.e.,* less volatile) racemates when columns with similar selector concentrations are used. The results also evidenced that increasing the amount of chiral selector had a less pronounced effect on enantioseparation than using a less polar diluting polymeric solvent.

This PM-β-CD/SE-54 column also afforded the separation of fenoxaprop ethyl ester enantiomers which were not resolved on the more polar phases. The same is true for enantiomers of metalaxyl. The general conclusion is that the column PM-β-CD/SE-54 had the more diverse enantiorecognition capacity, with most racemates of these chiral pesticides being satisfactorily resolved.
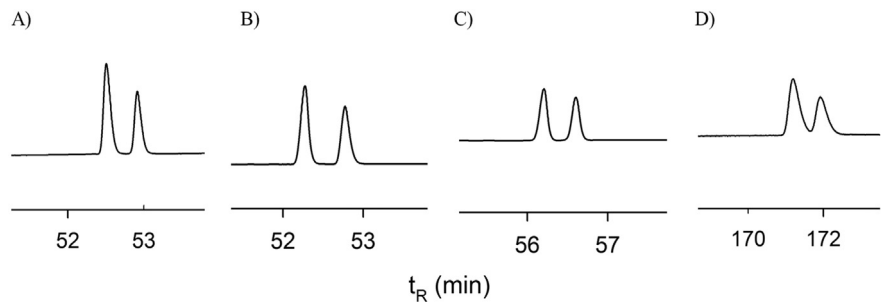
Acknowledgements

Fig. 5. Examples of herbicide enantioseparations on the column PM-β-CD/SE-54. Chromatograms of hydroprop-trifluoroethyl (A); hydroprop methyl (B); hydroprop ethyl (C) and of fenoxaprop ethyl (D). Temperature program as in Fig. 1, except for fenoxaprop ethyl, that was run initially at 70 °C for 2 min, followed by a temperature increase of 1 °C/min. The R-enantiomers of the four compounds were eluted first.

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