ANALYSIS OF ENCAPSULATED FENITROTHION IN CONIFER FOLIAGE

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K.M.S. SUNDARAM and J. FENG

Forest Pest Management Institute

Canadian Forestry Service

Environment Canada

Sault Ste. Marie, Ontario

P6A 5M7

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INTRODUCTION

Indiscriminate and excessive use of insecticides in Canadian forest pest control programs have often fallen into disfavour with environmentalists and politicians. A need for improved application methods and formulation development has been recognized by forestry scientists and pesticide manufacturers in many countries. Various innovative approaches are being developed here and elsewhere which could eventually lead to maximum efficiency in spray technology with minimum hazards to the environment as a whole.

Development of an in-flight microencapsulation technique used recently (Sundaram *et al.* 1982), although still in the development stage, may be considered as one of the innovative methods providing a more efficient delivery of chemicals to intended targets in forestry. Such a technique, its proponents say, could provide:

(1) extension of the duration of effectiveness of the insecticide without increasing the rate of application,

(2) reduction of the hazard associated with the toxicant by preventing volatilization, photolysis, hydrolysis, etc. due to polymer coating,

(3) prolongation of the optimum residual activity of the chemical at the target site by controlled release,

(4) improvement of the pest-control efficiency by maximizing the targetability of the chemical and

(5) minimization of environmental pollution by reducing drift and associated side effects.

Recently Sumitomo Chemical Company of Japan, manufacturers of fenitrothion insecticide, which is extensively used at present in Canada (Nigam 1980) to control spruce budworm, *Choristoneura fumiferana* (Clem.), introduced a new flowable formulation containing the active ingredient (AI) mixed with polymeric materials and water. Table 1 lists the composition of the various ingredients present in the fenitrothion flowable (FF) formulation.

In a recently conducted experimental study, to investigate the distribution pattern and persistance of the new formulation in conifer trees, FF was mixed with water (64.4 wt %) and sprayed onto single white spruce trees [*Picea glauca* (Moench) Voss] using a reagent sprayer (Desaga Spray Gun, from Nachf. Erich Feeht. GmbH and

Table 1

Composition of Fenitrothion Flowable (FF) Formulation

Ingredients	Percent composition by wt.
Sumithion® Tech.	21.6
Polymeric materials	14.0
Water	64.4

Co., D-6900 Heidelberg 1, P.O. Box 101969). The technique of spray application onto single conifer trees was similar to the one discussed earlier (Sundaram and Hopewell 1977) except that the spray cloud was released in almost still air (maximum wind speed 8 m/min)

as a single puff in the centre portion of the tree canopy at *ca.* 40 cm above the apex. The spray droplets diffused in both horizontal and vertical directions, underwent partial evaporation, lost some of their volatile components and deposited on the conifer needles as partially encapsulated droplets which then eventually adhered to the foliar surface. Since no suitable method has been reported so far to quantify fenitrothion residues present in encapsulated materials on conifer needles, a need to develop a rapid and sensitive analytical method arose. This report presents a simple cleanup procedure, using ethyl acetate as extraction solvent with final determination by NPD-GLC for quantifying the AI in the encapsulated droplets found on spruce needles. The method is fast, simple and economical and should provide a basis for the analysis of fenitrothion from a large number of different forestry substrates with few modifications.

MATERIALS AND METHOD

Reagents

(a) Solvents

Ethyl acetate and acetone redistilled from glass (available from Caledon Laboratories Ltd., 40 Armstrong Ave., Georgetown, Ontario L7G 4R9).

(b) Acid-treated charcoal:

Prepared as per the method used by Watts *et al.* (1969) and Brown (1975). Slurry 200 g Nuchar SN (Fisher Sci. Co.) charcoal with 500 mℓ concentrated HCℓ, stir with a magnetic bar and boil for 1 hr. Cover the mixture with a watch glass while heating. Add 500 mℓ

distilled water, stir, and boil for an additional 30 min. Collect the charcoal in a Buchner funnel and wish it with distilled water until washings are neutral to universal indicator paper.

(c) Whatman CF-11 cellulose powder.

Available from Fisher Scientific Co.

(d) Silane-treated glass wool.

Supplied by Applied Science Lab. Inc. or Chromatographic Specialties Ltd.

(e) Adsorbent mixture.

Mix in the following weight proportions: 4 parts acid-treated charcoal and 10 parts cellulose powder. Grind and mix well for homogenity. Keep sealed.

(f) Fenitrothion standard.

Analytical grade of 99.9% purity supplied by Sumitomo Chem. Co. of Japan. Prepare the standard solutions in ethyl acetate containing 3.85 and 0.385 µg/mℓ.

(g) Eluting solution.

Ethyl acetate redistilled from glass.

(h) Sodium sulphate. (anhydrous, granular and A.C.S. certified)

Supplied by Fisher Scientific Co., Cat. No. S-421.

Apparatus

(a) Hobart food cutter (Model No. 84142)

Supplied by Hobart Mnf. Co., Toronto.

(b) Polytron PT-20.

Supplied by Brinkmann Instruments (Canada) Ltd., 50 Galaxy Blvd., Rexdale, Ontario M9W 4Y5.

(c) Evaporative concentrator. Büchi Rotavapor RE

Supplied by Canlab, 80 Jutland Road, Toronto, Ontario M8Z 2H4

(d) Nalgene Tefzel ETFE® centrifuge tubes (50 mℓ).

Supplied by Canlab.

(e) Centrifuge. Damon/IEC Division HN-S model

Supplied by Fisher Scientifc Co., 184 Railside Road, Don Mills, Ontario, M3A 1A9

(f) Mini-chromatographic columns. Pasteur type Fisherbrand® pipets 0.8 x 15 cm size supplied by Fisher Scientific Co. (Cat. No. 13-678-8).

(g) Gas Chromatograph

Type	:	Hewlett Packard model 5710A
Detector:	:	N/P specific
Detector mode	:	P
Detector temp.	:	300°C
Inlet Temp.	:	250°C
Oven Temp.	:	200°C
Column	:	120 cm x 4.0 mm I.D. glass coiled borosilicate glass with 1.5% OV-17 + 1.95% OV-210 on Chromosorb W "HP", 80/100 mesh (supplied by: Chromatographic Specialties Ltd. 300 Laurier Blvd., Brockville, Ontario K6V 5W1).
Carrier gas	:	He at 30 mℓ/min
Hydrogan flow rate	:	4 mℓ/min
Air flow rate	:	70 mℓ/min

Sample Preparation and Extraction

Carefully remove the conifer needles from twigs using scissors and shred the foliage in a Hobart food chopper. Weigh 5 g aliquots of the foliage in Nalgene Tefzel centrifuge tubes. Extract four times with ethyl acetate (20 mℓ each time) by homogenizing 1 min for the first extraction and 30 sec for the subsequent extractions using a high speed blender (Polytron PT-20). Centrifuge each homogenate at 1250 x g for 5 min. Decant all the liquid carefully through a 1 x 3 cm Na_2SO_4 (granular, anhydrous) column having a silanized glass wool plug at the bottom. Collect the pooled ethyl acetate extract (*ca.* 80 mℓ) in a 100 mℓ volumetric flask. Rinse the column with 10 mℓ of the extractant and make up the solution to 100 mℓ. Shake well for uniform concentration (1 mℓ = 0.05 g of foliage).

Microcolumn Cleanup

Plug the microcolumn (Pasteur pipet) with a small quantity of silane-treated glass wool. Place 3 cm adsorbent mixture, tamp well for uniform packing and top it with a small wad of the glass wool. Pre-wash the column with 5 mℓ of ethyl acetate. Transfer (pipet) 5 mℓ (0.25 g foliage, fresh weight) aliquot of sample extract onto the column. Elute with 20 mℓ of ethyl acetate. Collect the eluate in a 50 mℓ round bottom flask and flash evaporate to a small volume. Transfer quantitatively the concentrated eluate to a graduated centrifuge tube (15 mℓ capacity) and concentrate under a gentle air jet to 2 mℓ or less for GC analysis.

Prepare a calibration curve for fenitrothion by injecting into GC different volumes (1 to 5 μℓ) of the standard solution at suitable concentrations and plot peak heights against insecticide mass in ng. Inject 2 or 4

µℓ aliquots of the cleaned up extract, measure the peak height and compute the concentration of fenitrothion in the foliage from the calibration curve.

The typical set up of the microcolumn cleanup used in this analysis and the chromatograms obtained for the standard, blank and fortified foliar extracts and a field sample following the cleanup procedure are given in Figs. 1 to 5.

RESULTS AND DISCUSSION

Pre-spray as well as untreated control samples of spruce foliage were fortified with fenitrothion at two different levels and subsequently analysed as described. The rates of recovery were quantitative and are given in Table 2. No gas chromatographic response interfering with fenitrothion (retention time, RT 5 min) was detected in the pre-spray and control foliage samples. The detection limit for the chemical was 0.005 ppm based on wet weight. Under the experimental conditions discussed above, the method reported here is rapid, economical and suited for analyzing conifer needles which contain appreciable amounts of coextractive impurities such as terpenes and plant waxes. The active material was well separated and resolved (RT 5 min) from other impurities (Figs. 2 to 5) present in the final concentrate which indicates that the cleanup technique developed and utilized in this study is applicable and deserves consideration for analyzing forestry substrates. The method is especially useful when large numbers of samples have to be analyzed with speed, accuracy and economy soon after the field season.

Work is currently progressing in the following areas to improve the microcolumn cleanup technique.

(1) Evaluation of different adsorbents (alumina, silica, Florisil®, synthetic resins, etc.).

(2) Optimum length and volume of adsorbents or adsorbent mixtures to maximize cleanup efficiency and minimize the loss of AI.

(3) Extension of the technique for multiresidue analyses incorporating insecticides with a wide range of polarity by selecting appropriate solvent and adsorbent systems.

(4) Comparison of the present technique with the other similar approaches utilized by Brown (1974) and Getz and Hill (1980).

(5) Extension of the technique to encompass herbicides along with insecticides to develop a wider multiresidue methodology for pesticides used in forestry.

Extracts of sprayed conifer needles were analysed after cleanup using the microcolumn method described here. Results are given in Table 3. The recoveries were good and did not appear to vary much within each analysis.

Ethyl acetate appears to be an excellent extracting solvent for fenitrothion in conifers. Not much of the wax is removed from the needle and the little that is extracted is predominantly retained by the column and is not precipitated when the solution is concentrated prior to analysis.

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Table 2
Recovery of Fenitrothion from Untreated Fortified Spruce Foliage

Fortification level (ppm)	Percent recovery ($\bar{X}$ ± S.D., n = 4)
0.385	93.7 ± 2.9
3.85	102.3 ± 5.8

Table 3
Fenitrothion Residues in Spruce Foliage After Spraying with the New Flowable Formulation

Time after spraying (days)	Fenitrothion concn. (ppm - fresh wt.)*
0.25	216.3
1.0	154.6
3.0	8.92
12.0	5.20
35.0	1.38

*Mean of multiple separate analyses and the deviation from the mean was less than 5%.

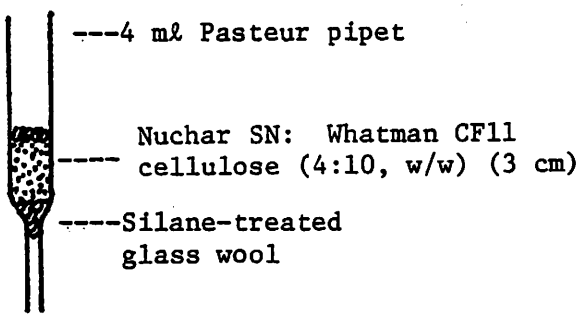

Fig. 1. Micro cleanup column.

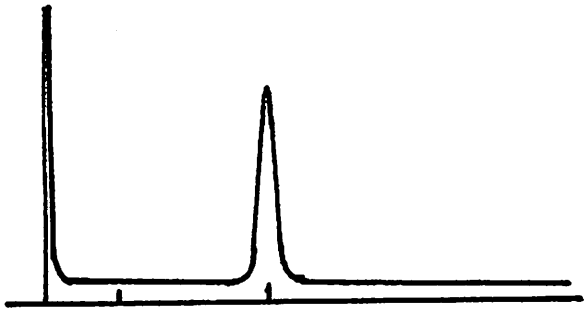

Fig. 2. Chromatogram of fenitrothion standard (4 ng in 4 µℓ)

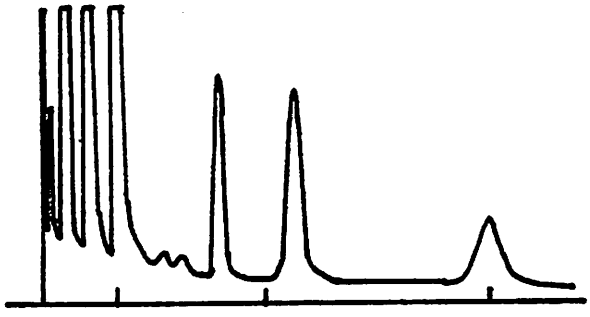

Fig. 3. Chromatogram of unfortified foliar extract without cleanup.

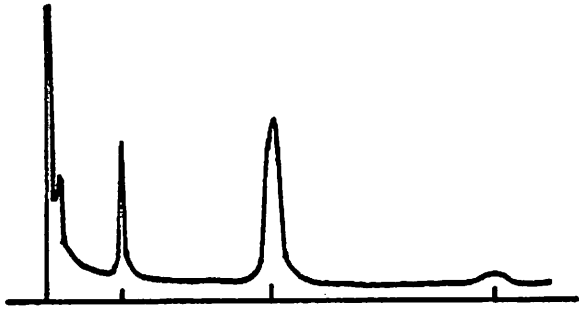

Fig. 4. Chromatogram of fenitrothion fortified foliar extract following micro-column cleanup.

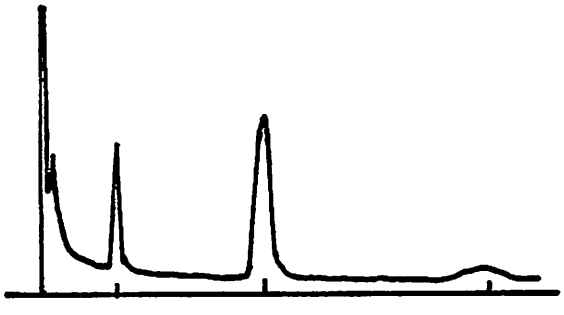

Fig. 5. Chromatogram of a field sprayed foliar sample following microcolumn cleanup.