Determination of *m*-sec-butylphenyl *N*-methyl-*N*-thiophenylcarbamate (RE-11775) in Water, Soil and Vegetation

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Since the compound m-sec-butylphenyl N-methyl-N-thiophenylcarbamate (RE-11775, Chevron Chemical Co.) is of interest in California as a moquito larvacide, a method suitable for measuring its residues in the order of 0.01 ppm is required to determine its persistence in aquatic environments. A procedure is reported here suitable for the extraction, cleanup, and determination by gas chromatography of RE-11775 at levels of 0.01 ppm in water, soil, and grass and 0.1 ppm in alfalfa. As no cleanup was required for very dirty pond water at the 0.01 ppm level, it appears that much lower levels could be measured, if desired, by using larger samples and perhaps some cleanup. Lower levels could probably be determined in alfalfa, too, but this possibility was not investigated.

Materials and Procedures

Water. Samples of very turbid pond water, irrigation water, and tap water were fortified with RE-11775 at levels of 0.01, 0.1, 0.2, and 1.0 ppm. At the 0.01 ppm level, 300 ml of water was shaken in a separatory funnel with consecutive 50, 25, and 25 ml portions of methylene chloride. The combined extracts were passed through a 5-cm layer of anhydrous sodium sulfate, then taken almost to dryness in a rotary vacuum evaporator at 50°C water-bath temperature. The last traces of solvent were removed with a gentle current of air and the residue was taken up in benzene for injection into the gas chromatograph. At levels of 0.1 ppm and above 50 ml of water was extracted by shaking with 50 ml of chloroform; methylene chloride and chloroform are equally satisfactory for extraction of the compound from water.

There were no interfering glc peaks in tap water, irrigation water, or reasonably clean pond water. One pond water sample, highly colored, and containing considerable quantities of decaying organic matter, required cleanup. This was accomplished by passing the benzene solution (5 ml volume) through a 5-g column of Florisil deactivated by adding 15% water and eluting

with 100 ml of benzene. The eluate was concentrated as before to proper volume for injection into the gas chromatograph.

Soil. Fifty g samples of soil were mixed with 50 g of anhydrous sodium sulfate and blended with 150 ml of methylene chloride for 10 minutes. The solvent was decanted through a filter into a round-bottomed flask and the blending repeated two more times with 150 ml of solvent each, filtering the extracts into the same flask. The solvent was removed as described previously and the residue was dissolved in 5 ml of benzene. At the 0.01 ppm level, 100-g samples were used, with 200-ml volumes of solvent. Samples were cleaned up by the procedure used for water.

Pond bottom mud required a different procedure because of the high water content and the large amount of decomposing organic matter and miscellaneous debris. A 50-g sample of mud was blended with 250 ml of acetonitrile for 10 minutes and the solvent-water mixture was filtered through a 5 mm layer of Hyflo Supercel in a Buchner funnel, with suction. The solution was transferred to a separatory funnel, 700 ml of water was added, and the solution was extracted by shaking with 3 successive 50-ml portions of hexane. The combined hexane extracts were evaporated almost to dryness in a rotary vacuum evaporator at 50°C, the residual solvent was blown off, and the residue was dissolved in 5 ml of ethyl acetate.

A column (20-22 mm diameter) was prepared by pouring into it a slurry of 8 g of silicagel (Woelm, activity grade 1) in 50 ml of ethyl acetate. When the solvent level reached the top of the adsorbent a slurry of 6 g of Nuchar-Attaclay was added and the solvent head was again just allowed to reach the top of the adsorbent. The sample solution was then poured into the column, eluted with 200 ml of ethyl acetate, and the eluate was concentrated to one ml with a rotary vacuum evaporator.

Grass and Alfalfa. The plant material was chopped and 50-g subsamples were blended for 10 minutes with 300 ml of acetonitrile containing 30% water. The macerate was filtered on a Buchner funnel through a 5 mm pad of Hyflo Supercel, the filtrate was transferred to a separatory funnel, and 400 ml of water and 20 ml of saturated sodium sulfate solution were added. The solution was then equilibrated with 3 successive 50-ml portions of hexane that were passed through a 2-cm layer of anhydrous sodium sulfate and combined, then concentrated to about 5 ml in a rotary vacuum evaporator.

A 20-22 mm diameter column containing 20 g of alumina, activity grade II, was packed dry, pre-wet with benzene, and the sample was introduced and eluted with 200 ml of benzene. The eluate was then concentrated to the required volume for injection for glc analysis.

Gas Chromatography. A gas chromatograph equipped with a Melpar flame photometric detector operated in the sulfur-sensitive mode was used although some samples were also run in an instrument equipped with an electrolytic conductivity detector for nitrogen, with equally good results. Both instruments were equipped with 3-ft columns packed with 5% OV-225 on Gas Chrom Q, 60/80 mesh. A ¼" stainless steel column was used for the sulfur detector and a 6 mm OD glass column for the nitrogen detector. The columns appeared to be equally acceptable. For sulfur detection the column, detector, and injection port temperatures were 242°C, 200°C, and 252°C, respectively; the carrier gas was nitrogen at 100 ml/min. For nitrogen detection the column, injection block, and furnace temperatures were 195°C, 240°C, and 840°C, respectively; hydrogen carrier and sweep gas flow rates were 100 ml/min and 125 ml/min, respectively.

The conditions for operation are not critical and the optimums may differ in different instruments. With the above operating parameters for sulfur detection, the retention time was 2.2 min and the peak was sharp with only slight tailing. Only one peak was observed with either detector, suggesting that there was no breakdown of the compound on the columns. The minimum detectability was 3 ng of RE-11775, this amount giving a signal more than 5 times the noise level.

Results and Discussion

The recoveries of RE-11775 from the various substrates are given in Table I. The recovery levels were all reasonably consistent and at acceptable levels, the pond bottom mud being the most difficult to extract and cleanup.

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TABLE I

Percent recoveries of RE-11775
(meta-isomer) added to various substrates

Substrate	Level of fortification (ppm)						
	1	0.5	0.2	0.1	0.05	0.02	0.01
Tap water	99-107						
Ditch water				110			
Pond water			120		95-104		
Pond Water (very dirty)					98-104		105
Hanford loamy sandy	99						85
Mocho silt loam				93-98			
Sandy loam, high organic matter				89			
Mud				80-122			
Alfalfa	80-83			80-85			
Grass		70-76		75-76		81	