ANALYSIS OF SOIL DISINFECTANTS CONTAINING CARBOFURANE AS ACTIVE PRINCIPLE, BY AN IR SPECTROPHOTOMETRIC METHOD

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Summary

The paper describes the infra-red spectrophotometric methods not requiring separation that have been developed by us for the analysis of soil disinfectants containing the active principle carbofurane (3,3-dihydro-2,2-dimethyl-7-benzofuranoyl-N-methyl carbamate) and various accompanying components as well as the mathematical statistical characteristics of the methods. Our experience showed our procedures to be simple, quick and suitable to qualify these products, the accuracy achieved is satisfactory. The active principle present in concentrations between 5 and 10% could be assayed with an error of $\pm 0{,}3-0{,}5\%$.

Carbofurane was measured, in the presence of dimethyl formamide, at 775 cm^{-1} and in the presence of fugrane, pearl granule and perlite at 1730 cm^{-1}.

The paper describes the infrared spectrophotometric methods not requiring separation that have been developed by us for the determination of the carbofurane content of preparations used as soil disinfectants containing the active principle carbofurane (3,3-dihydro-2,2-dimethyl-7-benzofuranoyl-N-methyl carbamate) and the performance of the methods estimated by mathematical statistical procedures.

In the literature several authors have reported on the physical and chemical properties [1], the infra-red spectrum [2] as well as the infra-red spectrophotometric determination of carbofurane requiring preliminary extraction separation [3, 4]. Simple colorimetric methods lending themselves for control purposes during manufacture [5, 6] can also be found.

In relation to the quantitative measurement of this compound most authors report on gas chromatographic [7—45] and high pressure liquid chromatographic [46—48] methods, but some spectrophotometric procedures can be found as well [49—51].

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Beside these, thin-layer chromatographic methods [52—56] are suitable to the quantitative estimation of carbofurane in biological matrices.

Out of the procedures mentioned several ones are suited to measure carbofurane in plants [30], animals [33, 55], in waters [42, 48, 56] and soils [44, 48, 54].

The ever spreading application of plant protecting agents made it necessary to develop — beside the existing ones — methods simpler and quicker than those, but of similar or approximately similar accuracy.

In the course of our work we have developed an infra-red spectrophotometric method not requiring previous seperation which permits to determine carbofurane, the active principle, in various soil disinfectants.

Beside carbofurane, dimethyl-formamide, fugrane, pearl granule or perlite might occur in commercial preparations, separately or jointly.

Experimental conditions and the measuring instrument

Infra-red spectra were prepared of the active principle of several soil disinfectants, carbofurane and the accompanying components, dimethyl-formamide, pearl granule and perlite as well as of soil disinfectants containing the above components.

The spectra of dimethyl formamide were taken in film form, between sodium chloride cuvette windows, for the rest of the substances the potassium bromide pastille technique was applied. Weighing of the samples was performed at the accuracy of 0,1 mg, homogenization was carried out in a vibrational mill, applying in all the cases a 3-min milling time. Finally, the pastilles of 13 mm ø with a sample ratio of 1 mg to 300 mg potassium bromide, were obtained in a hydraulic press, under vacuum. The spectra were taken in a Zeiss UR-10 type infra-red spectrophotometer.

Experimental methods and results

The infra-red spectrum of carbofurance is shown in Fig. 1 and the interpretation of the absorption bands in Table 1. Beside the absorption spots, the interpretation indicates the modes of vibration the vibrational character of which is the dominating or the only prevailing one in the corresponding normal vibration. The symbol system of Sohár, Holly, Varsányi [57] was used to denote the modes of oscillation.

The spectra of the accompanying components were also taken and the interpretation of the spectral bands carried out, but these will not be dealt with here.

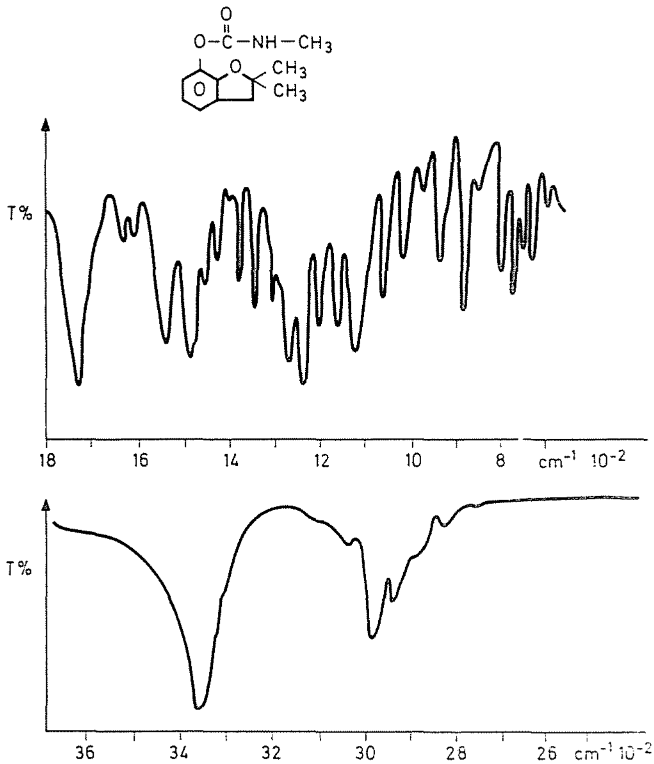

Fig. 1. Infra-red spectrum of carbofurane (C)

Our methods developed for determining the active principle in various kinds of soil disinfectants will be shown below. Soil disinfectants of the following composition were analysed:

1. Carbofurane and dimethyl formamide
2. Carbofurane, dimethyl formamide and fugrane
3. Carbofurane, dimethyl formamide and pearl granule
4. Carbofurane and fugrane, as well as
5. Carbofurane, dimethyl formamide, perlite and fugrane

1. First we will report on the analysis of a system containing 50% carbofurane and 50% dimethyl formamide not used as soil disinfectant, but as model substance in investigating the properties of carbofurane, therefore it is important that there be a possibility of measuring its carbofurane content.

The infra-red spectra of the components and the selection of the analytical spot to determine carbofurane in the presence of dimethyl formamide can be seen in Fig. 2. In the range of appearance of the maximum

Table 1
Interpretation of the IR spectrum bands of carbofurane

Absorption spots (cm^{-1})	Interpretation
3363	νNH
3037	$\nu(=CH)$
2979	$\nu_{as}CH_3$
2934	$\nu_{as}CH_3$
2815	$\nu_s CH_3$
1730	νCO
1629	νCC
1610	νCC
1540	βNH
1487	νCC
1454	$\delta_{as}CH_3$
1397	$\delta_s CH_3$
1380	$\delta_s CH_3$
1237	$\nu_{as}COC$
1118	$\nu_s COC$
1061	$\beta(=CH)$
1017	$\beta(=CH)$
973	$\beta(=CH)$
777	$\gamma(=CH)$
736	$\gamma(=CH)$

absorption band of carbofurane at 775 cm^{-1}, dimethyl formamide shows an absorption of background character only, therefore, if a system contains but these two components, the absorbance of this band depends only on the carbofurane concentration.

For calibration, 2 g of the above system were accurately weighed with a microbalance and diluted to 100 cm^3 with dimethyl formamide. From the stock solution thus obtained volumes of 0,5—9 cm^3 were removed and made up with dimethyl formamide to 10 cm^3. The infra-red spectra of the solutions obtained were taken and the absorbance values determined at the analytical spot by the method of baseline correction.

From the concentration — absorbance data pairs obtained, the equation of the calibration curve was determined by the least squares method as well as the residual standard deviation which is equal to the standard deviation of the absorbance estimated on the basis of all the measured signals.

The linear calibration curve obtained was used for the analysis of systems of unknown carbofurane content. The concentration of the sample was estimated from its analytical signal measured, the absorbance at 775 cm^{-1}, using the calibration curve. The confidence limits of the estimation of the concentration at the level of 95% were given as well. Table 2 contains the equation of the linear calibration curve, the value of the residual standard deviation, the carbofurane concentration values occurring most frequently in

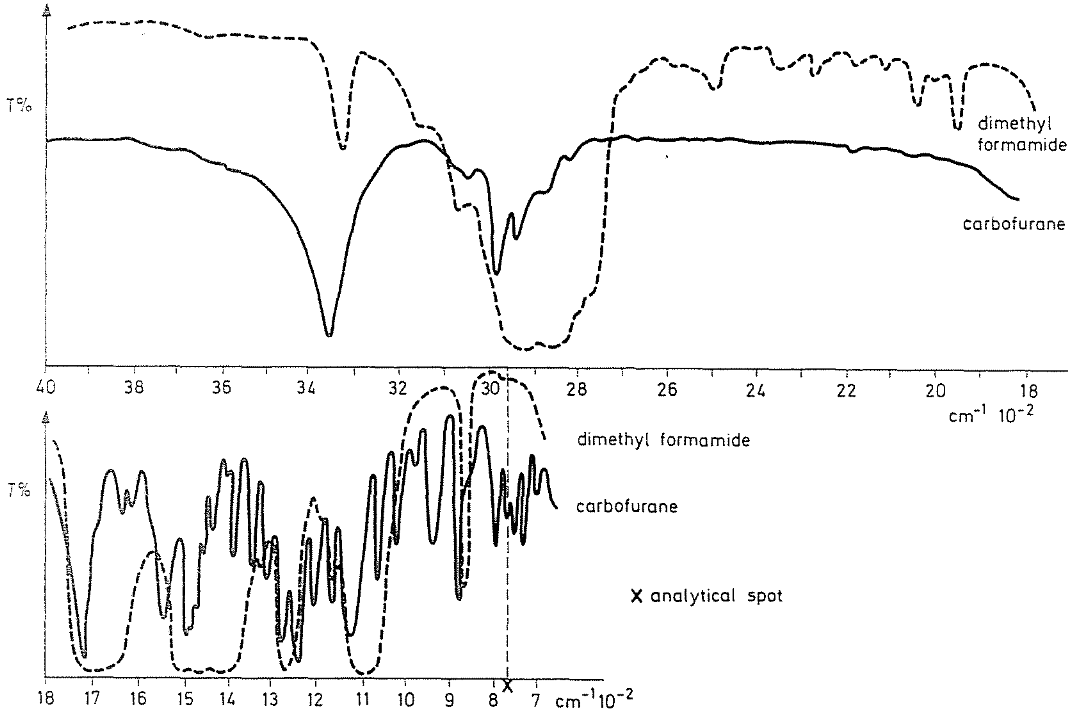

Fig. 2. Determination of the analytical spot for the assay of carbofurane in the presence of dimethyl formamide

the samples analysed, as well as the 95%-level confidence limits under consideration of the error of the estimation of concentration.

The residual standard deviation was calculated from the following expression:

$$s_{res} = \sqrt{\frac{\sum_{i=1}^{n} (Y_i - y_i)^2}{n-2}}$$

where $Y_i =$ the absorbances calculated from the equation of the curve
$y_i =$ the absorbances measured
$n =$ the number of the calibration measurements.

The 95%-level confidence limits of the estimation of concentration were calculated from the following formula:

$$x_{upper} \text{ and } x_{lower} = \bar{x} - \frac{\bar{Y} - \bar{y}}{(1-\alpha^2)b} \pm$$

$$\pm \frac{\alpha}{(1-\alpha^2)b} \sqrt{\left(\frac{1}{m} + \frac{1}{n}\right) b^2 (1-\alpha^2) \sum_{i=1}^{n} (x_i - \bar{x})^2 + (\bar{Y} - \bar{y})^2}$$

Table 2

Equations of the linear calibration curves of the carbofurane determination methods, residual standard deviations and errors of concentration estimation

Components occurring beside carbofurane	Equation of the calibration curve	Residual standard deviation (in absorbance)	The most frequent carbofurane concentration in the samples and the 95% confidence interval
dimethyl formamide	$y=0.044+0.031x$	0.018	$15.0\pm0.5\ \frac{mg}{cm^3}$
dimethyl formamide +fugrane 2+17	$y=0.018+0.023x$	0.009	10.0±0.5%
dimethyl formamide +pearl granule 2+17	$y=0.023+0.025x$	0.007	10.0±0.3%
fugrane	$y=0.019+0.023x$	0.006	10.0±0.3%
dimethyl formamide +perlite +fugrane	$y=0.011+0.024x$	0.010	10.0±0.5%

where x_{upper} and x_{lower} = the upper and lower confidence limits,

$\bar{Y}$ = the mean absorbances obtained in measuring the unknown sample

$\bar{y}$ = the mean of the absorbances obtained in the calibration measurements

$$\alpha = \frac{t_{n-2}^2 s_{res}^2}{b^2 \sum_{i=1}^{n} (x_i - \bar{x})^2}$$

t = the probability variable of Student's distribution belonging to the number of measurements (n−2) and the probability required (95%)

m = the number of measurements concerning the unknown sample

$\bar{x}$ = the mean of the concentrations of the calibration series

b = the slope of the calibration curve.

The error of the estimation of concentration was calculated as given below and the concentration was given in the following way:

$$x \pm \frac{x_{upper} - x_{lower}}{2}$$

2. In the following we describe our methods developed for determining the carbofurane content of soil disinfectants, first the one related to the system containing carbofurane, dimethyl formamide and fugrane. In these soil disinfectant systems carbofurane is present to 5—10% and the restly 95—90% are made up of fugrane and dimethyl formamide in the ratio of 17+2.

Fugrane is an organic carrier of plant protecting agents, prepared from agricultural wastes (corn cob, waste wood, sunflower seed hulls) by disintegration, hydrolysis with dilute acetic acid, drying and granulating.

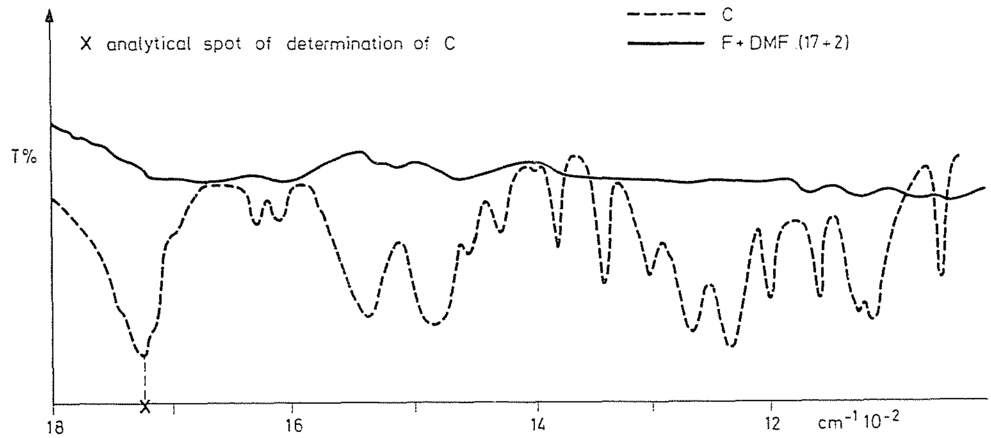

Fig. 3. Determination of the analytical spot for the assay of carbofurane (C) in the presence of fugrane (F) and dimethyl formamide (DMF)

In order to select the analytical spot of the determination procedure, the infra-red spectrum of carbofurane was compared to the spectra of the accompanying components (Fig. 3) and it was established that in the range of the valence oscillation band of CO appearing at 1730 cm^{-1} the absorbance of the accompanying components is of background character, therefore the absorbance calculated at this spot from the spectrum of the system containing these three components, depends solely on the carbofurane concentration.

For calibration a "stock mixture" was prepared from the components by exact weighing and addition of potassium bromide, and by appropriately mixing these, a series was obtained in which carbofurane concentration varied between 2 and 20%. The concentration to be expected in the samples to be analysed was between 5 and 10%.

All the components except carbofurane were added to the pastilles in the light path of comparison. By the fact that our calibration series contains all the components but the one to be determined, in concentrations adapted to those of the samples to be analysed, the elimination or minimization of the matrix effect can be achieved.

The concentration dependence of the absorbance values calculated from the infra-red spectra prepared with the members of the calibration series and the mathematical statistical characteristics of the method developed are shown in Table 2.

A great number of analyses of soil disinfectants of this type were carried out with the method developed.

3. We dealt with determining carbofurane in the presence of the accompanying components dimethyl formamide and pearl granule as well. In this system the carbofurane content to be expected is also between 5 and 10%,

and the ratio of the pearl granule and dimethyl formamide is also 17+2. The determination of the analytical spot is shown in Fig. 4. The principle underlying the composition of the calibration series necessary to develop the method is identical with those described above. The equation of the linear calibration curve of the method and its statistical characteristics are to be found in Table 2. The method developed was used for the analysis of several soil disinfectants.

4. There are soil disinfectants containing, beside carbofurane, only fugrane as accompanying substance, and having a carbofurane content of 5 to 10%. The selection of the analytical spot can be found in Fig. 5, the equation of

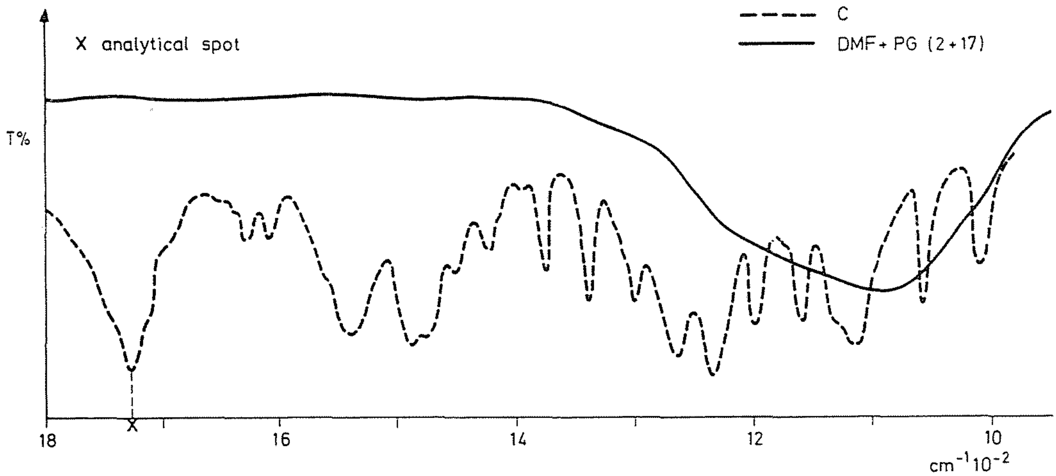

Fig. 4. Determination of the analytical spot for the assay of carbofurane (C) in the presence of dimethyl formamide (DMF) and pearl granule (PG)

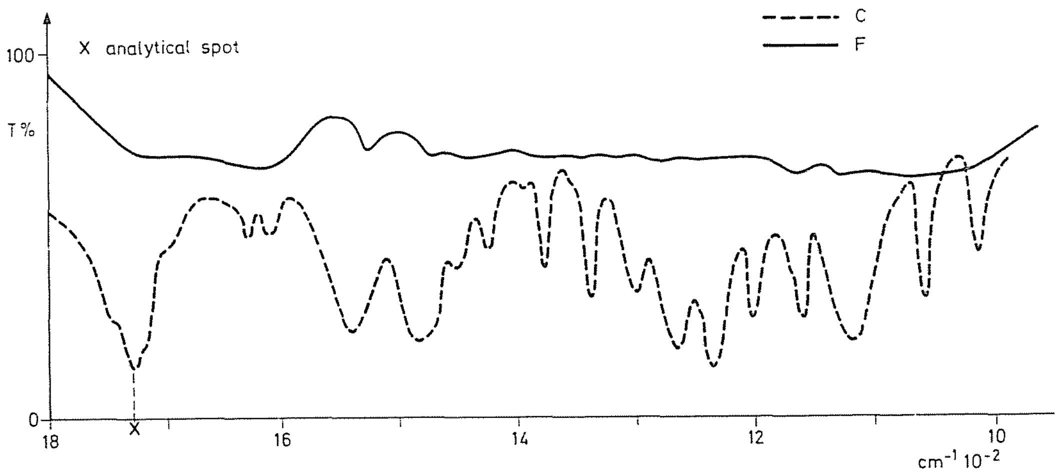

Fig. 5. Selection of the analytical spot for the assay of carbofurane (C) in the presence of fugrane (F)

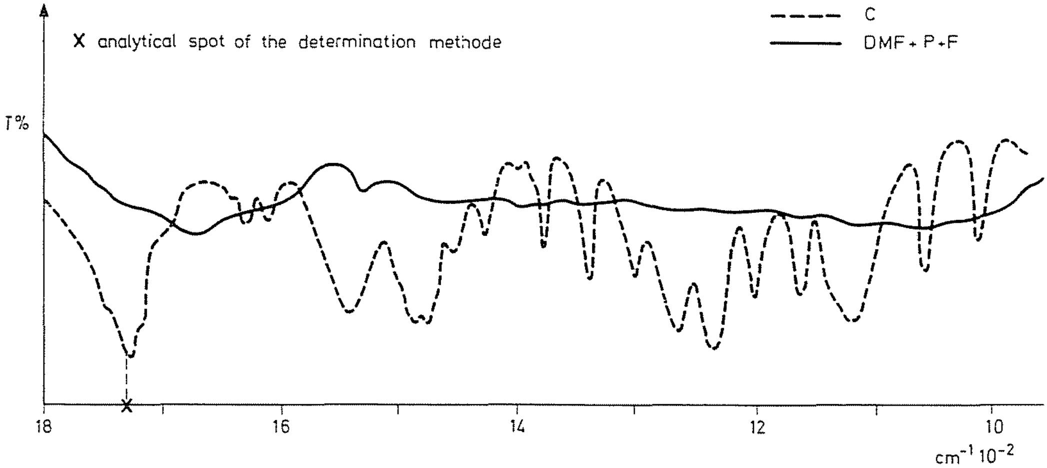

Fig. 6. Selection of the analytical spot for the assay of carbofurane (C) in the presence of dimethyl formamide, (DMF) perlite (P) and fugrane (F)

the calibration curve and its statistical characteristics in Table 2. The method developed proved, in this case too, suitable for the analysis of the preparations.

5. Finally, we describe our method developed for the determination of carbofurane in the presence of dimethyl formamide, perlite and fugrane as components. Perlite is a rock of volcanic origin whose main component is silicon dioxide. The selection of the analytical spot can be seen in Fig. 6, the equation of the calibration curve and the statistical characteristics in Table 2. This method, too, proved suitable to analyse the samples.

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