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## Note

# Gas chromatographic determination of fenitrothion and some other organophosphorus pesticides in technical materials and formulations

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Fenitrothion (Sumithion) is an organophosphorus compound widely used in many countries for agricultural, public health and household purposes. It is formulated as emulsifiable concentrates, water-dispersible powders, dusts and other products, and also in combination with other insecticides and fungicides.

In this paper we describe a gas chromatographic (GC) method for the determination of fenitrothion and some other organophosphorus pesticides in technical materials and formulations.

## EXPERIMENTAL

The GC conditions are given in Figs. 1 and 2. The pesticides analysed were products of the author's company and fluoranthene was purchased from Tokyo Kasei (Tokyo, Japan).

## RESULTS AND DISCUSSION

Generally, organophosphorus compounds are labile at higher temperatures and we tested various GC columns and conditions to establish the optimal parameters for the reliable analysis. We checked fourteen packed columns containing 10% Apiezon L (1 m), 10% Apiezon N (1 m), 10% SF-96 (1 m), 10% HV grease (1 m), 10% SE-52 (1 m), 2% OV-17 (1 m), 2% XE-60 (1 m), 2% QF-1 (2 m), 7.5% OV-210 (1 m), 0.5% castor wax (1 m), 2% LAC-2R-446 (0.5 m), 0.5% FFAP (1 m), 3% PPE-7R (1 m) and 3% PPE-6R (1 m). Fenitrothion technical materials contain positional isomers due to the nitrocresol moiety and it is important to separate them from the fenitrothion peak. Although many of the columns tested gave poor separations and partial decomposition of fenitrothion was observed, QF-1, OV-210, PPE-6R and PPE-7R gave successful chromatograms. Analytical methods with QF-1 and OV-210 have already been reported[1,2]. Dibutyl sebacate is used as an internal standard for both columns, but it contains small amounts of impurities that emerge after the peak of the internal standard and interfere in the analysis. Therefore, we selected PPE-7R as the liquid stationary phase and fluoranthene as the internal standard. The separation of fenitrothion and the internal standard is better than with OV-210 or QF-1, and one chromatogram can be completed within 40 min.

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Fenitrothion like other organophosphates tends to decompose at high temperatures, and it is important to set the temperatures of the injection port and column oven at the optimal values. The peak-area ratios of fenitrothion to the internal standard were measured at various temperatures. When the injection port temperature was set at 220°C the peak-area ratio was almost constant at column temperatures between 170 and 190°C, but at 200°C it decreased markedly, which was attributed to partial decomposition of fenitrothion in the gas chromatograph. Therefore, the column temperature was selected as 180°C. For injection port temperatures between 200 and 250°C the peak-area ratios were constant but at 270°C marked degradation was observed. Therefore, the injection port temperature was selected as 220°C. We have used a 3% PPE-7R column for checking the quality of technical materials for several years. However, as PPE-7R may not be available in the future, we recommend

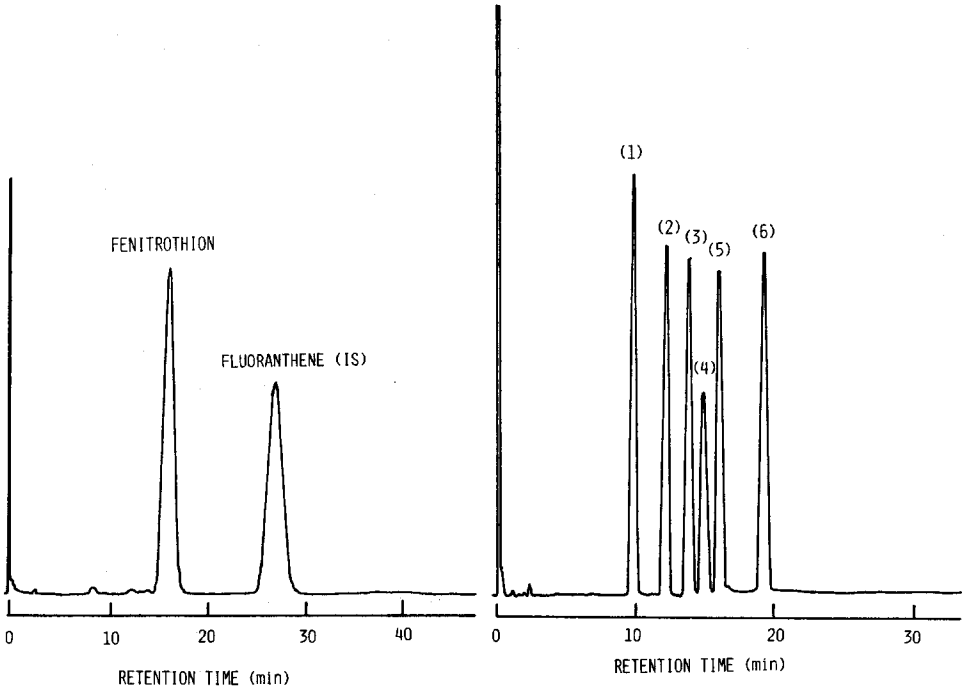


Fig. 1. Gas chromatogram of technical-grade fenitrothion. GC conditions: Shimadzu GC-7A chromatograph equipped with a flame-ionization detector; glass column, (1 m × 3 mm I.D.), packed with 3% PPE-6R on Chromosorb W AW, DMCS (60–80 mesh); column temperature, 180°C; injection and detector temperatures, 220°C; carrier gas, nitrogen at 50 ml/min; hydrogen, 50 ml/min; air, 700 ml/min; sensitivity, $10^2 \times 16$ ($1.6 \cdot 10^{-9}$ A full scale); injection volume, 1 μl (8.5 mg/ml, chloroform).

Fig. 2. Gas chromatogram of organophosphorus pesticides. (1) 2-Methoxy-4H-1,3,2-benzodioxaphosphorin 2-sulphide (fenfosphorin); (2) O-4-cyanophenyl O,O-dimethylphosphorothioate (cyanophos); (3) O-2,6-dichloro-4-methylphenyl O,O-dimethylphosphorothioate (tolclofos-methyl); (4) diethyl (dimethoxythiophosphorylthio)succinate (malathion); (5) O,O-dimethyl O-4-nitro-*m*-tolylphosphorothioate (fenitrothion); (6) O-ethyl O-5-methyl-2-nitrophenyl-*sec*.-butylphosphoramidothioate (butamifos). GC conditions as in Fig. 1 except column packed with 3% PPE-7R on Chromosorb W HP (80–100 mesh); column temperature, programmed from 150 to 220°C at 4°C/min; sensitivity, $10^3 \times 4$ ($4 \cdot 10^{-9}$ A full scale); and injection volume, 1 μl (10 mg/ml, chloroform).

PPE-6R instead of PPE-7R, as it is recommended as a liquid stationary phase for WHO collaborative work (November 1982).

A successful chromatogram has been obtained with PPE-6R as shown in Fig. 1, which is almost identical with the chromatogram obtained with PPE-7R phase. A linearity check was carried out under the recommended GC conditions by using a 3% PPE-6R column. Fenitrothion standard solutions gave almost the same correction factors, and the plots of the peak-area ratio of fenitrothion to fluoranthene against their weight ratio were straight lines passing through the origin. Good results were obtained for technical materials, emulsifiable concentrates and water-dispersible powders, with precisions of 0.2–0.3%.

Other pesticides such as fenfosphorin, cyanophos, butamifos and tolclofos-methyl were also analysed by GC. They are labile at higher temperatures and under alkaline conditions and the GC conditions were tested in the same manner as for fenitrothion by taking into account both the separation of impurities from the active ingredients and the reproducibility of the chromatogram. A PPE-7R column was found to be the most suitable for these purposes. Fig. 2 shows a temperature-programmed gas chromatogram. The technical materials were analysed with a precision of 0.2–0.3% with suitable internal standards: dibutyl phthalate for fenfosphorin, dipropyl phthalate for cyanophos, dibutyl terephthalate for tolclofos-methyl and *p*-benzyldiphenyl for butamifos.

We conclude that a PPE-7R or 6R column is suitable for the analysis of both fenitrothion and other organophosphates.

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