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Note

Determination of phosmet by high-performance liquid chromatography

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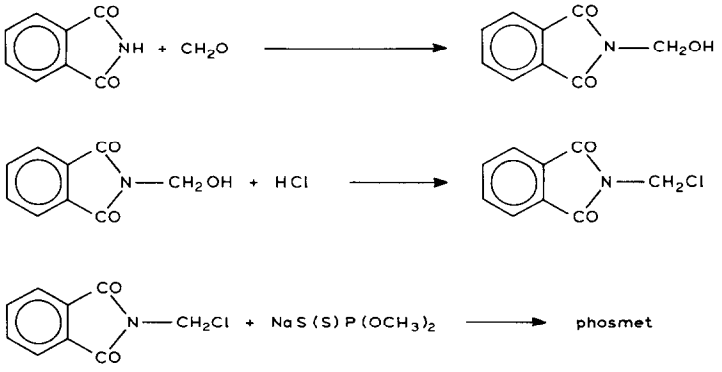
O,O-Dimethyl-S-phthalimidomethylphosphorodithioate, common name phosmet, is the active ingredient of an organophosphorus insecticide and acaricide known under the commercial names Imidan, Prolate, etc.

Since its discovery, a number of methods for its determination have been reported. A review of methods dealing with this compound in general was published by Batchelder *et al.*[1]. The spectrophotometric method[2,3] is currently the most commonly used for the analysis of technical samples. Although high-performance liquid chromatographic (HPLC) methods[4,5] have been described for the determination of the active ingredient of phosmet in mixtures with other pesticides, the methods do not include the determination of the most frequently occurring impurities in the technical product. Methods for the determination of residues of phosmet[6–10] are not applicable to the determination of technical product.

The HPLC method reported here permits the determination of phosmet and accompanying by-products, and the analysis of every stage of the synthesis of phosmet illustrated in the following scheme:



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EXPERIMENTAL

Chromatographic equipment

All separations were carried out on a Varian Model 8500 liquid chromatograph equipped with a syringe pump, connected to a dual-beam ultraviolet (UV) detector (Aerograph 254/280) and an A-25 dual-channel strip-chart recorder. Retention data and peak areas were measured and calculated by a Model 101 chromatography data system (Varian, Palo Alto, CA, U.S.A.).

A MicroPak CN-10 cyanopropyl-bonded phase column (Varian) (250 × 2 mm I.D.) with *ca.* 4500 theoretical plates was used.

Chemicals

The chemicals were of analytical-reagent grade. Solvents were freshly distilled before use and were purified by recommended methods[11]. The standards of phosmet, N-chloromethylphthalimide[12] and N-hydroxymethylphthalimide were prepared by the Division of Organic Chemistry of our Institute according to standard procedures. Their purities and structures were established by elemental analysis and standard physico-chemical techniques.

Mobile phase

The mobile phase consisted of 8% (v/v) of tetrahydrofuran in *n*-hexane.

Chromatographic conditions

The separations were performed in the isocratic mode at ambient temperature at a flow-rate 50 ml/h. The detector was operated at 280 nm and the chromatogram was recorded at a chart speed of 50 cm/h. The column pressure ranged between 4.5 and 5.0 MPa.

Internal standard solution

About 130 mg of diphenylamine were accurately weighed into a 100-ml volumetric flask, dissolved in tetrahydrofuran and diluted to the mark with THF.

Preparation of standard solution

About 130 mg of standard phosmet (or a mixture of phthalimide, N-chloromethylphthalimide and N-hydroxymethylphthalimide standards) were accurately weighed, dissolved in 5 ml of tetrahydrofuran in a 50-ml volumetric flask and exactly 10 ml of internal standard solution were added. The solution was then diluted to volume with *n*-hexane.

Sample solution

Into a 50-ml volumetric flask were accurately weighed about 150 mg of technical phosmet (or an appropriate amount of reaction mixture) and dissolved in 5 ml of tetrahydrofuran, then exactly 10 ml of internal standard solution were added and the solution was diluted to volume with *n*-hexane. A 1-g amount of anhydrous sodium sulphate was added to each solution and mixed well.

Chromatographic procedure

Volumes of 5 μl of the solutions were introduced on to the column with a microsyringe (Hamilton) through a stop-flow injector. Samples were prepared at concentrations such that 5-μl portions injected on to a column gave a suitable detector response. Standard solutions were injected until a precision of 1% was obtained for the peak-area ratio of phosmet to internal standard. To ensure that the same detector response and column conditions were maintained during the analysis time, duplicates of standards followed by duplicates of the sample were injected, then standards were injected at the end of the run.

Calculation

The internal standard method was used to convert peak areas into quantitative results.

RESULTS

The chromatographic separation of phosmet was carried out under a variety of conditions. Reversed-phase chromatography was found not to provide a satisfactory separation of phthalimide and N-hydroxymethylphthalimide and could cause a reaction of N-chloromethylphthalimide with the mobile phase. However, reversed-phase chromatography was useful in the HPLC analysis of the active ingredient. A MicroPak CH-10 column with methanol–water (1:1) as the mobile phase at a flow-rate 1 ml/min was satisfactory for the separation of phosmet.

The CN column with *n*-hexane–tetrahydrofuran (92:8) gave the best resolution. The chromatogram of a synthetic mixture is shown in Fig. 1.

Linearity of the chromatographic system was verified by injections of five solutions containing phosmet in the range 0.97–4.82 mg/ml plus 0.264 mg/ml of internal

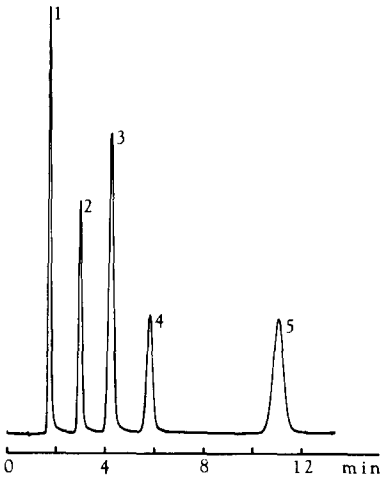

Fig. 1. High-performance liquid chromatogram of a synthetic mixture. Column, 250 × 2 mm I.D. MicroPak CN-10; eluent, *n*-hexane–tetrahydrofuran (92:8); flow-rate, 50 ml/h; detector, UV (280 nm). Peaks: 1 = diphenylamine (internal standard); 2 = N-chloromethylphthalimide; 3 = phthalimide; 4 = phosmet; 5 = N-hydroxymethylphthalimide.

standard. A correlation coefficient of 0.9998 was obtained when ratios of areas counts of phosmet divided by area counts of internal standard were plotted against concentration of phosmet.

The reproducibility of the method for a technical product and emulsifiable concentrate was checked on the basis of twelve repeated determinations and compared with the results of the spectrophotometric method. The range of reliability (for 95% and $n = 12$) was 83.31 ± 0.23% for the HPLC method and 82.06 ± 0.60% for the spectrophotometric method.

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