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# Comparative study of some columns for direct determination of carbofuran by gas–liquid chromatography with nitrogen-specific detection

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(First received December 6th, 1989; revised manuscript received June 7th, 1990)

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuranyl-N-methyl carbamate) is a broad-spectrum pesticide used for the control of insects, mites and nematodes in a variety of edible crops. Its determination may be carried out by several methods which involve gas liquid chromatography (GLC).

Direct determination of carbofuran may be accomplished by using micro-columetric detection [1], electrolytic conductivity detection [2] and nitrogen-specific detection [3,4]. Several methods make use of suitable derivatives for GLC, because these products are usually more sensitive and chromatographically stable. For this purpose, several procedures involving hydrolysis followed by trichloroacetylation of the phenolic moiety [5], trifluoroacetylation [6], thiophosphorylation [7] and mesylate derivatization [8] have been proposed, using electron-capture or flame photometric detection. The disadvantages of derivatization methods are that they are time consuming and increase the chances of errors due to extra sample manipulation.

Direct GLC of carbofuran may be of use for residue control in fruits or for controlling concentrations in irrigation water or nutrient solutions. For these reasons, the suitability of three GLC columns for the direct determination of carbofuran were tested for their efficiency and also to establish the extent of thermal degradation, if any.

## EXPERIMENTAL

### *Instrumentation*

Nitrogen-specific GLC was performed on a Perkin-Elmer gas chromatograph

equipped with a Perkin-Elmer 2B N-P thermionic detector run in the nitrogen mode at 220°C, a Sigma 10B integrator and a Model 550 terminal, using nitrogen as carrier gas. The chromatographic conditions were as follows: injector temperature, 220°C; column temperature, 170°C; hydrogen pressure, 10 p.s.i.; and air pressure, 10 p.s.i. Three columns were tested: 2% OV-101 on Chromosorb WP (100-120 mesh), 122 cm × 2 mm I.D., used by Leppert *et al.* [9] for the determination of carbofuran residues with nitrogen-specific detection; 5% OV-101 on Chromosorb WP (80-100 mesh), 122 cm × 2 mm I.D., used by Nelsen and Cook [4] for direct determination of carbofuran with nitrogen-specific detection; and 1.5% SP-2250 + 1.95% SP-2401 (100-120 mesh) (Supelco, Bellefonte, PA, U.S.A.), 200 cm × 4 mm I.D., described by Technokroma (Barcelona, Spain) for general analyses for pesticides [10].

### Reagents

A standard of carbofuran (99.6% purity) was obtained from FMC (Middleport, NY, U.S.A.). A standard of phosphamidon (95% purity) was obtained from PolyScience (Niles, IL, U.S.A.) and used for internal standard calibration. Ethyl acetate and benzene were used for preparing standard solutions of carbofuran and phosphamidon, respectively.

### RESULTS AND DISCUSSION

In order to check the linearity of the GLC response, the external standard procedure was used for all columns. In each instance, calibration graphs were obtained by injecting five different volumes of a solution of carbofuran in ethyl acetate (8.52 mg dm<sup>-3</sup>). Table I shows the nitrogen flow-rate used in the analyses, the mean peak areas corresponding to three injections of 3 μl and their standard deviations, the correlation coefficients for the calibration graph and the retention times for carbofuran. The results indicate that the 2% OV-101 column shows a higher response for a 3-μl injection and a higher correlation coefficient than the other two columns for the calibration graphs. Therefore, the sensitivity of the system using 2% OV-101 on a Chromosorb WP column for the direct determination of carbofuran was checked in

TABLE I  
COMPARATIVE BEHAVIOUR OF COLUMNS USED FOR DIRECT DETERMINATION OF CARBOFURAN

Parameter	Column		
	2% OV-101	5% OV-101	1.5% SP-2250 + 1.95% SP-2401
N <sub>2</sub> flow-rate (cm <sup>3</sup> min <sup>-1</sup> )	30	28	35
Mean peak area for 3-μl injections	28.2210	6.5100	8.6126
Standard deviation for 3-μl injections	0.4222	0.0195	0.0788
Correlation coefficient	0.9995	0.9835	0.9575
Retention time (min)	2.62	7.67	5.30

TABLE II

CORRELATION COEFFICIENTS FOR DIRECT DETERMINATION OF CARBOFURAN BY THE EXTERNAL STANDARD PROCEDURE WITH 2% OV-101 ON A CHROMOSORB WP (80-100 MESH) COLUMN

Range of concentration (mg dm <sup>-3</sup> )	Correlation coefficient
8.52-1.70	0.9948
1.70-0.34	0.9645

TABLE III

CORRELATION COEFFICIENTS FOR DIRECT DETERMINATION OF CARBOFURAN BY THE INTERNAL STANDARD PROCEDURE WITH PHOSPHAMIDON USING 2% OV-101 ON A CHROMOSORB WP (80-100 MESH) COLUMN

Range of carbofuran concentration (mg dm <sup>-3</sup> )	Phosphamidon (mg dm <sup>-3</sup> )	Correlation coefficient
43.03-8.60	7.12	0.9943
8.60-1.72	2.37	0.9958
1.72-0.34	0.19	0.9930

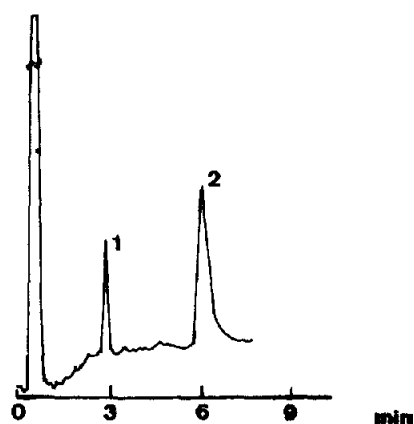


Fig. 1. Chromatographic separation of carbofuran (peak 1) and phosphamidon (peak 2) with 2% OV-101 on a Chromosorb WP column.

the range 8.52-0.34 mg dm<sup>-3</sup>. Table II gives the correlation coefficients obtained in these experiments for two ranges of concentration.

A similar study was made using phosphamidon as an internal standard. Table III gives the correlation coefficients for three different ranges of carbofuran concentration, with the concentration of phosphamidon used in each instance. High correlation coefficients were obtained for all three ranges of concentration. Fig.

TABLE IV

MEASURED VALUES, RELATED STATISTICAL PARAMETERS AND LIMITS OF DETECTION FOR DIRECT DETERMINATION OF CARBOFURAN WITH 2% OV-101 ON A CHROMOSORB WP COLUMN USING EXTERNAL AND INTERNAL STANDARD PROCEDURES

Parameter	External standard procedure	Internal standard procedure
Amount of carbofuran ( $\text{mg dm}^{-3}$ )	0.34	0.34
Analytical values ( $\text{mg dm}^{-3}$ )	0.39	0.31
	0.34	0.33
	0.37	0.34
	0.34	0.32
Mean value ( $\text{mg dm}^{-3}$ )	0.36	0.32
Standard deviation	0.0252	0.0129
Relative standard deviation (%)	7.00	3.97
Limit of detection ( $\text{mg dm}^{-3}$ )	0.12	0.05

1 shows a chromatogram corresponding to the separation of carbofuran (peak 1) and phosphamidon (peak 2), without noticeable interferences.

Table IV gives the limits of detection for both methods of calibration (external and internal standard procedures) using 2% OV-101 on a Chromosorb WP column and samples containing  $0.34 \text{ mg dm}^{-3}$  of carbofuran. A lower limit of detection was obtained when the internal standard procedure was used.

These studies show that GLC with 2% OV-101 on a Chromosorb WP column with nitrogen-specific detection may be a good choice for the direct determination of carbofuran using external or internal standard procedures.

#### ACKNOWLEDGEMENTS

The authors are grateful to the Caja Insular de Ahorros de Canarias for laboratory facilities and to the Excmo. Cabildo Insular de Gran Canaria for financial support.

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