DIRECT GAS CHROMATOGRAPHIC DETERMINATION OF CARBARYL

M. RIVA AND A. CARISANO

Research Laboratories Star Food Co., Ltd., Agrate Brianza, Milan (Italy)

(Received March 13th, 1969)

SUMMARY

The direct analysis of the carbamate Carbaryl by gas chromatography has many limitations, owing to its low thermal stability and its polarity. In some gas chromatographic methods described in the literature, Carbaryl is determined via its degradation product, α-naphthol. The use of stable N-substituted derivatives has also been suggested. A technique has now been devised for the direct analysis of Carbaryl in microgram and submicrogram amounts without decomposition. Flame-ionization detectors which have been modified with KCl and are sensitive to organic nitrogen respond selectively and sensitively to Carbaryl. The proposed conditions are particularly favourable for the determination of Carbaryl residues in foods.

INTRODUCTION

The increasing use of carbamates as insecticides, fungicides, and herbicides has raised the need for suitable gas chromatographic methods for their identification and determination. ZIELINSKI et al.[1-3] studied the gas chromatographic behaviour of simple and N-substituted carbamates, including 1-naphthyl N-methyl-carbamate. Under the conditions used, the latter compound underwent thermal decomposition, and lost its carbamate moiety. As a result, the peak given by this compound was that of α-naphthol.

To overcome this difficulty, FISHBEIN et al.[4] converted the carbamates into their more stable and less polar N-trimethylsilyl derivatives. SULLIVAN et al.[5] recommended the acetylation of the carbamate group in Carbaryl, so as to raise the thermal stability. Although FISHBEIN[4] mentioned the possibility of analysing Carbaryl without decomposition provided that a sufficiently low temperature is used, no results obtained in this manner have yet been published. However, it appeared likely that Carbaryl can be analysed directly by choosing the right conditions.

We were interested in a rapid method for the direct gas chromatographic determination of Carbaryl residues in foods of plant origin, and preliminary work on the identification of Carbaryl by the use of an SE-30 column was encouraging. Subsequently we studied the behaviour of this compound on apolar columns in greater detail, bearing in mind that recent improvements in flame-ionization detectors (F.I.D.), modified with alkali metal salts[6-10], and the silanization of the support for

the stationary phase permit the selective and sensitive detection of polar compounds with one or more nitrogen atoms.

We shall now describe the conditions and the results of the direct analysis of microgram and submicrogram amounts of Carbaryl.

EXPERIMENTAL

General considerations

In view of the limited thermal stability (Carbaryl tends to dissociate into α-naphthol and methyl isocyanate)[11] and the polar nature of the sample, it is advisable to choose a relatively low column temperature (150–170°) and the shortest elution time that still gives an acceptable separation. We chose a low-concentration (0.5–2%) apolar stationary phase such as Apiezon L or SE-30 on 100–120 mesh silanized Gas-Chrom P (ex John Mansville). The preliminary experiments were done at 130–200° with 1 and 2-m silanized glass columns (I.D. 3 mm) and a Fractovap DAI chromatograph (ex C. Erba). For the detection and the estimation of losses during the elution, we used a conventional F.I.D. and a KCl-treated thermionic flame-ionization detector (KCl-T.D.) which is specific for organic nitrogen. The sample was an equal mixture of Carbaryl and methyl pentadecanoate (a thermostable compound). The results obtained with the two detectors under suitable conditions show whether or not the carbamate group is cleaved off, and whether the hydrocarbon skeleton remains intact. The preliminary work was done to find the best conditions for the direct gas chromatographic analysis of Carbaryl.

Use of the KCl-treated thermionic detector

This detector[6,7] is highly sensitive to organic nitrogen and is therefore ideal for showing whether Carbaryl emerges from the column with or without its nitrogen atom.

The selectivity of the KCl-T.D. is generally defined by the ratio between the response of a KCl-T.D. and the response of a conventional F.I.D. to an organic nitrogen compound. According to TINDLE *et al.*[10] the selectivity ratio SR is best determined by the use of an internal standard containing no nitrogen; introduction of identical amounts in the tests by the two detectors is thus unnecessary. If A_{CHN} and A_{CH} denote the peak areas for the nitrogen compound and the standard containing no nitrogen (*e.g.* methyl pentadecanoate), respectively, the selectivity ratio of the KCl-treated detector is found by the formula:

$$SR = \frac{(A_{CHN}/A_{CH}) \text{ KCl-T.D.}}{(A_{CHN}/A_{CH}) \text{ F.I.D.}}$$

In the case of Carbaryl (N = 6.93% and ionizable CH = 53.6%), the relative selectivity of the KCl-T.D. is $SR = 75$ under the conditions used in the present work. This means that the single nitrogen atom accounts for a response in the KCl-T.D. 75 times greater than the hydrocarbon skeleton alone. Under fixed conditions, the selectivity ratio is a measure of the ratio between the nitrogen and the ionizable carbon in the molecule. Compounds with a higher nitrogen content and a lower ionizable carbon content (CH groups) have much higher SR values. Thus, the SR for Atrazine is 1645 (N = 32.5% and ionizable CH = 16.8%).

Use of the conventional F.I.D.

This detector[13] responds to organic carbon, and thus indicates the ionizable carbon content of the sample. Since only groups to which no oxygen is attached participate in the detection mechanism[14], only the nine asterisked carbon atoms in Carbaryl elicit a response in the detector.
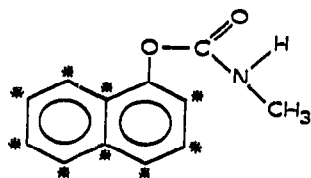
Carbaryl, mol. wt. = 201, ionizable carbon = 9 × 12 = 108 (108/201) × 100 = 53,6%.
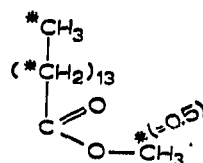
Methyl pentadecanoate, mol. wt. = 256, ionizable carbon = 14,5 × 12 = 174 (174/256) × 100 = 67.8%.

The ionizable carbon content of Carbaryl and methyl pentadecanoate is 53.6 and 67.8 wt-%, respectively. The two peak areas obtained in the elution of an equal mixture of these two compounds will therefore ideally be in a ratio of $R = 53.6/67.8 = 0.79$ (provided that the naphthalene nucleus is not destroyed or the substance fully absorbed or disintegrated). An experimental check of this theoretical value of $R = 0.79$ with various amounts of Carbaryl therefore enables one to estimate the recovery of the carbon skeleton of the molecule.

By the joint use of these two detectors, we can thus tell in what form the Carbaryl molecule is on leaving the column after elution under various conditions. It is said to retain its nitrogen if $SR = 75$, and its carbon skeleton if $R = 0.79$.

RESULTS AND DISCUSSION

The following emerged from the preliminary tests:·

The use of a 2-m column at 140–200° was unsatisfactory: R was close to zero or fluctuated when a few micrograms of Carbaryl were introduced, which indicated large losses on the column. Significantly better results were obtained with a shorter column having a smaller proportion of SE-30, and which had been silanized further.

. The silanization of the support by the usual method before the coating with the stationary phase[15] proved insufficient. The results could be markedly improved by resilanizing the column after its operation for a few hours. This was done by injecting four or five aliquots (10 μg in total injected) of pure hexamethyldisilazane. To prevent contamination of the detector with SiO_2, the electrodes were removed and the flame was burned at the end of a second burner, which is not used for the analysis. The importance of this additional, dynamic silanization is evident from a comparison of the two curves in Fig. 1, obtained at 168° with and without this resilanization. The latter made the value of R increase towards the theoretical 0.79 with all the Carbaryl samples.

Reproducible results with acceptable R values were obtained by the use of a 1-m glass column (I.D. 3 mm) packed with 0.5% of SE-30 on 100–120 mesh silanized Gas-Chrom P support, the column temperature being 168°. The glass vaporizer, incorporated in the column, was heated to 185°, by an auxiliary ceramic heating
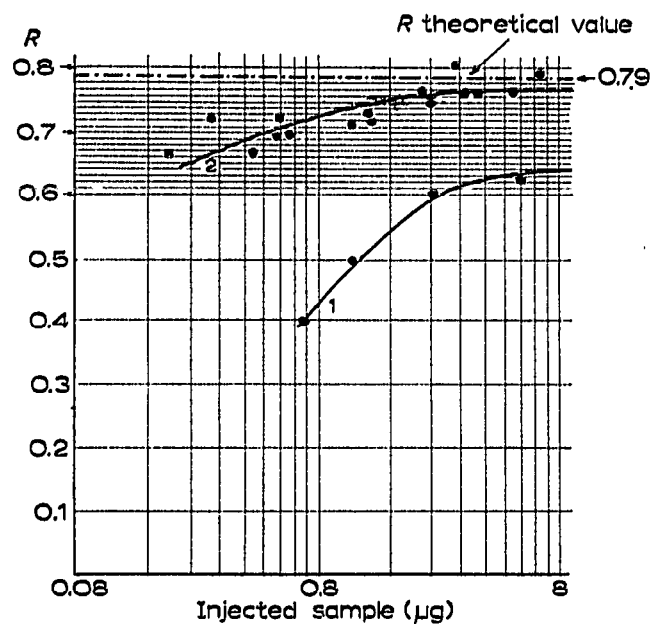
Fig. 1. Variation of R with the amount of the sample (R is the ratio between the peak area of Carbaryl and that of methyl pentadecanoate). A conventional flame ionization detector was used. The smaller the value of R, the greater the proportion of Carbaryl lost in the analysis. 1 = no dynamic silanization; 2 = dynamic silanization by injecting hexamethyldisilazane into the column.
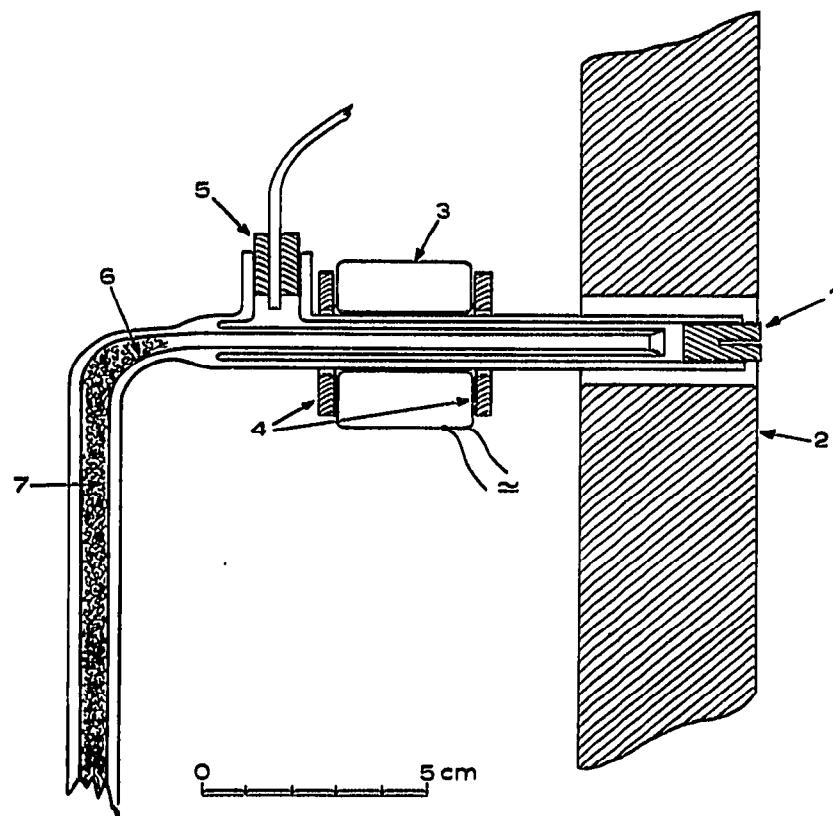

Fig. 2. Cross section of column inlet. (1) Injection port; (2) oven door; (3) ceramic heater element (12 watt); (4) asbestos washers; (5) carrier gas inlet; (6) silanized glass wool plug; (7) column packing.

element. The geometry of the inlet zone is shown in Fig. 2. After conditioning for one day, the column was resilanized as described above. The detector temperature was 250°, the flow rates of the carrier nitrogen and the detector hydrogen were respectively 50 and 55 ml/min, and that of the detector air was 300 and 600 ml/min for the F.I.D. and the KCl-T.D., respectively.

According to the need, we used either a conventional F.I.D., or KCl-T.D. (devised by GIUFFRIDA[6,7]), or a dual-channel flame ionization-cum-thermionic detector (PF.-T.D.), described in a previous article of ours[12]. Having an F.I.D. section and a KCl-T.D. section, this third detector monitored simultaneously the nitrogen and the hydrocarbon moiety of the Carbaryl molecule.
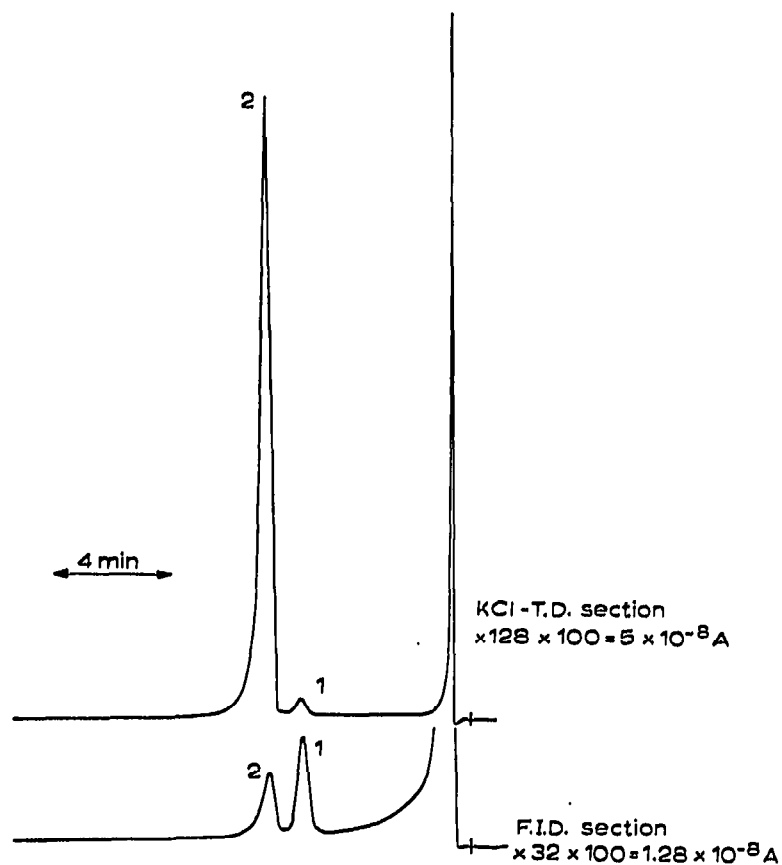

Fig. 3. Simultaneous analysis, separately recorded, of 2 μg of methyl pentadecanoate (peak 1) and 2 μg of Carbaryl (peak 2) with the two sections of the P.F.-T.D. The KCl-T.D. section is seen to have a high response to Carbaryl, owing to its nitrogen content.

The standard solutions were prepared by dissolving equal amounts of Carbaryl and methyl pentadecanoate in benzene, the concentration of each compound varying between 0.5 and 4 μg/ml. We used a 10-μl Hamilton microsyringe to inject samples of not more than 2 μl (1 μl of hexane and 0.5 μl of air had been introduced into the syringe before the sample).

The results are shown by curve 2 in Fig. 1 and by the chromatogram in Fig. 3. The former was obtained with a conventional F.I.D., and indicates, by means of the R value, the recovery of the hydrocarbon moiety of the molecule. The chromatogram in Fig. 3 gives the results of a series of tests with the P.F.-T.D. detector and 0.3-10 μg

of Carbaryl, and shows that the KCl-T.D. selectively responds to the nitrogen moiety, with an $RS = 75$. This proves that the nitrogen is not lost, and thus Carbaryl does not suffer considerable structural changes during the analysis. With Carbaryl samples exceeding 3 μg, the value of R becomes 0.79, which means that the recovery of Carbaryl is complete. With smaller samples, there is a small loss, and R decreases, reaching 0.65 in the case of 300 ng (the smallest sample used). This corresponds to a recovery of about 90%.

CONCLUSIONS

Under the conditions used, Carbaryl can be analysed by gas chromatography without having to convert it into a derivative. It can be detected by a conventional F.I.D. or preferably by a KCl-T.D. The latter is more sensitive to nitrogen and detects it selectively. This fact permits a distinction to be made between Carbaryl and interfering organic compounds. The selectivity can be further improved by the use of a dual-channel flame ionization-cum-thermionic detector[12], in which the hydrocarbon signal can be suppressed automatically by electronic means.

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