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Gas Chromatographic Determination of Benfuresate through On-column Injection

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On-column Injector를 이용한 benfuresate의 분석

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요약

Benfuresate의 잔류분석을 위해 GC-FPD (S-mode)를 이용하여 분석조건을 설정 중 열적 불안정으로 인해 열분해 산물과 모 화합물이 혼재됨이 확인되었다. 가스크로마토그라프를 이용한 열분해의 주된 요인은 주입구의 온도와 주입구내의 기화 정도인 것으로 판단되었으며, 주입구를 Chauhan과 Debre가 고안한 on-column으로 교체 후 분석한 결과 분해산물이 없는 단일 봉우리의 크로마토그램을 얻을 수 있었고, 절대량으로 0.6-4 ng의 정량 범위 내에서 유의성 높은 검량선을 얻을 수 있는 주입구 온도는 200°C였다.

Key words : Benfuresate, On-column injection, 열분해

INTRODUCTION

Benfuresate (2,3-dihydro-3,3-dimethylbenzofuran-5-yl ethanesulfonate) is a benzofuranyl alkanesulfonate class selective herbicide for control of purple nutsedge (*Cyperus rotundus* L.) in cotton (Anonymous, 1991). It is also applied in rice paddy to protect against *Echinochloa crus-galli*, Cyperus spp. (Kleifield *et al.*, 1992). GC and HPLC are most widely used instrument for multi-or single-residue methods to screen or determinate foods, water, soil, and other environmental samples for contamination. Thermally decomposed products during GC analysis have been reported, such as oxygen analogs of OP insecticides, acephate, methamidophos, azodrin. Co-injection of residual sample matrix presumably protects the analytes from thermal degradation and/or prevents adsorption of analytes by covering active sites in the gas chromatographic system (McMahon *et al.*, 1987). Loss of organophosphorus pesticides in vaporizing injectors was attributed to the thermal stress imposed on sample and the possibility of adsorption by liner (Stan, 1984; Stan, 1988). These factors vary with the chemical structure of pesticides and individual pesticides differently. Erney *et al.* (Erney, 1993)

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studied the influence of matrix-induced changes in the chromatographic response of OP pesticides using open tubular column gas chromatography and explored possible solutions for its irradiction or control under conditions suitable for the determination of pesticide residues in fatty foods. Moate and Jenkins (Moat and Jenkins, 1997) studied gas chromatographic determination of airborne residues of azinphosmethyl and azinphosmethyl-oxon through cool on-column injection as their previous work showed that azinphosmethyl-oxon undergoes sequential degradation in the hot split/splitless injection port of the GC. Several researchers (Park *et al.*, 1995; Yang *et al.*, 1995) reported on benfuresate residue analysis following Horne and Hoohstraten (Horne and Hoohstraten, 1980), who used packed column and flame photometric detector.

The purpose of the present study was to determine the influence of thermal decomposition on the chromatographic response of benfuresate using open tubular column gas chromatography and to explore possible solutions and conditions for the determination of benfuresate.

MATERIALS AND METHODS

Materials

Benfuresate standard was obtained from Novartis Agro Korea, and all solvents were pesticide-residue grade (J.T. Baker).

Instrumental analysis

A Hewlett-Packard 5890 series II with flame photometric detector (sulfur mode), a Hewlett-Packard 3396A integrator, a Hewlett-Packard 6890 with ^{63}Ni-electron capture detector, and HP GC Chemstation (Rev. A.06.01 [403]) were used for gas chromatography. The standard split/splitless injector was used for splitless injection and hot on-column injection by changing injection liners (Supelco, Bellefonte, PA, USA). On-column injections were carried out only for detection using the flame photometric detector following the Chauhan and Dabre's device (Jeninnings *et al.*, 1981) by changing the injection liner. For separation, a 5 m × 0.53 mm I.D., 2.65 μm film thickness, HP-1 fused silica open tubular column (Hewlett-Packard, USA) was used. Operating conditions varied greatly in different studies and relevant details are given in Table 1. For GC-MS analysis, the Finnigan GCQ GC/MS was employed at 70 eV. The chromatographic column was DB-5, 30 m × 0.25 mm I.D., 0.25 μm film thickness, J & W Scienti-

Table 1. Instrumental conditions of GC and GC/MS for benfuresate

Experiment 1: Instrumental conditions A

Instrument: HP 5890 series II equipped with HP 3396A Integrator (Hewlett Packard, U.S.)
Inj.: 70, 200, 250°C
Det.: FPD-S mode, 225°C
Oven: 30°C/min
70°C → 200°C
Column: HP-1, 5 m × 0.53 mm (i.d.) × 2.65 μm,
Carrier: N_2 14 ml/min.
Fuel: H_2 75 ml/min. Air 100 ml/min.
Injection volume: 2.0 μl, splitless/on-column injection

Experiment 2: Instrumental conditions B

Instrument: HP 6890 equipped with HP GC Chemstation (Rev. A. 06.01 [403]) (Hewlett Packard, U.S.)
Inj.: 200°C
Det.: ^{63}Ni-electron capture detector, 225°C
Oven: 30°C/min
70°C → 200°C
Column: HP-1, 5 m × 0.53 mm (i.d.) × 2.65 μm,
Carrier: N_2 14 ml/min.
Injection volume: 2.0 μl, splitless

Experiment 3: Instrumental conditions C

Instrument: Finnigan GCQ GC/MS (U.S.)
Column: DB-5, 30 m × 0.25 mm × 0.25 μm
Temp: Inj.: 70, 200, 250°C
MS: 225°C
Oven: ① 30°C/min
70°C → 200°C min
② 5°C/min 10°C/min
180°C → 200°C → 250°C (30 min)
Transfer line: 280°C
EI$^+$ mode: 70 eV
Analyzer: Ion-trap

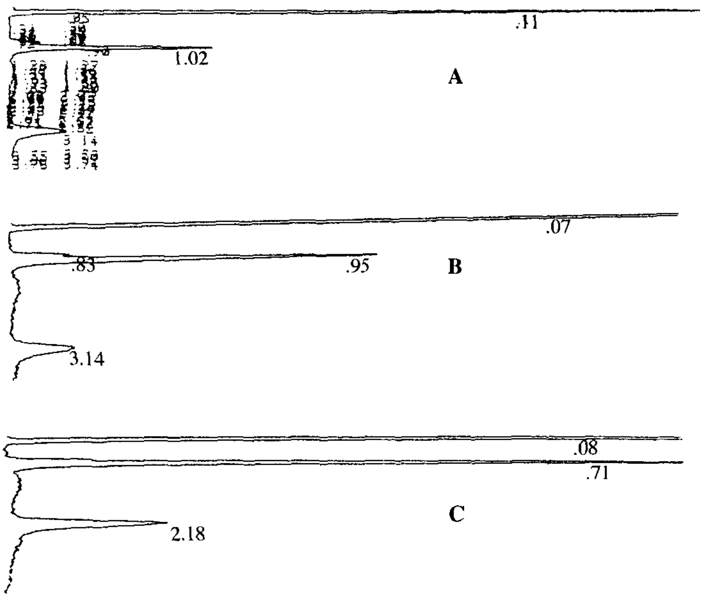

Fig. 1. Chromatograms of benfuresate at different injection temperatures without on-column injection system in GC-FPD. Injection temperature; A: 70°C, B: 200°C, C: 250°C

fic, Folsom, CA, USA), and sample injection was carried out with the split/splitless injector.

RESULTS AND DISCUSSION

GC analysis

Under the conditions of Experiment 1 (Table 1), benfuresate was not detected using the split/splitless injector, but there were possible evidences that benfuresate was decomposed during the analysis. Chromatograms showed the same pattern though experiments were carried out under different temperature conditions of the injector, there were two peaks were recorded at the same retention time and relatively different peak height at 70, 200, and 250°C of injector temperatures (Fig. 1). The solvent blank showed no peak except for solvent itself. Three assumptions were made: ① impurities of the standard material, ② decomposition or adsorption of benfuresate onto the injection liner, and ③ benfuresate is not sensitive and selective to the detector.

As the on-column injector was used, only a single

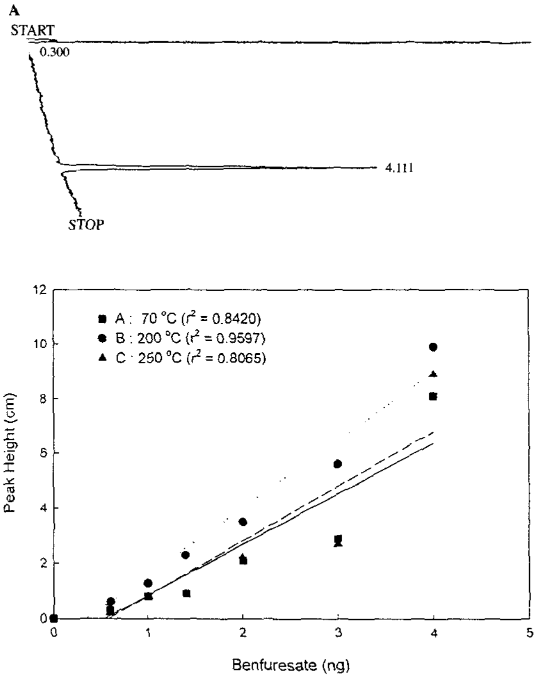

Fig. 2. A chromatogram and a standard calibration curve of benfuresate using the on-column injector at different injection temperatures.
Injection temperature; A: 70°C, B: 200°C, C: 250°C

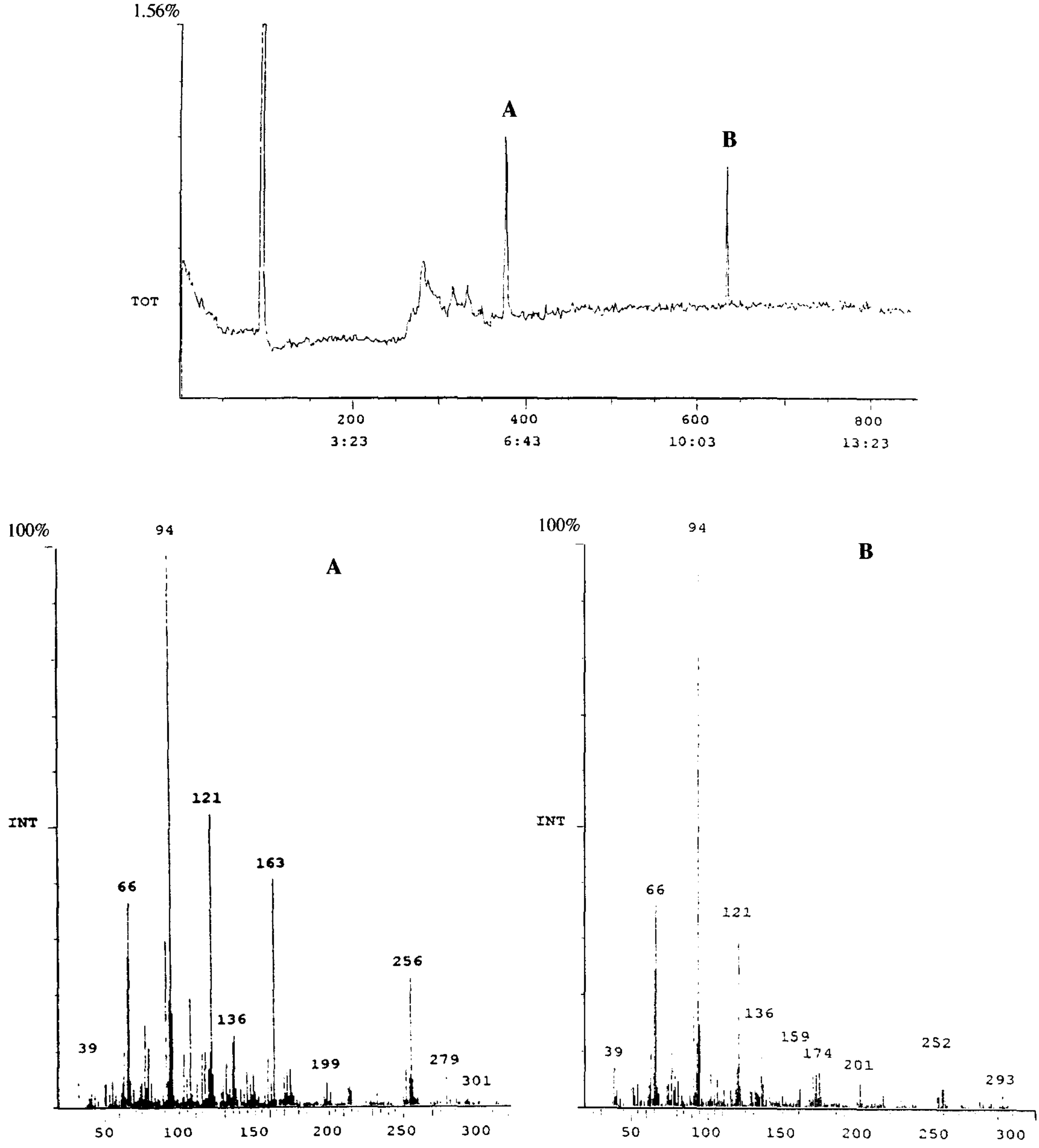

Fig. 3. A total ion chromatogram and MS spectra of benfuresate (A) and its decomposed compound (B).

peak was expected. However, at 70 and 250°C injector temperatures, linearity of the calibration curve of the benfuresate standard solution was not good as 200°C. However, at 200°C, only one single peak was observed, and the calibration curve showed a significant correlation at the level with $R^2 = 0.9597$ (Fig. 2).

Sulfur-containing compounds could be detected using the electron capture detector with a rather low sensitivity (Grob, 1977) To detect benfuresate using GC-ECD, experiments were carried out under the same conditions of Experiment 2. The similar chromatograms were obtained through the GC-FPD ana-

Table 2. Thermal decomposition ratio of benfuresate during the GC/MS analysis

Concentration (ng/μl)	Benfuresate (%±SD)	Decomposed benfuresate (%±SD)
0*	0	0
100	55.5±0.1	44.5±0.1
200	56.5±0.1	43.5±0.1
500	56.0±0.1	44.0±0.1
Mean	56.0±0.1	44.0±0.1

*solvent blank test

lysis. The on-column injection device could not be applied in this experiment due to instrumental installation problem related to electronic pressure control system. Hence clear-cut evidence for thermal decomposition of benfuresate at the injector was not observed, but GC/MS analysis without the on-column injection system showed decomposition of benfuresate at all injector temperatures tested. In particular, injector temperature 250°C, unknown compounds possessing m/z patterns similar to benfuresate (Fig. 3) was found at 44% portion of whole benfuresate (Table 2).

CONCLUSION

Thermal instability and readily decomposible characteristcs of benfuresate resulted in poor GC/FPD chromatograms. The major factors causing poor chromatogram were temperature of the injector and injector type, but these problems could be resolved using the on-column injector with the application of the Chauhan and Dabre's device. In the case of conventional injection in GC-FPD, GC-ECD, and GC/MS from 70 to 250°C, there were two peaks showing the similar patterns. Through the GC/MS analysis, decomposition was identified by the ratio of 56 : 44 (parent : decomposed benfuresate) The recommended GC injector type and temperature are on-column and 200°C.

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