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Determination of carbaryl and 1-naphthol in English apples and strawberries by combined gas chromatography–fluorescence spectrometry

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ABSTRACT

A rapid and selective method is reported for the determination of carbaryl (1-naphthalenol methyl carbamate) and its hydrolysis product, 1-naphthol, using combined gas chromatography–fluorescence spectrometry (GC–FS). The title compounds were detected and quantified as 1-methoxynaphthalene (λ_{ex} 282 nm, λ_{em} 334 nm) after derivatisation with trimethyl anilinium hydroxide. The method has been demonstrated for the analysis of English apples and strawberries. The limit of detection for carbaryl by GC–FS was 0.14 mg kg^{-1}.

INTRODUCTION

N-methyl carbamates are widely used as insecticides and maximum residue limits for carbaryl (1-naphthalenol methyl carbamate, **I**) in fruit and vegetables in the UK range from 0.2 to 10 mg/kg. A fast and efficient method for monitoring residues of these compounds in different agricultural products is therefore required. Carbamate pesticides have been determined using a variety of methods including gas chromatography (GC) [1–18], high-performance liquid chromatography (HPLC) [19–21] and combinations of these techniques with mass spectrometry [22–24]. Multiple residue methods for liquid chromatographic determination of N-methyl carbamates in crops [25], fruits and vegetables [26] have also been reported.

Ebing [1] reported that N-monomethyl carbamates were unstable during GC and carbaryl, which falls in this category, was degraded to 1-naphthol at a column temperature of 240°C. Nevertheless the direct GC detection of the intact carbamate has been carried out by minimising the effects of thermal instability and column substrate interaction [2,3], although some carbamate decomposition can occur even with careful selection of column conditions. The instability of the carbamates led to the development of thermally stable derivatives for quantitative gas chromatographic analysis. The trimethylsilyl (TMS) derivatives of several carbamates were prepared by Fishbein and Zielinski [4], by reaction with hexamethyldisilazane in pyridine in the presence of trimethylchlorosilane. Low levels of carbamates have also been measured by GC with electron-capture detection as N-perfluoroacyl [5] and N-trifluoroacetyl

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[6] derivatives. These derivatization procedures were applied to the detection of either the methyl amine moiety [7–11] or the liberated phenol moiety [12–16] of N-methylcarbamates. On-column transesterification of N-methylcarbamate with methanolic sodium hydroxide was investigated by Moye [17], who used a nitrogen/phosphorus detector to analyse mobam extracted from lettuce. Bowman and Beroza [18] hydrolysed carbaryl completely to 1-naphthol. They determined carbaryl (as 1-naphthol) in grass and milk using packed column GC combined with solution-phase fluorimetry.

The application of combined gas chromatography–vapour-phase fluorescence spectrometry has been demonstrated for the determination of polycyclic aromatic hydrocarbons [27,28] and the indirect detection of fluorescence quenchers [29]. In this paper, we report a rapid method for the determination of carbaryl, and its hydrolysis product 1-naphthol, as 1-methoxynaphthalene using combined gas chromatography–fluorescence spectrometry (GC–FS). The method is demonstrated for the analysis of English apples and strawberries.

EXPERIMENTAL

Instrumentation

A Perkin Elmer LS-5 luminescence spectrometer was interfaced to a Pye 104 gas chromatograph using a heated transfer line [27,28,30]. The column effluent was passed to a heated quartz flow cell (48 μl) via a zero dead volume coupling (SGE) located inside the oven of the gas chromatograph, and a length of fused-silica capillary tubing (60 cm × 0.3 mm I.D.) contained in the transfer line. A wide bore capillary column adaptor (SGE) was fitted to the injection port of the gas chromatograph. The column (25 m × 0.53 mm I.D. BP-5, SGE) was maintained isothermally at 170°C or programmed from 50°C to 180°C at 6°C min^{-1}, the transfer line at 200°C, the flow cell at 160°C and the injector at 235°C. The column head pressure was set at 53 kPa of oxygen free nitrogen. Data acquisition and processing was carried out using a Philips 3105 data station with Chromate PC software. The fluorescence spectrometer was operated in the time-drive mode for chromatographic analysis, with slit widths set to 15 and 20 nm at the excitation and emission monochromators respectively. Vapour-phase fluorescence excitation and emission spectra were recorded by the method described previously [30].

Reagents

The solvents, methanol (Fisons), chloroform (May & Baker) and dichloromethane (Fisons), were of HPLC grade, Analar and Pesticide grade respectively. Carbaryl (Prochem), 1-naphthol (Interchem) and 1-methoxynaphthalene (Aldrich) were obtained at 98% purity or better. Trimethylanilinium hydroxide (Methelute®) was purchased as a 0.2 *M* methanolic solution from Pierce.

Sample preparation and extraction

Apples (250–300 g) were chopped and blended with 100 ml Analar water, to form a homogenous mixture. Approximately 60 g of the resulting aqueous slurry (equivalent to 45–50 g of apple) was transfered to a 750-ml conical flask containing 50 grams of anhydrous sodium sulphate. To this slurry was added 150 ml of chloroform and the mixture was vigorously shaken for 10 min, before being filtered through

Whatman No. 1 paper. Four drops of diethylene glycol were added to the extract and the chloroform was removed by evaporation in a stream of dry air at room temperature. The residue was diluted to 1 ml with methanol. For the recovery experiments, the apple mixture was fortified with 1 ml of a 275-μg/ml solution of carbaryl in chloroform prior to extraction. Carbaryl and its hydrolysis product 1-naphthol were determined individually after separation by column liquid chromatography [31]. A 30 cm × 20 mm I.D. column was packed from the bottom with 5 g of anhydrous sodium sulphate, 10 g of alumina (70–230 mesh) and 10 g of anhydrous sodium sulphate. The column was prewashed with 50 ml of chloroform and the eluate discarded. A volume of 60 ml of the chloroform extract was added to the column and the carbaryl eluted with an additional 50 ml solvent to give a total volume of 110 ml. The column was then washed with 100 ml of methanol to elute the 1-naphthol. Four drops of diethylene glycol were added to the chloroform fraction, and the mixture was concentrated to near dryness. The residue was diluted to 1 ml with methanol. The methanol fraction was transferred to a 500-ml separatory funnel containing 50 ml of saturated aqueous sodium chloride. The container was washed with Analar water, and the washings were added to the separatory funnel. This solution was extracted twice with 100 ml of dichloromethane, and the extract dried through a plug of anhydrous sodium sulphate (3.5 cm × 2 cm I.D.). Four drops of diethylene glycol were added, the dichloromethane was removed and the residue dissolved in 1 ml of methanol.

Strawberry samples (150 g) were blended with 50 ml Analar water and 66 g of the resulting slurry (equivalent to 50 g strawberries) was extracted and pretreated by the same procedure as that used for apple.

Methylation procedure

A volume of 25 μl methelute (0.2 *M* trimethylanilinum hydroxide, TMAH, in methanol) was added to 50 μl of methanol extract and the mixture was shaken for a few seconds. Aliquots of 1.5 μl of each mixture were analysed directly by GC–FS.

RESULTS AND DISCUSSION

The fluorescence excitation and emission spectra of carbaryl in 95% ethanol solution show maximum intensity at 285 nm and 340 nm respectively, whilst for the hydrolysis product, 1-naphthol, the maximum excitation and emission wavelengths are shifted toward the red (λ_{ex} = 306 nm, λ_{em} = 362 nm) [32]. However, the vapour-phase fluorescence excitation and emission maxima of carbaryl in nitrogen at 160°C (λ_{ex} = 283 nm, λ_{em} = 338 nm) were found to be identical to that of 1-naphthol (Fig. 1a), probably as a result of the decomposition of carbaryl to 1-naphthol at high temperature in the vapour-phase. The difference between the maximum excitation and emission wavelengths of 1-naphthol on going from solution (95% ethanol) to vapour (nitrogen) may be attributed to matrix effects. Fluorescence excitation and emission wavelengths were therefore set at 283 nm and 338 nm respectively for the detection of 1-naphthol and carbaryl (Table I).

The direct analysis of carbaryl by GC with vapor-phase fluorescence detection yields two chromatographic peaks with retention times of 20.3 and 35.4 min (Fig. 2a). The longer retention time peak is assigned to the intact carbaryl, while the peak at 20.3 min arises from thermal decomposition of a portion of carbaryl (approximately

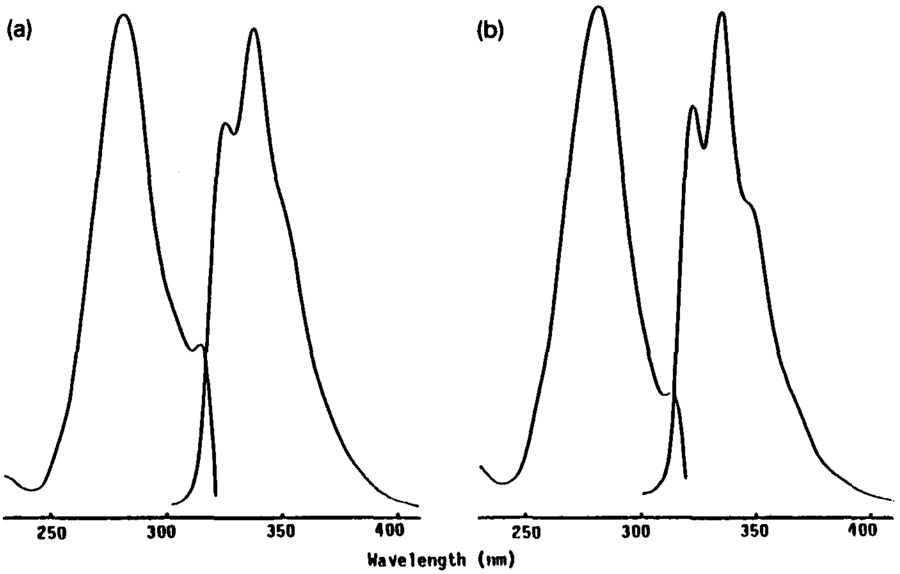


Fig. 1. Vapour-phase fluorescence excitation and emission spectra of (a) 1-naphthol and (b) 1-methoxynaphthalene.

45%) to 1-naphthol during GC (injector temperature at 235°C). The thermal decomposition of carbaryl to 1-naphthol, the high limit of detrection (115 ng) and long retention time (35 min) therefore make the direct determination of carbaryl at residue levels unreliable.

The possibility of the detection of intact carbaryl using cold on-column injection (temperature programming 50–180°C at 6°C/min) was investigated, using the combined GC–FS technique, but carbaryl was still partially hydrolysed to 1-naphthol under these conditions. Lowering the flow cell and transfer line temperatures resulted in increased tailing of the carbaryl peak with little change in the decomposition to 1-naphthol. However, quantitative conversion of carbaryl to the 1-naphthol was ob-

TABLE I

CHROMATOGRAPHIC AND VAPOUR-PHASE FLUORESCENCE CHARACTERISTICS FOR CARBARYL, 1-NAPHTHOL AND 1-METHOXYNAPHTHALENE

Compound	Retention time (t_R, min:s)[a]	limit of detection (LOD) (ng)	Tailing factor (TF)	$\lambda_{ex}/\lambda_{em}$
Carbaryl	35:42	115	1.6	283/338[b]
1-Naphthol	20:30	7.5	1.6	283/338
1-Methoxynaphthalene	19:18	2.5	1.1	282/334

[a] Conditions: temperature programming from 50 to 180°C at 6°C/min.
[b] Possible decomposition of carbaryl to 1-naphthol in the vapour phase.

served when a small piece of glass wool was inserted into the hot capillary injector. Fig. 2a and b compares the chromatograms obtained from the analysis of a carbaryl solution (λ_{ex} 283 nm, λ_{em} 338 nm) with, and without the presence of the glass wool in

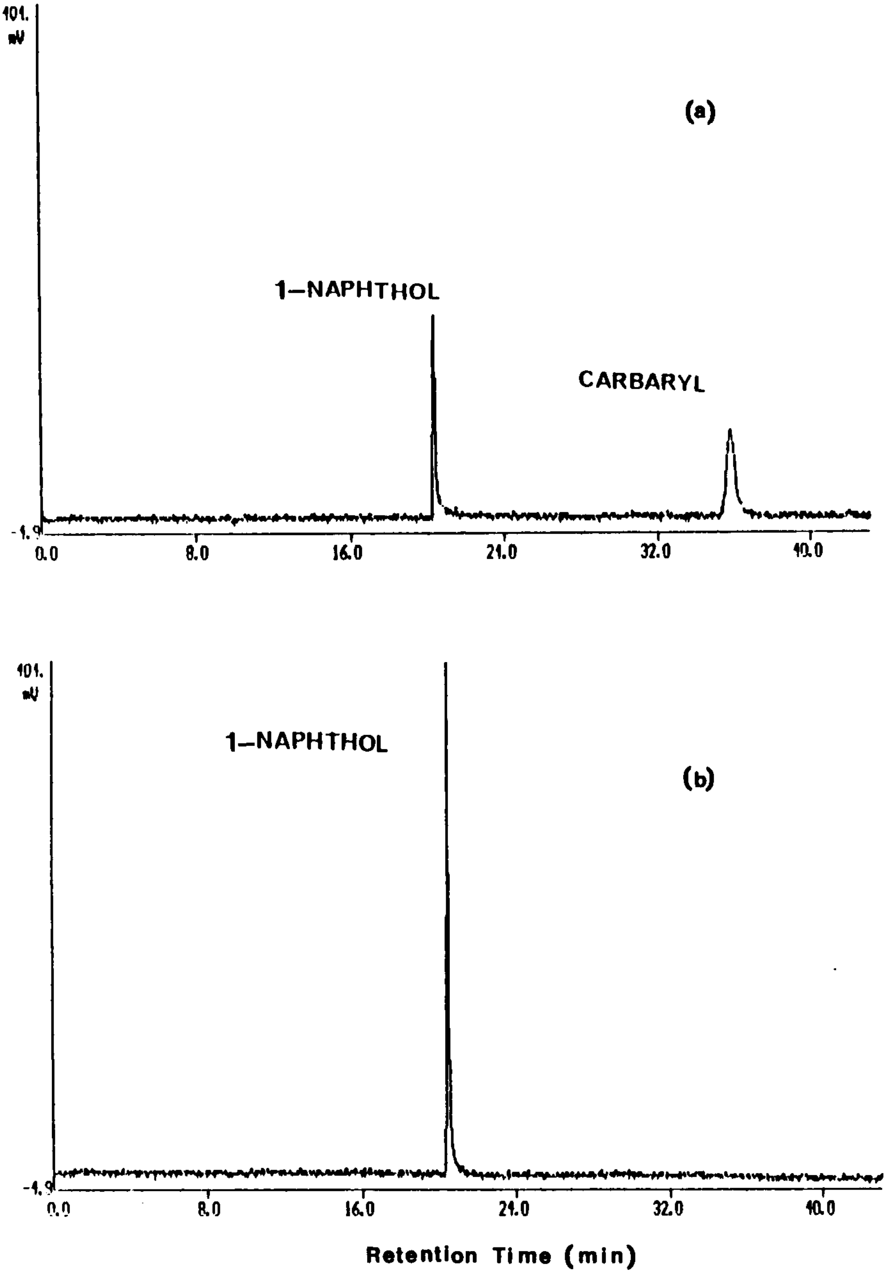
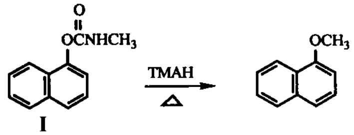


Fig. 2. GC–FS chromatograms of carbaryl without (a) and with (b) glass wool in the injector port (λ_{ex} 283 nm, λ_{em} 338 nm). Conditions: temperature programmed from 50°C at 6°C/min to a final temperature of 180°C.

the hot injector. A similar result was obtained by Bowman and Beroza [18] using a short plug containing 85% phosphoric acid at the head of a packed GC column. This suggested a convenient method for the determination of carbaryl after complete hydrolysis.

The thermal methylation of N-methyl and N-aryl carbamates with TMAH was investigated by Wien and Tanaka [33]. The reaction of N-aryl carbamates containing a single N–H group (*e.g.* propham) yielded the thermally stable N-methyl analogue, but the product of the thermal reaction of N-methyl carbamates (*e.g.* carbaryl) with TMAH was the aryl methyl ether. The methylation of 1-naphthol following carbaryl hydrolysis was therefore investigated for the detection of carbaryl as 1-methoxynaphthalene by GC–FS.



The vapour-phase fluorescence spectrum of 1-methoxynaphthalene shows maximum excitation and emission wavelengths at 282 and 334 nm (Fig. 1b) which were selected for subsequent quantitative detection. Table I gives data on retention times, limits of detection, tailing factors and maximum fluorescence excitation and emission wavelengths for carbaryl, 1-naphthol and 1-methoxynaphthalene. The limit of detection for 1-methoxynaphthalene (2.5 ng) was found to be lower than for 1-naphthol (7.5 ng) and a much improved peak shape was observed. A wide linear range for the detection of 1-methoxynaphthalene from the carbaryl/TMAH reaction (0.010–6.8 μg) was established.

The apple and strawberry extracts were prepared by a simple homogenisation and extraction procedure and the resulting methanol solution (1 ml) was mixed with the TMAH derivatizing reagent immediately prior to analysis by GC–FS. Detection of total carbaryl and 1-naphthol, as 1-methoxynaphthalene (λ_{ex} 282 nm, λ_{em} 334 nm) in a strawberry extract fortified with carbaryl (5.5 ppm) is shown in Fig. 3. The first peak is due to the presence of N,N-dimethylaniline from the derivatizing reagent, which fluoresces strongly, whilst the peak at 4:06 min arises from 1-methoxynaphthalene. This confirms the high selectivity of combined GC–FS for the rapid screening of total carbaryl/1-naphthol in sample extracts without pre-treatment. In order to quantify carbaryl and 1-naphthol separately in the apple and strawberry samples, 1-naphthol and carbaryl were separated on alumina using the method of Bowman and Beroza [31]. The analytical method recoveries for spiked samples of English apples and strawberries are given in Table II. The coefficients of variation (C.V.) for carbaryl and 1-naphthol are 11% and 8%, respectively. The results obtained from samples fortified with carbaryl and 1-naphthol at the 5.5-ppm level indicated that a total of 110 ml of chloroform (rather than 160 ml [31]) was sufficient to elute the carbaryl. A low recovery (31%) was observed for 1-naphthol for the apple samples, which may arise either from incomplete extraction or losses during the evaporation process. Recoveries of 73–78% have been reported [18] for 1-naphthol in milk which were lower than those for carbaryl (95–100%). Recoveries from corn samples were 89–93% and 16–34% for carbaryl and 1-naphthol, respectively. This indicates that the recovery is matrix dependent and varies between different samples. The recovery of

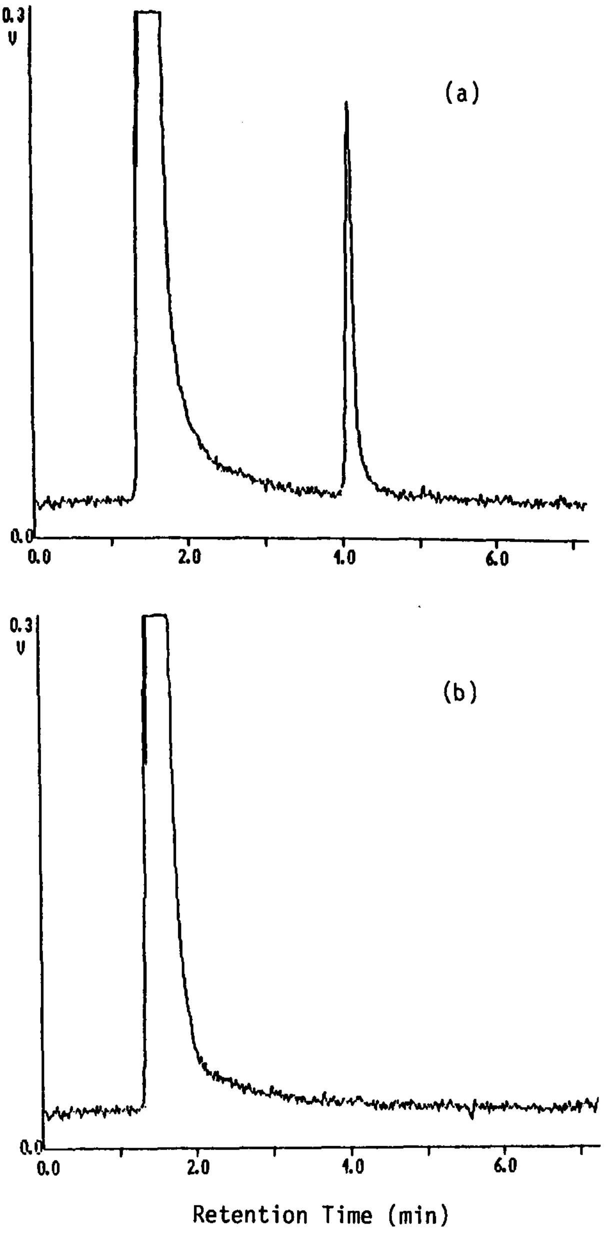


Fig. 3. Detection of carbaryl as 1-methoxynaphthalene in crude strawberry extract sample by GC–FS. (a) Sample spiked at 5.5 ppm, (b) unspiked sample; λ_{ex} 282 nm, λ_{em} 334 nm. Conditions: isothermal at 170°C.

TABLE II

RECOVERIES FOR CARBARYL AND 1-NAPHTHOL IN ENGLISH APPLES AND STRAWBERRIES USING GC–FS DETECTION

Compound[a]	Amount added (μg)	Amount recovered (μg)		Recovery (%)	
		Apple	Strawberry	Apple	Strawberry
Carbaryl	275 (5.5 ppm)	212	198	77	72
1-Naphthol	260 (5.5 ppm)	81	156	31	60

[a] Detected as 1-methoxynaphthalene (λ_{ex} 282 nm, λ_{em} 334 nm).

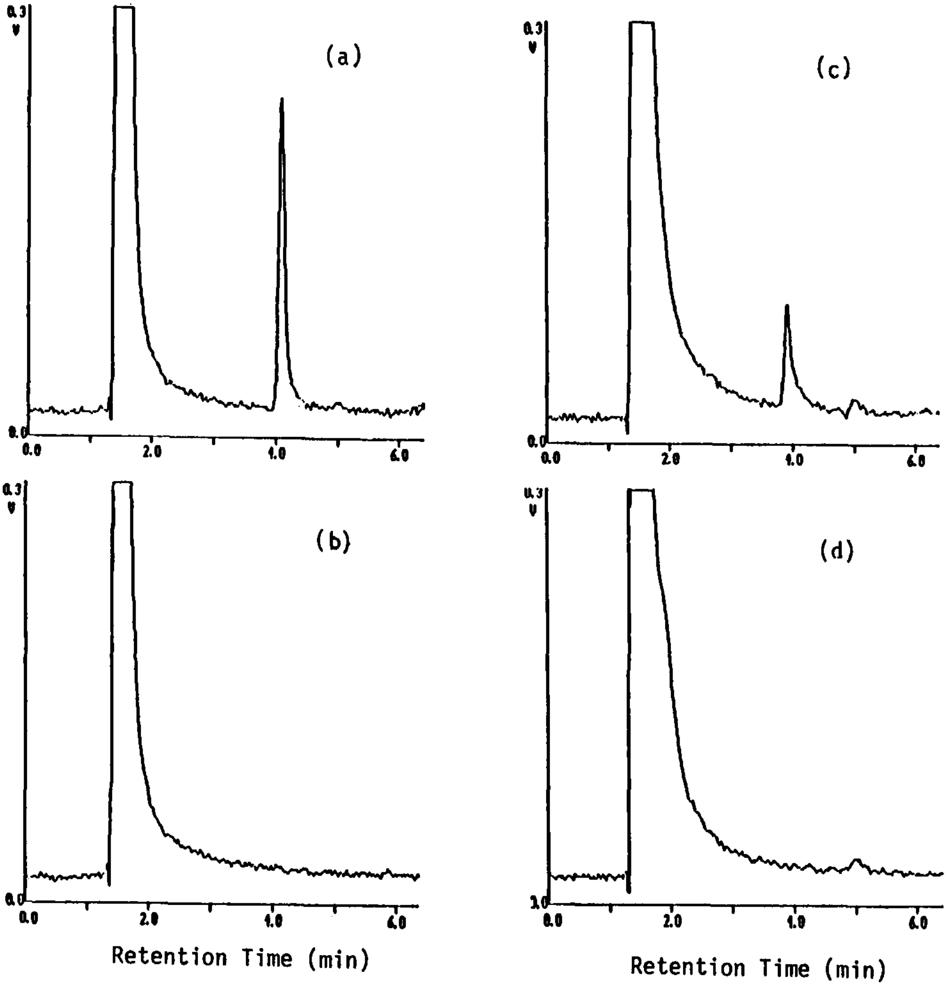


Fig. 4. Detection of carbaryl (a: spike, b: sample) and 1-naphthol (c: spike, d: sample) as 1-methoxynaphthalene in apple extract by GC–FS (λ_{ex} 282 nm, λ_{em} 334 nm). Conditions: isothermal at 170°C.

carbaryl from both fruit extracts is, however, satisfactory (>70%). The chromatograms obtained from the GC–FS analysis of an apple sample are shown in Fig. 4. The presence of carbaryl and 1-naphthol in this sample is not confirmed (Fig. 4b and d), although their levels may be below the GC–FS limit of detection (0.14 ppm). Samples spiked at the 5.5-ppm level were easily detected without interference (Fig. 4a and c). Maximum residue limits (MRL) for apple and strawberry in the UK are 5 and 7 mg/kg respectively.

The quantitative determination of carbaryl and 1-naphthol in real samples can be carried out with high sensitivity and selectivity using the combined GC–FS technique. The extracts examined in this study show no matrix interferences and require short analysis times (< 5 min at an isothermal column temperature of 170°C), providing a rapid and novel screening procedure for total carbaryl/1-naphthol, whilst both may be determined separately after alumina column separation.

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