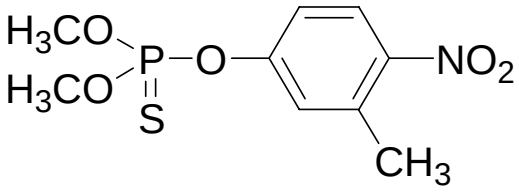
FENITROTHION

35



ISO common name	Fenitrothion
Chemical name	*O,O*-Dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate (IUPAC) *O,O*-Dimethyl *O*-(3-methyl-4-nitrophenyl)-phosphorothioate (CA)
CAS No.	122-14-5
Empirical formula	$C_9H_{12}NO_5PS$
RMM	277.2
b.p.	109°C at 13.3 Pa, 164°C at 133 Pa isomerizes on distillation
v.p.	700 mPa (6.0 x 10^{-6} Torr) at 20°C
d_4^{20}	1.308
Reflactive index n_D^{25}	1.5528
Solubility	Practically insoluble in water, soluble in most organic solvents, e.g. acetone, alcohol, chlorinated hydrocarbons
Description	Brownish yellow liquid
Stability	Hydrolyzed by alkali. Do not store at temperatures above 40°C because the material will isomerize

FENITROTHION

35/TC/m3/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 HPLC. Use the HPLC method below. The retention time of fenitrothion for the sample solution should not deviate by more than 0.2 min from that of the calibration solution.

2.2 Infrared. Prepare a film between NaCl plates and scan from 4000 to 600 cm^{-1}. The spectrum produced from the sample should not differ significantly from that of the standard.

3 Fenitrothion

OUTLINE OF METHOD Fenitrothion is determined by normal phase high performance liquid chromatography using a CN column, UV detection at 268 nm and external standardisation.

REAGENTS

n-Hexane HPLC grade

1-Butanol

Diluting solvent *n*-hexane – 1-butanol, 50 + 50 (v/v)

Mobile phase *n*-hexane – 1-butanol, 100 + 1 (v/v)

Fenitrothion working standard technical product of certified purity. Store refrigerated.

Calibration solution Prepare calibration solutions in duplicate. Weigh (to the nearest 0.1 mg) into a volumetric flask (100 ml) approximately 100 mg (*s* mg) of fenitrothion working standard. Make up to volume with diluting solvent. Mix thoroughly. Transfer by pipette 5.0 ml of this solution into a volumetric flask (20 ml) and make up to volume with diluting solvent. Mix thoroughly (Solutions C_A and C_B).

APPARATUS

High performance liquid chromatograph equipped with a detector suitable for operation at 268 nm, constant-temperature column compartment and an injector capable of delivering 10 µl.

Column 250 x 4.6 (i.d.) mm, stainless steel, packed with Zorbax CN (5 µm), or equivalent.

Electric integrator or data system

PROCEDURE

(a) Liquid chromatographic conditions (typical):

Column	stainless steel, 250 x 4.6 (i.d.) mm, packed with Zorbax CN (5 μm), or equivalent.
Mobile phase	*n*-hexane – 1-butanol, 100 + 1 (v/v)
Temperature	40°C
Flow rate	1.0 ml/min
Detector wavelength	268 nm
Injection volume	10 μl
Retention time	fenitrothion: about 10 min

(b) Linearity check. Check the linearity of the detector response by injecting 10 μl of solutions with fenitrothion concentrations 0.5, 1 and 2 times that of the calibration solution before conducting analysis.

(c) System equilibration. Prepare two calibration solutions. Inject 10 μl portions of the first one until the peak areas obtained for two consecutive injections differ by less than 1.0 %. Then inject a 10 μl portion of the second solution. The response factor for this solution should not deviate by more than 1.0 % from that for the first calibration solution, otherwise prepare new calibration solutions.

(d) Preparation of sample solution. Prepare sample solutions in duplicate for each sample. Weigh (to the nearest 0.1 mg) into a volumetric flask (100 ml) sufficient sample to contain about 100 mg (*w* mg) of fenitrothion. Make up to volume with diluting solvent. Mix thoroughly. Transfer by pipette 5.0 ml of this solution into a volumetric flask (20 ml) and make up to volume with diluting solvent. Mix thoroughly (Solutions S_A and S_B).

(e) Determination. Inject in duplicate 10 μl portions of each sample solution bracketing them by injections of the calibration solutions as follows; calibration solution C_A, sample solution S_A, sample solution S_A, calibration solution C_B, sample solution S_B, sample solution S_B, calibration solution C_A, and so on. Measure the relevant peak areas.

(f) Calculation. Calculate the mean value of each pair of response factors bracketing the two injections of a sample and use this value for calculating the fenitrothion contents of the bracketed sample injections.

$$f_i = \frac{s \times P}{H_S}$$

$$\text{Fenitrothion content} = \frac{f \times H_w}{w} \text{ (g/kg)}$$

where:

f_i = individual response factor
f = mean response factor
H_s = peak area of fenitrothion in the calibration solution
H_w = peak area of fenitrothion in the sample solution
s = mass of fenitrothion working standard in the calibration solution (mg)
w = mass of sample taken (mg)
P = purity of fenitrothion working standard (g/kg)

Repeatability r = 22 g/kg at 940 g/kg active ingredient content
Reproducibility R = 29 g/kg at 940 g/kg active ingredient content

4 *S*-METHYL FENITROTHION. As for **35**/TC/m3/3 except:

change 'REAGENTS' as follows:

S-Methyl fenitrothion analytical standard of known purity. Store refrigerated.

Calibration solution Prepare calibration solutions in duplicate. Weigh (to the nearest 0.1 mg) into a volumetric flask (100 ml) approximately 100 mg (s mg) of *S*-methyl fenitrothion analytical standard. Make up to volume with diluting solvent. Mix thoroughly. Transfer by pipette 5.0 ml of this solution into a volumetric flask (100 ml) and make up to volume with diluting solvent. Mix thoroughly. Furthermore, transfer by pipette 5.0 ml of this solution into a volumetric flask (200 ml) and make up to volume with diluting solvent. Mix thoroughly. (Solutions C_A and C_B).

change 'PROCEDURE' as follows:

(a) Liquid chromatographic conditions (typical):
Retention time *S*-methyl fenitrothion: about 20 min

(b) Linearity check. Check the linearity of the detector response by injecting 10 µl of solutions with *S*-methyl fenitrothion concentrations 0.5, 1 and 2 times that of the calibration solution before conducting analysis.

(c) System equilibration. Prepare two calibration solutions. Inject 10 µl portions of the first one until the peak areas obtained for two consecutive injections differ by less than 5.0 %. Then inject a 10 µl portion of the second solution. The response factor for this solution should not deviate by

more than 5.0 % from that for the first calibration solution, otherwise prepare new calibration solutions.

(f) Calculation. Calculate the mean value of each pair of response factors bracketing the two injections of a sample and use this value for calculating the *S*-methyl fenitrothion contents of the bracketed sample injections.

$$f_i = \frac{s \times P}{H_S} \times \frac{1}{200}$$

$$S\text{ - Methyl fenitrothion content} = \frac{f \times H_w}{w}\text{ (g/kg)}$$

where:

f_i = individual response factor
f = mean response factor
H_s = peak area of *S*-methyl fenitrothion in the calibration solution
H_w = peak area of *S*-methyl fenitrothion in the sample solution
s = mass of *S*-methyl fenitrothion analytical standard in the calibration solution (mg)
w = mass of sample taken (mg)
P = purity of *S*-methyl fenitrothion analytical standard (g/kg)

Repeatability r = 0.15 g/kg at 2.39 g/kg *S*-methyl fenitrothion content

FENITROTHION WETTABLE POWDER
35/WP/m3/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 HPLC. As for **35**/TC/m3/2.1

2.2 Infrared. Extract the sample with a suitable solvent, filter and evaporate the solvent with a stream of clean dry air. Proceed as for **35**/TC/m3/2.2.

3 FENITROTHION. As for **35**/TC/m3/3 except:
add 'APPARATUS' as follows:
Ultrasonic bath

change 'PROCEDURE *(d) Preparation of sample solution.*' as follows:
Prepare sample solutions in duplicate for each sample. Weigh (to the nearest 0.1 mg) into a volumetric flasks (100 ml) sufficient sample to contain about 100 mg (*w* mg) of fenitrothion. Add by measuring cylinder diluting solvent (80 ml) and place the flasks in an ultrasonic bath for about 10 min and allow to cool to ambient temperature. Make up to volume with diluting solvent. Mix thoroughly. Transfer by pipette 5.0 ml of this solution into a volumetric flask (20 ml) and make up to volume with diluting solvent. Mix thoroughly. Filter the supernatant through a 0.45 μm filter (Solutions S_A and S_B).

Repeatability r = 6 g/kg at 414 g/kg active ingredient content
Reproducibility R = 7 g/kg at 414 g/kg active ingredient content

4 *S*-METHYL FENITROTHION. As for **35**/TC/m3/4 except:

add 'APPARATUS' as follows:
Ultrasonic bath

change 'PROCEDURE *(d) Preparation of sample solution.*' as for **35**/WP/m3/3.

Repeatability r = 0.06 g/kg at 2.84 g/kg *S*-methyl fenitrothion content

FENITROTHION EMULSIFIABLE CONCENTRATE
35/EC/m3/-

1 Sampling. Take at least 100 g.

2 Identity tests
2.1 HPLC. As for **35**/TC/m3/2.1
2.2 Infrared. Evaporate to dryness with a stream of clean dry air. Proceed as for **35**/TC/m3/2.2.

3 FENITROTHION. As for **35**/TC/m3/3

Repeatability r = 18 g/kg at 476 g/kg active ingredient content
Repeatability r = 22 g/kg at 768 g/kg active ingredient content
Reproducibility R = 18 g/kg at 476 g/kg active ingredient content
Reproducibility R = 29 g/kg at 768 g/kg active ingredient content

4 *S*-METHYL FENITROTHION. As for **35**/TC/m3/4

Repeatability r = 0.07 g/kg at 3.02 g/kg *S*-methyl fenitrothion content
Repeatability r = 0.25 g/kg at 12.81 g/kg *S*-methyl fenitrothion content

FENITROTHION ULTRA-LOW VOLUME LIQUID
35/UL/m/-

1 Sampling. Take at least 100 g.

2 Identity tests
2.1 HPLC. As for **35**/TC/m3/2.1
2.2 Infrared. Evaporate to dryness with a stream of clean dry air. Proceed as for **35**/TC/m3/2.2.

3 FENITROTHION. As for **35**/TC/m3/3

Repeatability r = 29 g/kg at 466 g/kg active ingredient content
Repeatability r = 24 g/kg at 789 g/kg active ingredient content
Reproducibility R = 27 g/kg at 466 g/kg active ingredient content
Reproducibility R = 28 g/kg at 789 g/kg active ingredient content

4 *S*-METHYL FENITROTHION. As for **35**/TC/m3/4

Repeatability r = 0.04 g/kg at 1.30 g/kg *S*-methyl fenitrothion content
Repeatability r = 0.11 g/kg at 2.11 g/kg *S*-methyl fenitrothion content

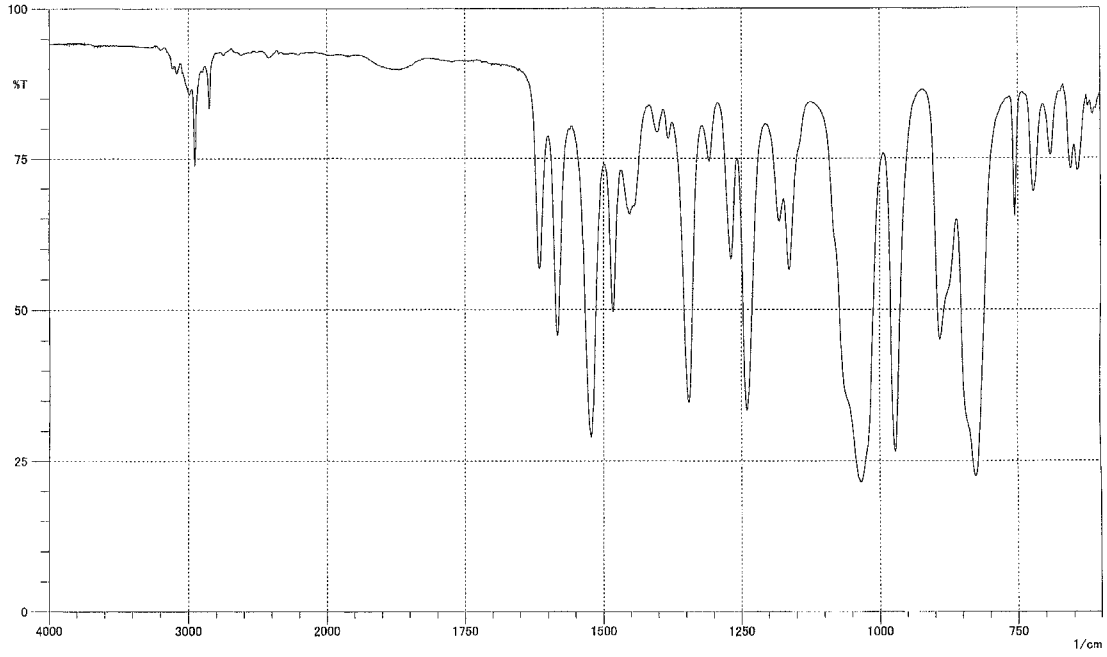


Fig.1 Infrared Spectrum of Fenitrothion

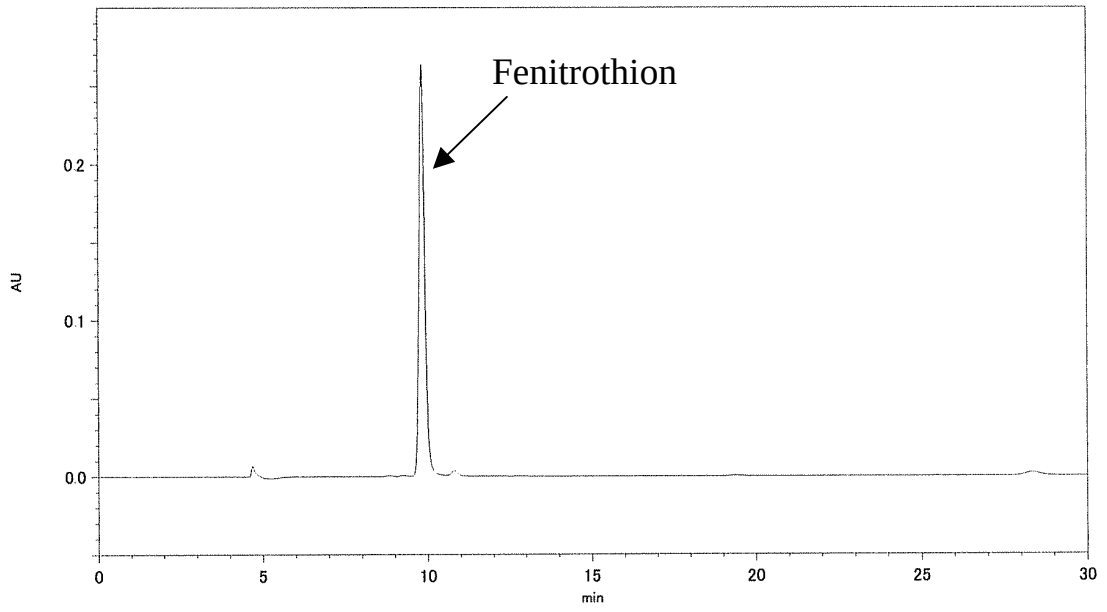
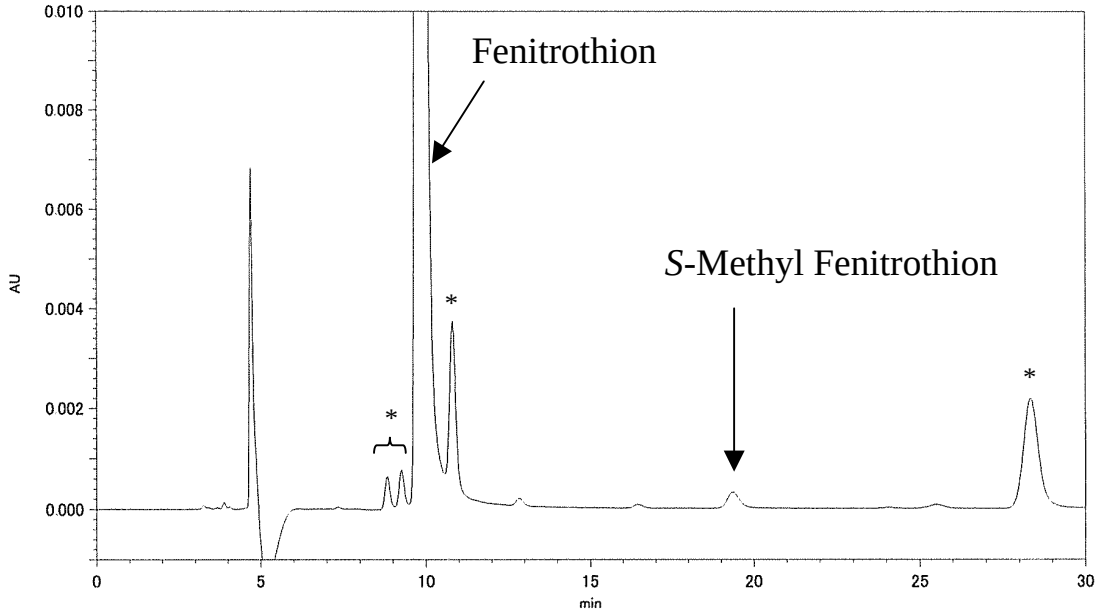


Fig.2 Example of Chromatogram of Fenitrothion



*: Impurities in Fenitrothion TC

Fig.3 Example of Chromatogram of *S*-Methyl Fenitrothion