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Short Communication

Carbosulfan in technical concentrates and formulated products

Liquid chromatographic determination with photodiode-array detection

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ABSTRACT

A reversed-phase high-performance liquid chromatographic method, based on the Food Machinery Corporation/Collaborative International Pesticides Analytical Council (FMC/CIPAC) method, has been developed for the determination of carbosulfan in technical and formulated products. With this method both time and solvents are saved and much more information on peak purity is obtained when compared with the FMC/CIPAC method. Accuracy, tested by application of the standard addition method, allowed recoveries from 99.0 to 101.3% of theoretical. Precision, determined by analysis of 22 samples prepared at concentrations of about 0.08 and 0.24 g/l, was 1.00 and 0.53%, respectively.

INTRODUCTION

Carbamate pesticides have been intensively used during recent years because of their broad spectrum, effectiveness and moderate mammalian toxicity.

Their thermal instability makes their analysis by gas chromatography difficult and thus numerous high-performance liquid chromatographic (HPLC) methods have been developed for this purpose [1–5]. Nevertheless, except for the Food Machinery Corporation/Collaborative International Pesticides Analytical Council (FMC/CIPAC) method [6], none has been found to be useful for the analysis of carbosulfan.

Carbosulfan is a systemic insecticide largely used in Spain to control soil-dwelling insects and foliar pests on maize, potatoes and sugar beet.

For the reasons indicated above and also because of a saving in both time and solvents compared with the FMC/CIPAC method, as well as to obtain more information on peak purity, we have developed an internal standard, reversed-phase HPLC method for the determination of carbosulfan.

EXPERIMENTAL

Apparatus

Filters. Millipore Type HAWP for water and Type FHLP for acetonitrile, pore size 0.5 μm (Millipore, Bedford, MA, USA).

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Liquid chromatograph. Hewlett-Packard 1090 as described in a previous paper [7].

Reagents

Solvents. Acetonitrile and water, both liquid chromatographic grade.

Eluent. Acetonitrile–water (85:15).

Internal standard solution. A 1.8-g aliquot of *n*-nonaphenone (Parish Chemical, Orem, UT, USA) was weighed into a 500-ml volumetric flask, dissolved and diluted to volume with acetonitrile.

Calibration solution. An aliquot of 100–110 mg of carbosulfan analytical standard of known purity (FMC Europe, Belgium) was weighed into a 50-ml flask. A 25.0-ml aliquot of the above internal standard solution was added and the carbosulfan dissolved quantitatively. A 5.0-ml volume of this solution was transferred to a 25-ml volumetric flask and diluted to volume with acetonitrile. A 2.0-ml volume of the latter solution was pipetted into a 20-ml volumetric flask and made up to volume with acetonitrile. The resulting solution was filtered through an appropriate Millipore filter into a small vial and capped.

Sample solutions

Sufficient sample (tehnical or formulated carbosulfan) to contain *ca.* 100–110 mg of carbosulfan was weighed and treated as described above for the calibration solution.

Chromatographic conditions

The chromatographic conditions were as follows: stainless-steel column, 100 × 2.1 mm I.D.; stationary phase, ODS-Hypersil 5 μm; guard column, 20 × 2.1 mm I.D. packed with ODS-Hypersil 30 μm; temperature, 40°C; flow-rate, 0.3 ml/min; stop time, 4.5 min; injected volume, 5 μl; detector wavelengths, 280–450 and 254–450 nm; spectra setting in apex, base and slope, from 240 to 350 nm; chart speed, 2 cm/min; attenuation, automatic.

The FMC/CIPAC method uses a 250 × 4.6 mm

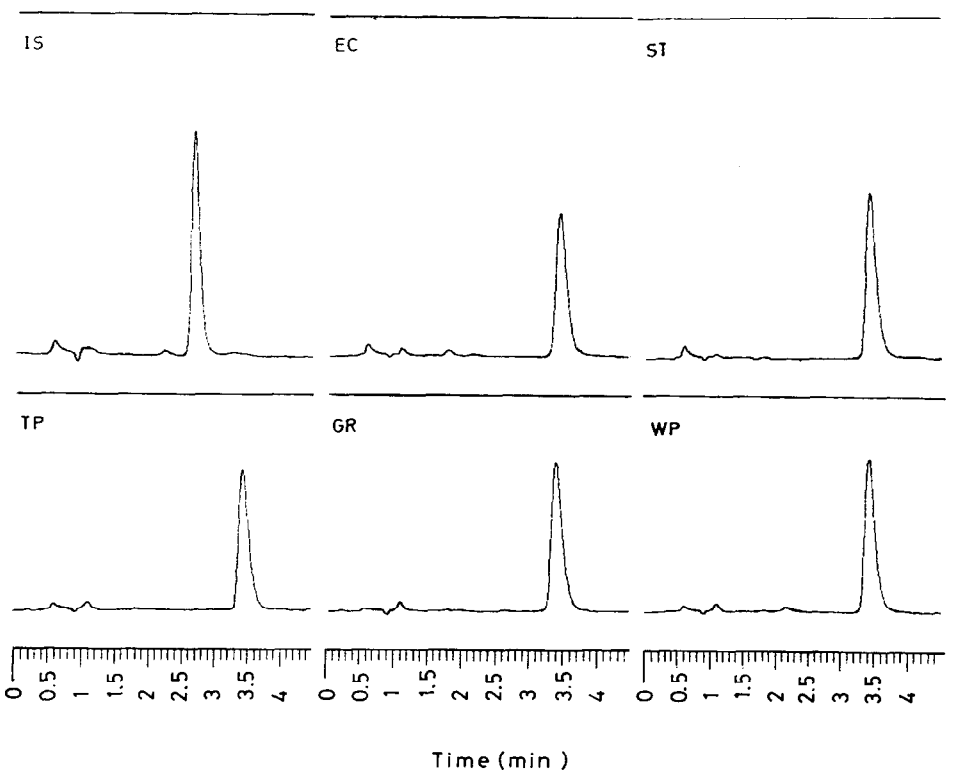

Fig. 1. Chromatograms of the different samples: TP = technical product; GR = granule; WP = wettable powder; ST = powder; EC = emulsifiable concentrate; IS = internal standard. See text for chromatographic conditions.

C_8 column and methanol–water (88:12) as eluent at a flow-rate of 1 ml/min. Detection is performed at 280 nm. The minimum chromatographic time is 13.5 min and it does not provide any test to prove peak purity.

Calibration and quantitation

The specified volumes of calibration solution were injected until the variation in peak areas did not deviate from the mean by more than 1%. After calibration, sample solutions were injected for analysis. Concentrations were proportional to peak areas at the concentration levels discussed in this paper.

RESULTS AND DISCUSSION

The calibration curve, obtained by plotting absorbance *versus* carbosulfan concentration, was linear over the range 0.02–0.34 g/l for 5-μl injections. The curve passed close to the origin and the data fitted the equation $y = 4700.0508x - 2.8067$, with a correlation coefficient of 0.9999.

Chromatograms of the different samples, technical product (TP), granule (GR), wettable powder (WP), powder (ST), emulsifiable concentrate (EC) and internal standard (IS) are shown in Fig. 1. It can be seen that in no case is here interference between samples and internal standard. In Figs. 1, 2 and 3 the y-axis shows absorbance.

Fig. 2 shows the signal plus spectra plot of a technical product added with internal standard. The identity of the three spectra, between 243 and 347 nm (each tick = 5 nm), for every peak, measured just prior to, at and after their respective maxima (upper left) shows their purities.

The carbosulfan spetrum shows a maximum absorbance at 280 nm, and both carbosulfan and *n*-nonaphenone present a considerable absorbance at 254 nm. These were the two wavelengths chosen for simultaneous integration. Fig. 3 shows the ratio of the signals obtained at those two wavelengths *versus* time for the same chromatogram as in Fig. 2. The linear relationship of the ratio of signals for

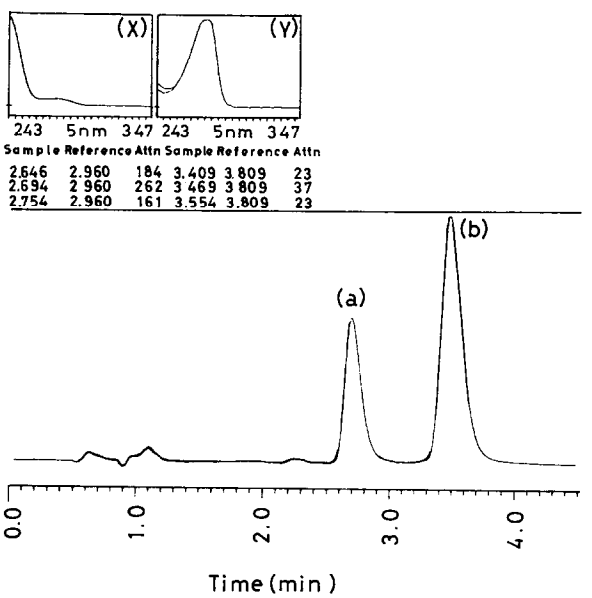

Fig. 2. Signal plus spectra plot of a technical product added with internal standard. (a) Internal standard peak; (b) carbosulfan peak; (X) three superimposed spectra obtained at different times of chromatographic peak a; (Y) three superimposed spectra obtained at different times of chromatographic peak b.

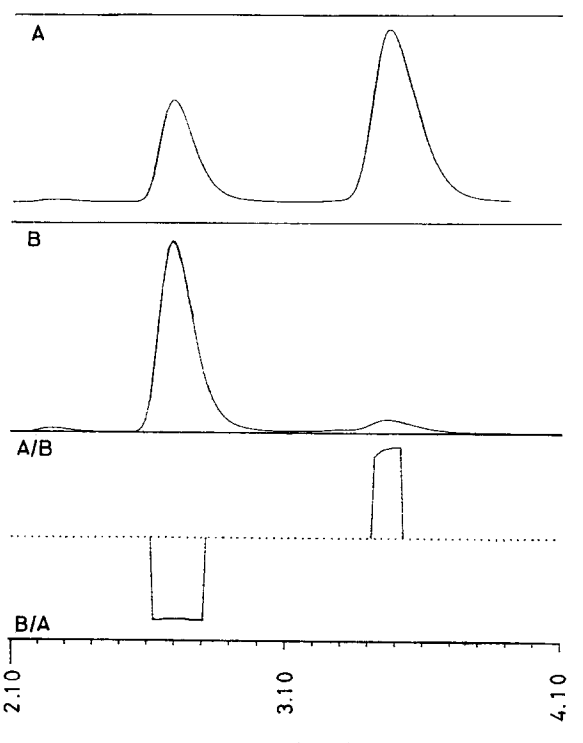

Fig. 3. Signals ratio of the chromatogram from Fig. 2, for both peaks, measured at (A) 280 nm and (B) 245 nm, and A/B ratio of the two signals.

TABLE I

RECOVERY OF CARBOSULFAN (STANDARD ADDITION METHOD)

Added (ng/5 μl)	Found (mean ± s_r)[b] (ng/5 μl)	Recovery (%)	R.S.D.[a] (%)
61.5	62.3 ± 6.0	101.3	2.25
122.9	121.7 ± 6.2	99.0	1.15
184.4	184.4 ± 7.9	100.0	0.98
245.8	244.6 ± 6.8	99.5	0.65

[a] Relative standard deviation of three determinations.
[b] $s_r = \sigma_{n-1} \cdot t_{n-1}$.

both peaks is a further demonstration of peak purity.

The standard addition method was used to test the accuracy of the method. To five 8-ml aliquots of a carbosulfan–nonaphenone solution in acetonitrile, at concentrations of 0.1121 and 0.1443 g/l, respectively, were added 0, 1, 2, 3 and 4 ml of a 0.1475 g/l carbosulfan solution in acetonitrile and, correspondingly 4, 3, 2, 1 and 0 ml of acetonitrile. Recoveries ranged from 99.0 to 101.3%. Details are given in Table I.

A total of 22 samples of a technical product were prepared and analysed. The details are given in Table II and they show that the relative standard deviation of the method is 1.00% for a carbosulfan concentration of about 0.08 g/l and 0.53% for a concentration of about 0.24 g/l.

It can be concluded that the method is specific, accurate and precise, provides a lot of information on peak purity and saves on operating costs (time and solvents).

TABLE II

CARBOSULFAN CONTENT IN A TECHNICAL PRODUCT, DETERMINED AT TWO DIFFERENT CONCENTRATIONS

0.08 g/l		0.24 g/l	
Weight (mg)	Percentage	Weight (mg)	Percentage
100.0	88.039	100.4	89.303
100.5	87.847	100.4	88.590
100.4	88.145	100.9	88.769
102.0	87.950	100.7	89.723
102.3	88.548	100.3	88.558
102.2	88.814	99.9	88.377
100.4	88.441	100.4	88.232
100.1	90.510	100.0	88.518
100.7	90.221	100.0	88.357
99.6	88.519	99.6	88.158
101.5	89.064	99.5	88.807
Mean ± s_r	88.736 ± 0.596		88.672 ± 0.317
R.S.D. (%)	1.00		0.53

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