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## Note

# Gas chromatographic determination of raspberry ketone and malathion in insect bait concentrates

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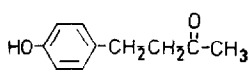
Raspberry ketone, 1-(4'-hydroxyphenyl)-3-butanone (I), is a natural flavour constituent of many berries including the raspberry. Furthermore, synthetic raspberry ketone is commonly added to raspberry flavoured foods such as yoghurts, juices, desserts, milk drinks and confectionaries. The strong pervasive raspberry odour of the ketone acts as a fruit fly attractant and when added to malathion (II) dissolved in a suitable solvent an excellent fruit fly bait is obtained —the fly is attracted to the raspberry ketone and succumbs to the toxic affects of malathion. The bait is normally prepared by adding an ethanolic solution of raspberry ketone and malathion to a suitable absorbent material.

Methods so far published on the determination of raspberry ketone have concentrated on its determination in foods or food products such as those listed above. These methods are not particularly suitable for the routine determination of raspberry ketone in insect bait concentrates, either because they are unduly long for routine use, or because they involve expensive instrumentation such as mass spectrometry (MS).

Utilising its solubility in acetone and diethyl ether as well as thin-layer chromatography (TLC), Gallois[1] was able to determine the content of raspberry ketone in 22 cultivers in the range 20–370 μg/g fruit. In addition to presenting infra-red, nuclear magnetic resonance and MS data for pure raspberry ketone, Schmidlin-Meszaros[2] determined the raspberry ketone content of raspberry yoghurt, raspberry essence and raspberry pulp by TLC and vacuum sublimation after extraction with pentane–diethyl ether (1:5). While this author states that raspberry ketone is by its non-volatile character not readily detected by gas chromatography (GC), neither Bruchmann and Klob[3], Braun and Hieke[4] nor the present author found volatilization to be a problem. In addition to direct GC several GC–MS methods have been de-



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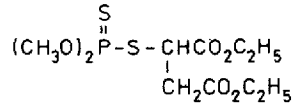

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scribed for the determination of raspberry ketone in various matrices[5–7]. More recently, Holzer[8] has described the use of high-performance liquid chromatography (HPLC) for determination of raspberry ketone in numerous food products.

A brief review of the various methods used for the determination of malathion has been published elsewhere[9] and will not be elaborated on here. The majority of these methods have been based on UV-spectrophotometry, or GC, although several HPLC procedures are now also available[9–11].

As the methods thus far published for the determination of raspberry ketone and malathion were not found suitable fo routine determination in the insect bait concentrate a GC method was developed in this laboratory for their simultaneous determination in a concentrate consisting of 20% (w/v) raspberry ketone and 25% (w/v) malathion. The method which requires no sample preparation other than appropriate dilution, involves the separation of the two active components on a column of 3% XE-60 on Chromosorb W HP followed by detection with a flame-ionisation detector (FID). The complete analysis time is approximately 1 h and gives a recovery of 99% and 100% for raspberry ketone and malathion respectively.

## EXPERIMENTAL

### *Apparatus*

A Varian 3700 gas chromatograph equipped with a FID (Varian, Sydney, Australia) and 1.8 m × 4 mm I.D. glass column packed with 3% XE-60 on Chromosorb W HP (80–100 mesh) was used. The detector was connected to an Omniscribe B5117-2 recorder (Activon Scientific Services, Granville, Australia). All injections were made with an S.G.E. 10-$\mu$l syringe (Activon).

### *Reagents and standards*

Malathion (95.5%) from Cheminova (Lenvig, Denmark). Raspberry ketone (99.0%) from Givaudan (Dee Why, Australia). Ethanol (AR Grade) from Ajax Chemical (Sydney, Australia).

### *Preparation of concentrates*

Three samples of concentrate were prepared containing different concentrations of raspberry ketone and malathion (as shown in Table I) by dissolving the appropriate amount of the two components in ethanol.

### *Peparation of standards*

A working standard was prepared by dissolving 0.2126 g of malathion and 0.1645 g of raspberry ketone in ethanol and diluting to 100 ml with ethanol.

In addition four solutions were prepared consisting of 0.1, 0.2, 0.3 and 0.4 g each of malathion and raspberry ketone in 100 ml of ethanol. These solutions were used to test the linearity of detector response to those compounds.

### *Preparation of samples*

The samples were prepared by diluting 1.0 ml of each concentrate to 100 ml with ethanol in separate volumetric flasks.

*Chromatographic conditions*

Column temperature: 190°C. Injection temperature: 200°C. FID temperature: 220°C. Detector setting: $16 \cdot 10^{-10}$ A $mV^{-1}$. Chart speed: 0.25 cm $min^{-1}$.

*Procedure*

Duplicate 5-$\mu$l injections were made of the standard working solution and each sample and the ratio of the respective peak height of raspberry ketone and malathion in each sample to that of the standard determined. The respective ratios were then used to calculate the concentration of both components in the samples, as well as their recovery.

*Reproducibility*

Six samples of commercially produced concentrate consisting of 20% (w/v) raspberry ketone and 25% (w/v) malathion were diluted and analysed by the above procedure and the mean recovery and reproducibility of the method calculated.

## RESULTS AND DISCUSSION

As shown in Table I, the mean recovery of raspberry ketone and malathion is 99.3% and 99.7% respectively for laboratory prepared samples containing 15–25% raspberry ketone and 20–30% malathion. The four standard ethanolic solutions consisting of 0.1, 0.2, 0.3 and 0.4 g (corresponding to 10, 20, 30 and 40%) each of raspberry ketone and malathion were found to give a linear calibraton line, justifying the use of a single standard mixture for quantitation of the five components in the range likely to be encountered in normal commercial batches of concentrate. Fig. 1 is a typical chromatogram of a standard solution consistidng of 0.2130 g raspberry ketone and 0.2720 g malathion per 100 ml of ethanol, while Fig. 2 is the chromatogram of a commercially produced bait concentrate containing 20% raspberry ketone and 25% malathion when diluted and chromatographed as described. Under the described conditions the retention time of raspberry ketone and malathion is 4.0 min and 5.6 min respectively.

The method described gives excellent recovery and reproducibility for both components. This is seen in Table II where the mean recovery of both is 100%, while

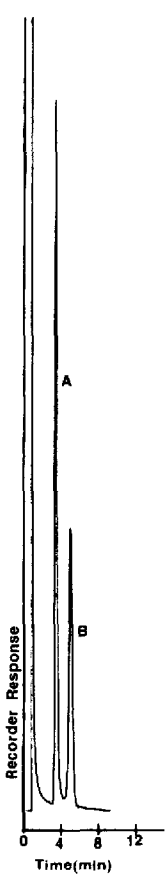
TABLE I

RECOVERY OF RASPBERRY KETONE AND MALATHION FROM LABORATORY PREPARED INSECT BAIT CONCENTRATES

As determined from duplicate 5-$\mu$l injections.

| | *Rasberry ketone (%)* | | | *Malathion (%)* | | |
|---|---|---|---|---|---|---|
| | *Added* | *Found* | *Recovery* | *Added* | *Found* | *Recovery* |
| 1 | 15.0 | 14.8 | 98.7 | 20.0 | 19.9 | 99.5 |
| 2 | 20.0 | 20.1 | 100.5 | 25.0 | 25.2 | 100.8 |
| 3 | 25.0 | 24.7 | 98.8 | 30.0 | 29.6 | 98.7 |

Mean recovery: raspberry ketone, 99.3%; malathion, 99.7%.



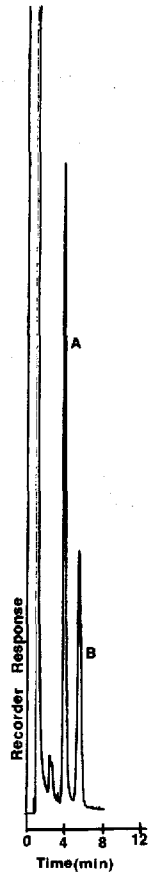




Fig. 1. Gas chromatogram of a standard ethanolic solution containing 0.2130 g raspberry ketone (A) and 0.2720 g malathion (B) per 100 ml ethanol. Chromatographic conditions as described in Experimental section.

Fig. 2. Gas chromatogram of typical commercial bait concentrate containing 20% raspberry ketone and 25% malathion in ethanol when diluted and chromatographed as described in Experimental section.

TABLE II

RECOVERY OF RASPBERRY KETONE AND MALATHION FROM COMMERCIALLY PRODUCED INSECT BAIT CONCENTRATE CONTAINING 20% RASPBERRY KETONE AND 25% MALATHION IN ETHANOL

As determined from duplicate 5-μl injections.

| *Raspberry ketone (%)* | | *Malathion (%)* | |
|---|---|---|---|
| *Found* | *Recovery* | *Found* | *Recovery* |
| 20.0 | 100.0 | 25.1 | 100.4 |
| 20.1 | 100.5 | 25.2 | 100.8 |
| 20.1 | 100.5 | 25.0 | 100.0 |
| 19.8 | 99.0 | 25.1 | 100.4 |
| 20.0 | 100.0 | 24.8 | 99.2 |
| 20.1 | 100.5 | 25.0 | 100.0 |
| Mean | 100.1 | | 100.1 |
| S.D. | 0.59 | | 0.55 |

their standard deviation is 0.59% and 0.55% for raspberry ketone and malathion respectively. The complete analysis time (preparation of standard and sample and duplicate injections of each) is approximately 1 h.

## CONCLUSION

A gas chromatographic method has been developed for the simultaneous determination of raspberry ketone and malathion in insect bait concentrates. The method involves no sample preparation other than an appropriate dilution and gives a recovery in excess of 99% for both components with a standard deviation of 0.59% and 0.55% for raspberry ketone and malathion respectively. Linearity in the concentration range 10–40% of both components has been established.

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