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Microdetermination of 3,3′-Dimethyl-4-methoxybenzophenone (NK-049) in vegetable by Mass Fragmentography

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A simple and sensitive mass fragmentographic method for quantitative determination of 3,3′-dimethyl-4-methoxybenzophenone(NK-049) in lettuce, carrot and sweet potato was developed. After gas chromatographic separation, NK-049 was determined by a mass spectrometer (MS) with a multiple ion detector (MID), The lower limit for detection by this method was 0.004 ppm, and the average recoveries of NK-049 were 83–92%.

INTRODUCTION

Application of gas chromatography-mass spectrometry (GC–MS) technique was popular in the biochemical and biomedical field. In contrast, only a few reports on the application of GC–MS in pesticide residue analysis have been published.[1,2] We developed the analytical method using MID for quantitative determination of trace level of NK-049 in lettuce, carrot and sweet potato.

EXPERIMENTAL

1. *Reagents*

Pure NK-049 was obtained from Nippon Kayaku Co. Ltd., and all other chemicals used in this study were of reagent grade.

2. *Instrumentation*

GC–MS analysis: A Shimadzu LKB-9000 GC/MS system and a Shimadzu High-Speed MID-PM 9060S were employed. The *glc* parameters, MS, and MID settings were listed in Table 1.

glc analysis: *glc* settings were given in Table 2.

3. *Extraction of NK-049 from Vegetable*

A 50-g sample of the homogenized vegetable was transferred to 500-ml Elenmeyer flask followed by 30-min shaking with 150 ml of acetonitrile at room temperature. The sample was filtered and the filtrate was washed with *n*-hexane (100 ml). The acetonitrile was evaporated under vacuum at 40°C. The residue was dissolved in saturated sodium chloride (100 ml) and re-extracted twice with chloroform (100 ml+50 ml). Then the chloroform layer was separated, dried over anhydrous sodium sulfate and evaporated to dryness under vacuum at 40°C. The residue was dissolved in 3 ml of *n*-hexane and applied to a column (10 cm×1.8 cm i.d.) of Florisil (Floridine Co.). The column was washed through with 100 ml of 10% chloroform in *n*-hexane and then with 30 ml of 30% chloroform in *n*-hexane. Then NK-049 was eluted with 100 ml of 30% chloroform in *n*-hexane. The solvent of the effluent was removed under vacuum at 40°C, and blown to dryness with a stream of nitrogen, and the residue was dissolved in *n*-hexane. An aliquot of this solution was then injected into *glc* and GC–MS.

RESULTS AND DISCUSSION

The mass spectra of NK-049 are shown in Fig. 1. A relatively strong peak of the molecular ion was observed at *m/e* 240 and this ion was used for monitoring of NK-049.

Calibration curve was prepared by known

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Table 1 GC–MS and MID operating conditions.

GC–MS	
GC column	glass (25 cm × 3 mm i.d.)packed with 5% PEG 20 M on Gas-chrom Q (80–100 mesh)
Temperature	Sample: 260°C Separator: 260°C Column oven: 220°C Ion source: 270°C
Electron energy	70 eV
Trap current	60 μA
Accelerating voltage	3.5 kV
Carrier gas	helium, 30 ml/min
Sample size	2 μl
MS gain	5
MID	
Mass on MID	240
MID gain	30
Additional voltage	3500 V for mass 230 (BG) 3354.167 V for mass 240

Table 2 GC operating conditions.

Instrument	Yanako G–1800 ECD (^{63}Ni), glass (2 m × 2 mm i.d.), packed with 5% OV–17 on Gas–chrom Q (60–80 mesh)
Temperature	Column: 240°C Injection: 250°C Detector: 250°C
Carrier gas	nitrogen, 1.0 kg/cm^2 (6.6 ml/min)
Chart speed	5 mm/min

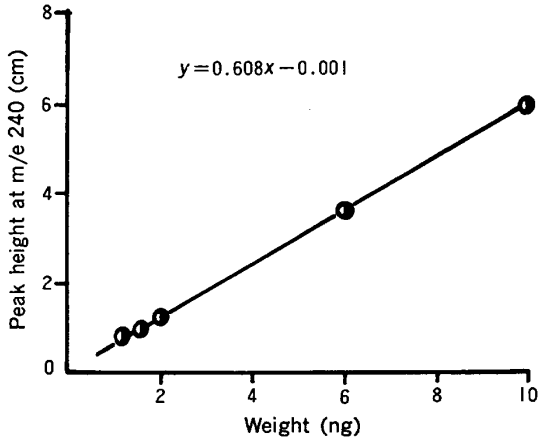

Fig. 2 Standard curve of NK–049.

amounts of the chemical without internal standard. The calibration curve obtained showed excellent linearity, as seen in Fig. 2.

Figure 4 shows the mass fragmentogram of NK–049 in the vegetable. The separation by *glc* was not complete for the quantitative determination of NK–049 as shown in Fig. 3, because of the existence of interfering compound in the vegetable. And, a troublesome process for clean-up was required for precise analysis. On the contrary, MF analysis was free from any interfering compound, and gave completely separated peaks of NK–049 (Fig. 4). The sensitivity of this method is at the nanogram level.

The data in Table 3 indicated the good reliability of this method. This method proved substantially simple and specific.

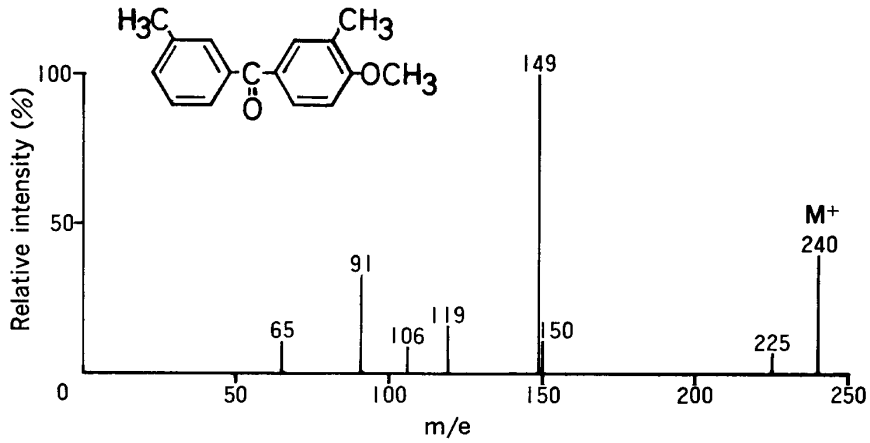

Fig. 1 Mass spectrum of NK–049.

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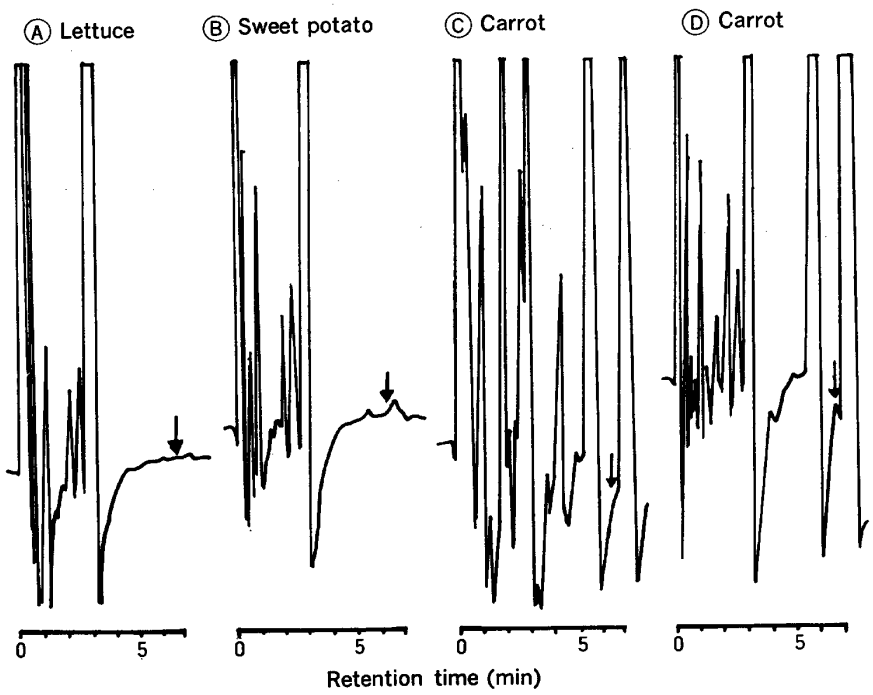
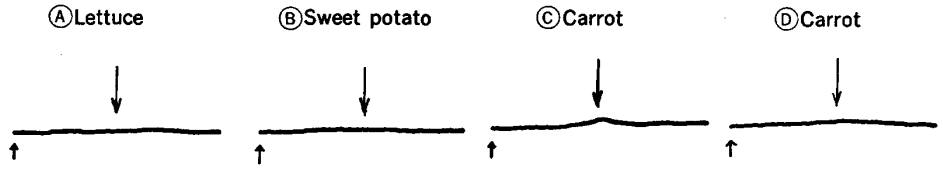


Fig. 3 Gas chromatograms of crop extracts.
Ⓐ, Ⓑ, Ⓒ……control samples, Ⓓ……field-treated carrot



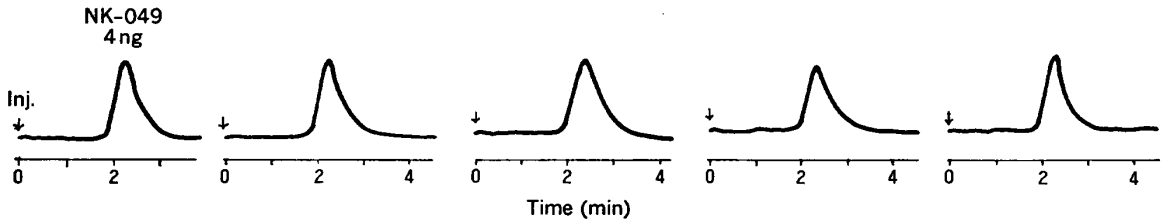


Fig. 4 Mass fragmentograms of standard NK–049 and crop extracts.
above: control samples
below: fortified with 0.2 ppm (Ⓐ, Ⓑ, Ⓒ) and field treated carrot (Ⓓ)
recording: *m/e* 240

Table 3 Recoveries by MF and *glc* analysis.

	MF	*glc*
Lettuce	92.1±4.1	83.8±2.3
Sweet potato	86.9±1.5	72.8±3.8
Carrot	82.8±1.1	73.6±7.1

fortification: 0.2 ppm

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2) R. A. Chapman & J. R. Robinson: *J. Chromatogr.* **140**, 209 (1977)

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要　　約

Mass Fragmentography による野菜中の 3,3′-dimethyl-4-methoxybenzophenone (NK-049) の微量分析

小林裕子，俣野修身，後藤真康

作物中の3,3′-dimethyl-4-methoxybenzophenone (NK-049) の定量に際し，選択性の高い方法である mass fragmentography (MF) の応用を試み，レタス，にんじん，かんしょ中の NK-049 を ECD と同感度で，より選択的に定量する方法を確立した．最小検出量は，0.004 ppm であり，平均回収率は，83～92% であった．

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