



FENITROTHION RESIDUES IN
THE AQUATIC ENVIRONMENTS OF
NEW BRUNSWICK FORESTS

by

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INTRODUCTION

Fenitrothion (0, 0-dimethyl 0-4-nitro-m-tolyl phosphorothiate) was introduced in 1959 as an experimental insecticide by the Sumitomo Chemical Company, Japan. Since 1969, it has been used in operational sprays in Canada to control lepidopterous defoliators. Its use as an operational larvicide has caused direct and indirect contamination of the aquatic ecosystem (Eidt and Sundaram, 1974; Kingsbury, 1973).

Constant vigilance is needed to protect this environment. A good method of monitoring the aquatic habitat for pesticide contamination is by analysing water samples collected from sprayed areas for fenitrothion residues by gas liquid chromatography (g.l.c.). G.l.c. is generally the method of choice for quantitation of fenitrothion and the use of specific phosphorus detectors, such as the flame photometric detector (f.p.d.), eliminates the need of cleaning up water extracts.

During the 1976 spray program, twenty-seven water samples were collected from the fenitrothion sprayed forest areas in New Brunswick Forests by Dr. Eidt of the Maritimes Forest Research Centre (M.F.R.C.) and sent to the Pesticide Laboratory at the Chemical Control Research Institute (C.C.R.I.) in Ottawa for analysis. This report contains a brief summary of the analysis made at C.C.R.I.

MATERIALS

Anhydrous granular sodium sulphate (Baker analysed) was obtained from Canlab. It was heated overnight at 160°C to remove moisture, cooled in a dessicator and stored in tightly sealed glass stoppered reagent bottles. All solvents used were either nanograde or glass distilled supplied by Caledon Laboratories Ltd.

METHOD

Twenty-seven water extracts in chloroform from M.F.R.C. were received June 15, 1976 in good condition and stored immediately in a cold room (0°C) until analysis could be performed. The samples were to be analysed for fenitrothion. Background information included date, time of sampling, pH and temperature as well as the grade and amount of chloroform used in the extraction.

Each sample bottle was checked for leakage and the contents was measured. Since almost all samples contained noticeable amounts of water, it was necessary to pass the extractant through a 20g column of sodium sulphate. This being done the sample was flash evaporated gently to dryness. The residues were dissolved in benzene and transferred quantitatively to a centrifuge tube for g.l.c. analysis. Concentrations of the insecticide were determined by measuring the chromatogram height and reading the concentration from a calibration curve prepared to same day using standard fenitrothion solutions (analytical grade, supplied by Sumitomo Chemical Co.). Results are recorded in Table 1.

G. L. C. CONDITIONS

Column:	20% OV-101 on Chromosorb W Mesh 80/100 4' x 0.25" o.d. x 2mm i.d. glass column
Instrument:	5710A H.P.
Detector:	FPD - P mode
Temperature (°C):	Oven - 214 Detector - 200 Injection Port - 250
Gas Flows (ml/min.):	H ₂ - 210 Air - 60 O ₂ - 30
Carrier Gas (ml/min.):	N ₂ - 30
Attenuation:	64
Range:	100
Chart Speed (in/min.):	0.5
Chart Span (mV):	1.0
Retention Time (min.)	4.00

DISCUSSION

Samples

The chloroform extracts of the water samples received from M.F.R.C. varied significantly from the theoretical value (see Table 1, Column 3). In one particular case, only 10% of sample was received and no bottle contained the theoretical amount of the extract. The average content of chloroform in the bottles was *ca* 64%. The losses have been probably due to evaporation while extraction and storage. It was reported that water samples contained considerable amount of natural detergents in them causing heavy foaming during the partitioning with chloroform. While separating the phases, loss of chloroform could have occurred.

The original water samples had been divided into duplicate samples. One set of samples were analysed here at C.C.R.I. the others were analysed by the Moncton Lab. There was agreement between the two labs. in all but one sample M-1 (21/76/344/329). Our value was 0.22 ppb while the Moncton Lab. was 0.001 ppb. The value and calculations of M-1 were checked. It was concluded that there was no error on our part.

G.L.C.

Various stationary phases have been used for the analysis of fenitrothion such as SE 30, DC 200, OV 17 and SE 30/QF 1. It has been found advantageous to use a 20% OV 101. The high loading provides a longer time for the pesticide to remain in the liquid thus a better partitioning and the OV 101 has an upper limit of 350°C compared to 250°C for DC 200 thereby providing a low bleed rate and minimizing detector contamination. The OV 101 also separates the metabolites fenitrooxon and S-methyl fenitrothion from the parent compound. The relative retention times of fenitrooxon, fenitrothion, and S-methyl are 0.78, 1.00, and 1.45 respectively.

The chromatogram was relatively free from extraneous peaks except for samples extracted with A C S grade chloroform. In these cases the fenitrothion peak was shouldered by secondary peaks. (See figures 2 and 3). It is advisable to use only nonograde or glass distilled solvents in the future to avoid this problem.

There was a slight increase in sensitivity as seen in the calibration curve (figure 4) during the second day of fenitrothion quantitation by g.l.c. This was probably due to the longer column conditioning done at the laboratory.

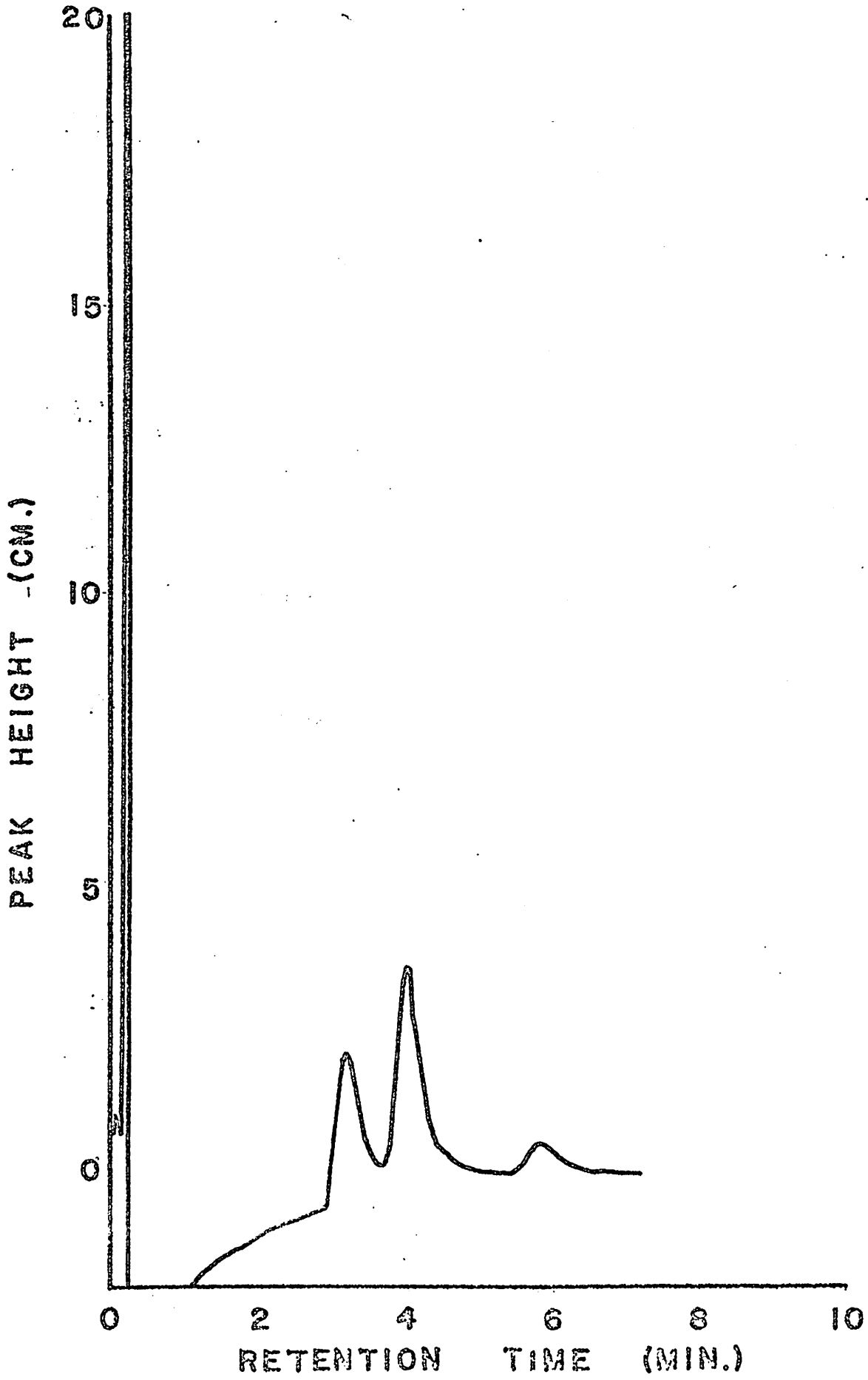


Figure 1. Fenitrothion mixed standard.

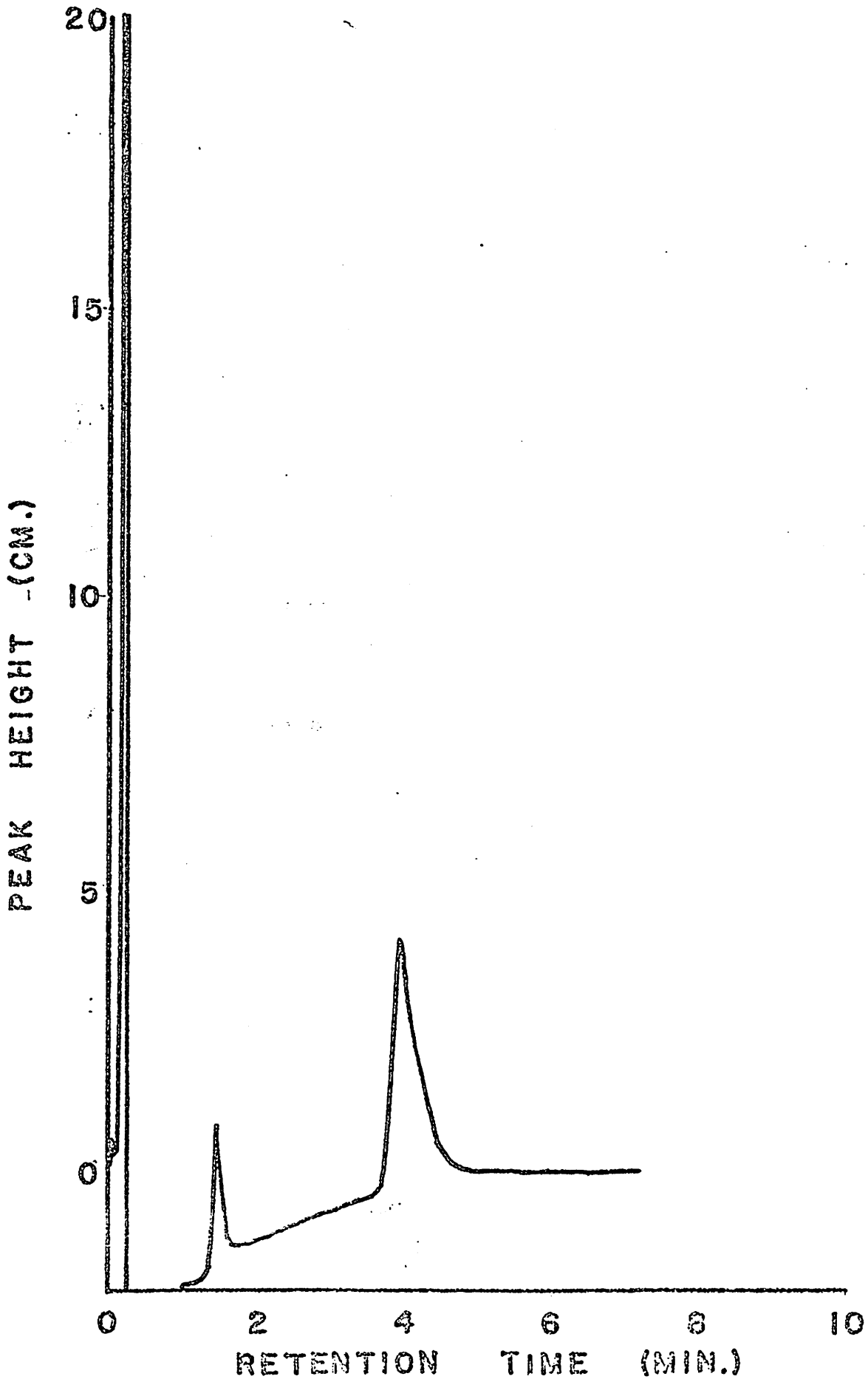


Figure 2. Sample H4 (21/76/340/325) extracted with nongrade chloroform.

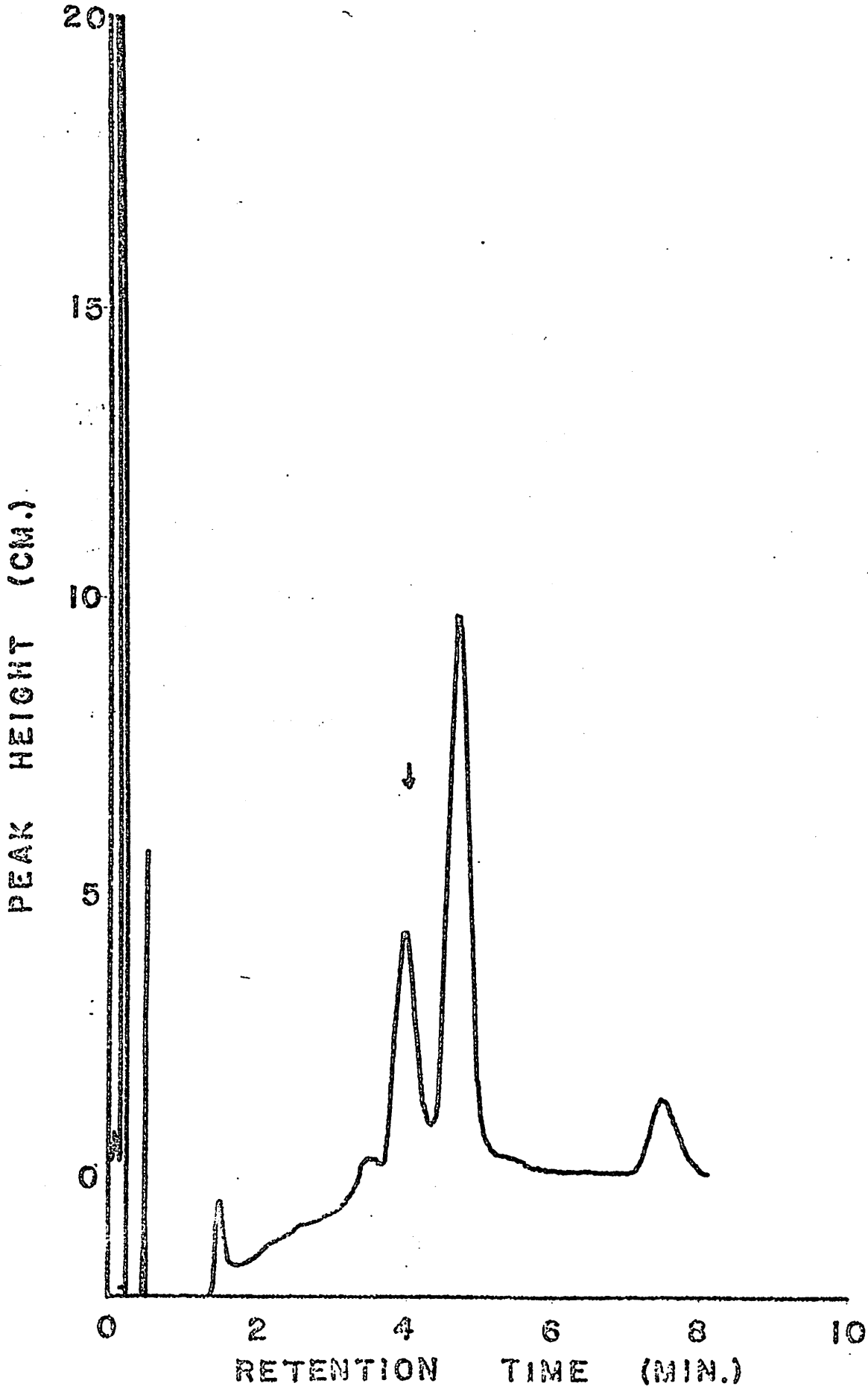


Figure 3. Sample 4M10 (21/76/354/339) extracted with A C S grade chloroform.

PEAK HEIGHT (cm.)

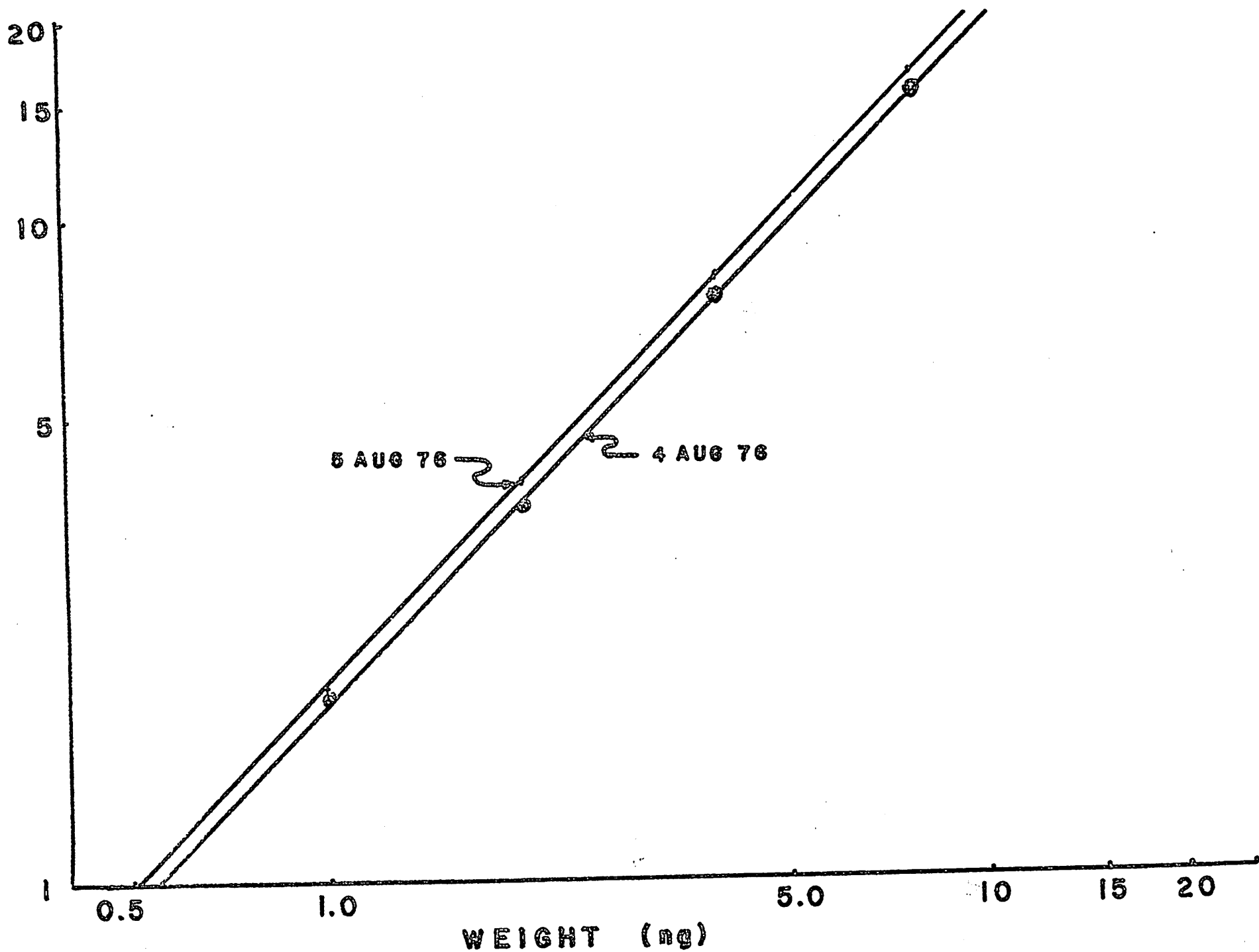


Figure 4. Fenitrothion calibration curve prepared 4th and 5th of August, 1976.

CONCLUSION

The results of any residue study are only as good as the sampling technique, extraction and clean-up methodology used. When large variations occur (> 20%) one must check each step of a procedure to insure minimum losses. Sample losses due to transportation can easily be rectified by checking that the screw caps are tightly closed. Losses incurred during the extraction process can be minimized by changing to a less volatile solvent. It is extremely important to use only nonograde or glass distilled solvents since impurities in lower grade solvents often mask the results. If efforts are made to improve areas of concern the final results will be meaningful.

REFERENCES

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