Matacil Residue Determination in Foliage, Fish, Soil, and Water

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A method for detecting Matacil residue in foliage, fish, soil, and water has been developed. After the residue was extracted from the sample, the Matacil was partitioned between organic and aqueous solutions for cleanup. Matacil was then derivatized with 1-fluoro-2,4-dinitrobenzene and detected by gas chromatography with an electron capture detector. Recoveries from foliage, fish, and soil fortified at 0.05 ppm and from water fortified at 0.01 and 0.005 ppm ranged from 68 to 127%. The lower limit of detection was <0.01 ppm for foliage, fish, and soil and was <0.001 ppm for water.

Matacil [4-(dimethylamino)-3-methylphenol methylcarbamate; aminocarb] is an insecticide which is being used in various experimental and operational forest spray programs in the United States and Canada for the control of insect pests such as the spruce budworm (*Chlorestoneura fumiferana* Clemens). There is a need for a method to determine any residue of Matacil in samples such as foliage, fish, soil, and water so that the distribution and persistence of Matacil in different components of the forest environment can be determined.

A method for residues of Matacil in foliage, soil, water, and fish was developed (Sundaram et al., 1976). The sensitivity of this method was 0.5 ppm in foliage, because of an interference peak, 0.1 ppm in soil, and 0.001 ppm in water. In addition, Matacil was derivatized with heptafluorobutyric anhydride to provide a compound which could be detected with high sensitivity with an electron capture detector; this procedure necessitates the removal of all water from the sample prior to derivatization. The reagent is moisture sensitive, the temperature at which the derivatization is done is critical, and the derivative of heptafluorobutyric anhydride and Matacil is unstable.

This paper describes a method for detecting the residue of Matacil in foliage, fish, soil, and water which does not require the use of a moisture-sensitive reagent for derivatization of Matacil, the temperature at which the derivatization is done is not critical, and the resultant derivative is stable.

EXPERIMENTAL SECTION

Apparatus. A Perkin-Elmer Sigma 3 gas chromatograph equipped with a ^{63}Ni electron capture detector was used. Borosilicate glass columns, 0.7 m × 2 mm i.d., were packed with 10% DC-200/2% OV-225 on 80–100-mesh Chromosorb W (HP) for the standard column and with 10% DC-200/1.5% QF-1 on 80–100-mesh Chromosorb W (HP) for the confirmatory column. Both phases were solution coated (Applied Science Laboratories, Inc., 1967), and each column was conditioned prior to use by purging the column with helium to remove oxygen, heating the column at 250 °C for 1 h with no carrier gas flow, and then heating the column at 250 °C for 16 h with carrier gas flow. Operating parameters were as follows: oven temperature, 250 °C; injection port temperature, 280 °C; detector temperature, 280 °C; carrier gas, 95% argon–5% methane, 40 mL/min.

A centrifuge equipped with a head and carriers suitable for 125-mL separatory funnels is desirable. If such a centrifuge is not available, the volumes during partitioning may have to be increased.

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A water bath at 38 °C and a silicone oil bath at 90 °C were needed.

Reagents. All organic solvents were pesticide grade. 1-Fluoro-2,4-dinitrobenzene (Aldrich Chemical Co.) was used for derivatization. (Do not allow this chemical to contact the skin as it is a skin irritant and cancer suspect agent.) Bromothymol blue indicator was prepared by dissolving 100 mg of bromothymol blue in 3.2 mL of 0.05 N sodium hydroxide and diluting the solution to 200 mL with deionized water. Phosphate buffer, pH 6, 0.07 M, was prepared by mixing 210 mL of pH 4.2 buffer (9.07 g of KH_2PO_4/1000 mL) and 40 mL of pH 8 buffer (17.8 g of $Na_2HPO_4 \cdot 7H_2O$/1000 mL). Sodium tetraborate, 5%, was prepared by dissolving 50 g of $Na_2B_4O_7 \cdot 10H_2O$ in water and diluting the solution to 1000 mL with deionized water. Sodium hydroxide, 0.1 and 1 N, and sulfuric acid, 0.1 N, solutions were prepared from reagent-grade chemicals.

Standards. A primary standard of Matacil was prepared by dissolving 20 mg of Matacil in 20 mL of ethyl acetate. Working standards were prepared by diluting the primary standard solution with ethyl acetate to obtain 2.5 and 2.0 μg/mL.

Procedure. *Extraction. Foliage, Fish, and Soil.* A 25-g sample was weighed into a 1000-mL boiling flask, 300 mL of 1,2-dichloroethane-methanol (1:1) (400 mL for foliage) was added to the flask, and the sample was heated at reflux for 1 h. The sample was cooled nearly to room temperature and filtered through a 9-cm Whatman No. 1 filter paper in a Büchner funnel. The filtrate was transferred to a 1000-mL flask and evaporated on a rotary vacuum evaporator at 38 °C to dryness or to any residual water.

The walls of the flask were rinsed with 40 mL of pH 6 buffer, and the rinse was transferred to a 125-mL separatory funnel. The flask was rinsed with 40 mL of dichloromethane, and the rinse was transferred to the separatory funnel. The separatory funnel was shaken for 30 s and centrifuged for 3 min if necessary. The dichloromethane was drained into another 125-mL separatory funnel which contained 40 mL of 0.1 N sulfuric acid. The second separatory funnel was shaken for 30 s and centrifuged for 3 min if needed, and the dichloromethane was discarded. The above partitioning procedure was repeated twice with fresh portions of dichloromethane, using the same sulfuric acid solution.

Extraction. Water. A 200-g sample was transferred to a 500-mL separatory funnel. The pH was adjusted to 7 with 0.1 N sodium hydroxide or 0.1 N sulfuric acid as needed. The water was then partitioned with 100 mL of dichloromethane by shaking the separatory funnel for 30 s. The phases were allowed to separate, and the dichloromethane was drained into a 250-mL separatory funnel which contained 50 mL of 0.1 N sulfuric acid. The second separatory funnel was shaken for 30 s, the phases were allowed to separate, and the dichloromethane was

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Table I. Percent Recovery of Matacil

sample	level, ppm	recovery, %
spruce foliage	0.05	84
maple twigs	0.05	74
maple leaves	0.05	127
leaf litter	0.05	83
fish, whole	0.05	68
fish, edible portion	0.05	94
fish, nonedible portion	0.05	79
soil	0.05	82
pond water	0.01	98
pond water	0.005	104
stream water	0.005	88

discarded. The above partitioning procedure was repeated twice with fresh portions of dichloromethane, using the same sulfuric acid solution.

Cleanup. Forty milliliters of ethyl acetate (50 mL for water samples) was added to the separatory funnel containing the sulfuric acid, and the separatory funnel was shaken for 30 s. The separatory funnel was centrifuged for 3 min if needed, and the sulfuric acid was drained into a 250-mL separatory funnel. Four drops of bromothymol blue was added to the solution, and 1 N sodium hydroxide was added dropwise until 1 drop turned the indicator blue. Then, 25 mL of pH 6 buffer was added. The solution was partitioned 3 times with 50-mL portions of dichloromethane. The dichloromethane was combined in a 300-mL flask and evaporated to dryness on a rotary vacuum evaporator at 38 °C. The last traces of solvent were removed with a stream of nitrogen.

Derivatization. A standard of Matacil (2.5 μg for foliage, soil, or fish or 2.0 μg for water) was begun here. The solvent was evaporated with a stream of nitrogen.

To a 125-mL separatory funnel were added 1 mL of acetone, 0.1 mL of 1-fluoro-2,4-dinitrobenzene, 10 mL of sodium tetraborate, and 10 mL of 2,2,4-trimethylpentane.

The separatory funnel was shaken for 30 s, the phases were allowed to separate, and the aqueous layer was drained into the flask containing the residue after evaporation of solvent. One milliliter of 1 N sodium hydroxide was added to the flask, and the flask was stoppered securely and heated in the oil bath for 30 min. The flask was cooled to room temperature, the contents were transferred to a 125-mL separatory funnel, and 5.0 mL of 2,2,4-trimethylpentane was added to the separatory funnel. The separatory funnel was shaken for 30 s, the phases were allowed to separate, and the aqueous phase was discarded. The 2,2,4-trimethylpentane was washed twice with 10-mL portions of 1 N sodium hydroxide and twice with 10-mL portions of water. About 4 mL of the 2,2,4-trimethylpentane was then transferred to a glass-stoppered tube, and the sample was reserved for GC.

Gas Chromatography. A 5-μL aliquot of derivatized Matacil standard or of sample was injected into the standard or confirmatory column. The derivatized Matacil was identified by its retention time (5.5 min on the standard column or 5.7 min on the confirmatory column), and the ppm of MATACIL was calculated by comparing the response of a sample to the response of the corresponding standard.

RESULTS AND DISCUSSION

Either a reflux or a Soxhlet extraction was necessary to remove Matacil residues from aged samples. The reflux extraction was chosen for the procedure as it was quicker and required simpler glassware than did the Soxhlet extraction.

Table II. Stability of Matacil Residue[a] under Frozen Storage Conditions

sample	interval, days	decomposition, %
spruce needles	187	11
fish	193	28
sandy loam	183	7
pond water	208	8

[a] Original concentration was 1 ppm.

In the separation procedure, Matacil was partitioned from aqueous solution into dichloromethane and from the dichloromethane into an acidic solution. The acidic solution was further cleaned up with an ethyl acetate wash, after which the acidity was adjusted to neutrality, and Matacil was partitioned from the aqueous solution into dichloromethane. This sequence of partitionings between aqueous and organic solutions provided good cleanup.

Other derivatizing reagents than heptafluorobutyric anhydride were considered as possibilities for the detection of Matacil residues. These reagents included benzenesulfonyl chlorides (Moye, 1975), trichloroacetyl chloride (Stanley et al., 1972), and 1-fluoro-2,4-dinitrobenzene (Holden, 1973). The derivatives formed with the first two were found to be unsuitable for Matacil whereas the 2,4-dinitrophenyl ether derivative formed with 1-fluoro-2,4-dinitrobenzene was found to be suitable. The derivatization procedure of Matacil with 1-fluoro-2,4-dinitrobenzene (Holden, 1973) was altered slightly to provide more consistent derivatization and better cleanup of the derivative. The reagent is washed with 2,2,4-trimethylpentane just before use to remove reagent peaks. The derivative is formed in aqueous solution, so there is no need to eliminate water from the sample before derivatization. The derivative is stable for at least 1 week.

The response of the electron capture detector was linear to at least 4 ng of Matacil. Samples containing Matacil at a level higher than 4 ng in the aliquot injected should be diluted and reinjected.

Recoveries of Matacil from duplicate samples of foliage, fish, and soil fortified at the 0.05-ppm level and from water fortified at the 0.01- and 0.005-ppm levels were better than 65% as shown in Table I. Control values were <0.01 ppm for foliage, fish, and soil and <0.001 ppm for water.

Loss of Matacil from samples which had been fortified with Matacil and stored at −20 °C for ~200 days was 7–11% for pond water, sandy loam, and spruce needles and was 28% for fish as given in Table II.

The described method for residues of Matacil in environmental samples is convenient and rapid and gives improved sensitivity and ease of operation over previous methods for Matacil.

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