

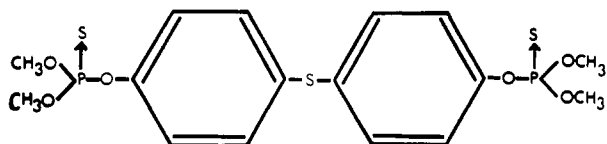
Gas Chromatographic Determination of Abate Residues in Water

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A gas chromatographic method for determining Abate (*O,O,O',O'*-tetramethyl-*O,O'*-thiodi-*p*-phenylene phosphorothioate) in water is described. After extraction and cleanup, the insecticide is concentrated in a small volume of chloroform. Average

recoveries of about 70% were obtained from water fortified with known amounts of the insecticide. The method will detect residues as small as 0.05 p.p.m.

Abate (*O,O,O',O'*-tetramethyl-*O,O'*-thiodi-*p*-phenylene phosphorothioate) is an insecticide that is to be used to control mosquito larvae in natural waters. The chemical structure for this compound is:



In practice, this insecticide is adsorbed on sand and added directly to the water to produce low concentrations, usually less than 1.0 p.p.m. This insecticide was studied by Blinn and Pasarela (1966) to determine its residual behavior in water and adjacent mud. Their procedure determines a hydrolysis product, 4,4-thiodiphenol, by a colorimetric method. These studies indicated the presence of only trace amounts of the metabolic products (Blinn and Pasarela, 1966).

The objective of this study was to develop a procedure for the glass chromatographic determination of Abate in water, with an immediate applicability to toxicity studies, in which the compound was added to the drinking water of cattle and sheep in amounts up to 20 p.p.m.

MATERIALS AND METHODS

Reagents. **EXTRACTION SOLVENT.** The chloroform used was redistilled in glass.

ABATE (COMPOUND 52,160). *O,O,O',O'*-tetramethyl-*O,O'*-thiodi-*p*-phenylene phosphorothioate 93.3% standard, 86.2% technical, and 43% emulsifiable concentrate (American Cyanamid Co., Princeton, N.J.).

EMULSIFIER. Triton X-100 (Rohm and Haas, Philadelphia, Pa.).

NITROGEN. Repurified (Matheson Co., Inc., LaPorte, Tex.).

Apparatus. **CHROMATOGRAPH.** Wilkens Aerograph Model 204 equipped with hydrogen flame ionization detector (Varian Aerograph, Walnut Creek, Calif.).

RECORDER. Westronics, Model LD11A, Dual Pen (Micro-Tek, Baton Rouge, La.).

COLUMN. Coiled stainless steel, 1/8-inch O.D. × 6-foot packed with 60- to 80-mesh Chromosorb W coated with 5% Dow 11 silicone. Preconditioned for at least 24 hours prior to use.

HYDROGEN GENERATOR. Aerograph Model 650 (Varian Aerograph, Walnut Creek, Calif.).

Standard Preparation. Prepare a series of Abate standards in redistilled chloroform ranging in concentration from 0.05 to 0.5 μg. per μl. Inject 2-μl. portions into the gas chromatograph and compare with those resulting from water extracts. Peak heights obtained were proportional to the concentration of Abate ranging from 8.0% for 0.10-p.p.m. standard to 53.0% for the 1.0-p.p.m. standard.

When Abate, adsorbed on sand, is placed in water, the insecticide is slowly mobilized into the water. If the compound is added directly to the water (not adsorbed on sand), it settles out rapidly. To keep the compound in suspension longer in the animal studies, one part of an emulsifier, Triton X-100, was mixed with two parts of the insecticide prior to adding to the water.

Extraction and Cleanup. Extract 1000-ml. aliquots for water samples expected to contain less than 5.0 p.p.m. Extract 100-ml. aliquots for water samples with expected concentrations greater than 5.0 p.p.m. Filter the aliquots

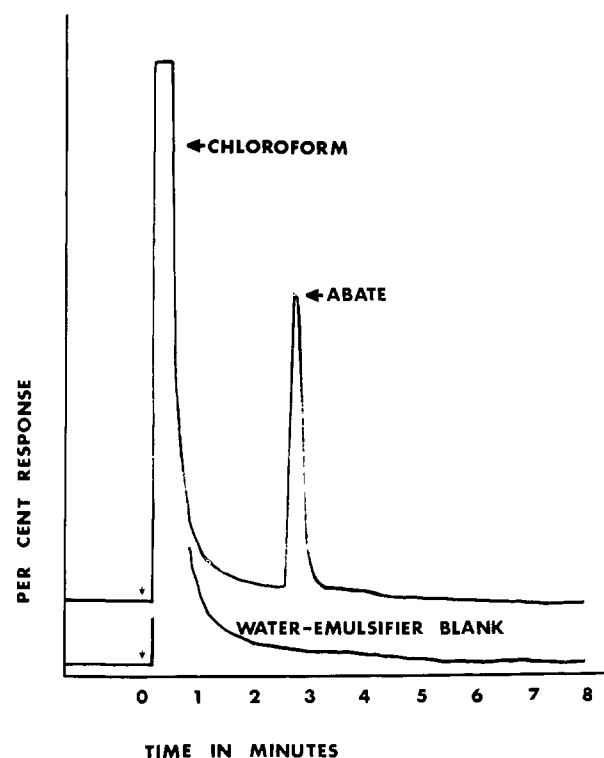


Figure 1. Gas chromatogram of extract of water sample containing Abate and emulsifier and water-emulsifier blank

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Table I. Per Cent Recoveries for Water Standards of Abate

Amount Added, P.P.M.	Volume Extracted, Ml.	Final Volume, Ml.	Amount Found, P.P.M.	Recovery, %
0.5	1000	1.0	0.34	68.0
1.0	1000	2.0	0.69	69.4
5.0	100	1.0	3.61	72.2
10.0	100	2.0	7.15	71.5
20.0	125	5.0	14.84	74.2

Triton X-100 was mixed with the insecticide (1 to 2) prior to addition to the water.

through glass wool into separatory funnels and make acid with 6*N* sulfuric acid (pH approximately 1.0). Extract the water samples with four successive portions of chloroform (one 50-ml. and three 25-ml. portions when extracting 1000-ml. samples; four 10-ml. portions when extracting 100-ml. samples). Wash the combined chloroform extracts with 0.1*N* sodium hydroxide (25 ml. for extracts of the 1000-ml. aliquots and 10 ml. for extracts of the 100-ml. aliquots). Evaporate the chloroform in a hood using an air stream and hot water bath to a volume expected to yield a concentration of approximately 0.5 mg. per ml. of Abate. Inject the concentrated extract (2 μ l. in the chromatograph used) into the gas chromatograph with the following conditions:

Detector. Hydrogen flame ionization detector; temperature, 300° C.

Column. 5% Dow 11 silicone on 60- to 80-mesh Chromosorb W in 6-foot \times $\frac{1}{8}$ -inch stainless steel.

Oven Temperature. Isothermal, 270° C.

Inlet Temperature. 305° C.

Carrier Gas. Nitrogen, 57 ml. per minute.

Chart Speed. 1.0 inch per minute.

DISCUSSION

The hydrogen flame detector response to various concentrations of the insecticide yielded a linear response for the range of concentration used.

The emulsifier, Triton X-100, did not interfere in the extraction or analysis of the insecticide (Figure 1).

The efficiency of the extraction procedure is shown in Table I. Average recovery for the water standards was approximately 70% from samples containing 0.05 to 20 p.p.m. of Abate.

To show that the peak in question was due to Abate rather than some of the inert materials in the technical material, chloroform standards of equal concentration were prepared from each of the available samples of Abate: technical (86.2 and 93.3%) and emulsifiable concentrate (43%). An identical single peak due to Abate with a retention time of less than 3 minutes was recorded on each chromatogram.

For water samples of unknown concentration, aliquots of at least 1000 ml. should be extracted. For extremely low levels of the insecticide, larger volumes of water can be extracted or the chloroform extract can be evaporated to a smaller volume.

In this study, the method detected concentrations of Abate as low as 0.05 p.p.m. in water. This method has been applied only to the drinking water of livestock that contained a minimum of organic materials. The probability of interference from organic materials that would be present in pond water is unknown.

LITERATURE CITED

Blinn, R. C., Pasarella, N. R., *J. Agr. Food Chem.* **14**, 152-6 (1966).

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