

The Determination of Ethyl *N,N*-Di-*n*-propylthiolcarbamate (EPTC) in Soil by Gas Chromatography

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A method of gas liquid chromatography (G. L. C.) analysis has been developed for residue quantities of ethyl *N,N*-di-*n*-propylthiolcarbamate (EPTC) in soil. This method has the advantage of being simpler and more rapid than previously reported methods. The principal limitation of the method is largely that of the sensitivity of the type of detector used in the gas chromatograph.

THE HERBICIDE ethyl *N,N*-di-*n*-propylthiolcarbamate, is commonly used as a preemergence or a preplanting herbicide. Its residual life in the soil depends upon soil type, moisture, temperature, degree of incorporation, and other factors (1, 3). For this reason, it is often of interest to determine the amount of EPTC remaining in the soil following treatment.

Analytical techniques for determination of EPTC have been developed by Batchelder and Patchett (2) and subsequently modified by Fang and Theisen (4). This method involves steam distillation of the sample followed by multiple extractions, hydrolysis of EPTC, and finally color development. Time could be saved and the multiple use of volatile flammable solvents avoided by a more direct method of analysis. The relatively low boiling point of EPTC indicates a high vapor pressure. This suggested that the chemical might be susceptible to determination by means of gas chromatography. The work reported here involves a study of the determination of residual amounts of EPTC in soil by gas chromatography. The apparatus used in this work was a Beckman Model GC-2 gas chromatograph.

Method

A weighed amount of soil (100 grams) and 80 ml. of water containing a known amount of EPTC were placed in a volatile oil determination apparatus as described by Fang and Theisen (4). The EPTC was then steam-distilled from the sample during a 4-hour interval. The distillate was continually extracted using 5 to 7 ml. of petroleum ether (Skelly F) which had been placed in the moisture trap. Since EPTC is appreciably soluble in water (402 p.p.m. at 28° C.), the volume of water used in the distillation should be as small as possible. At the end of the extraction

period, the water in the moisture trap was drawn off and the solvent was placed in a conical 15-ml. centrifuge tube. The centrifuge tube was then placed in a water bath and the solvent evaporated to reduce the volume to less than 0.5 ml., since sensitivity is increased by decreasing the sample volume. A small amount of anhydrous sodium sulfate was added to dry the solvent. A known amount of marker (5) or internal standard (*n*-nonyl ketone) was added in 50 μ l. of solvent. An aliquot of this sample was then injected into the GC-2 using a microliter syringe. The sample was chromatographed through a 4-foot Apiezon-L column which was packed with Celite, 80 to 200 mesh coated with Apiezon-L (25% w./w.). The ratio of the peak heights of the EPTC and the marker was then compared with the standard curve which had been previously prepared and the amount of EPTC present was determined.

The standard curve was obtained by plotting the ratio of the peak height of EPTC to the peak height of the marker as a function of the ratio of the amount of EPTC to a standard amount of marker in solution. In this way, by determining the ratio of peak heights in the unknown and knowing the amount of marker in the solution, it is possible to calculate the amount of EPTC in the solution without knowing the volume remaining in the centrifuge tube or the amount placed in the chromatograph.

For chromatography the column temperature was held at 160° C. with the attenuation set at 1, the filament current on the detector at 350 ma., and using helium, at 30 p.s.i., as carrier gas. Under these conditions, analysis of a sample required 15 minutes. A response of 5% full scale deflection was obtained with as little as 10 γ of EPTC introduced into the chromatograph. This was chosen as the limit of sensitivity of

the method, as it was felt that anything less than a 5% response was subject to too much error.

Results and Discussion

The partitioning of EPTC between water and solvent is an important factor determining the efficiency both of this method and that reported previously. However, preliminary experiments have shown that EPTC partitioned very favorably into the solvent, Skelly F. One hundred milliliters of water containing 20 p.p.m. of EPTC were partitioned against 10 ml. of Skelly F. In this case, 99.9% of the EPTC was extracted by the solvent. This indicated that a high degree of efficiency could be obtained in the distillation as described. However, it was found in the distillation procedure that recovery was lower as increasing amounts of water were used. In this work, EPTC was added to air-dry soil and only enough water was added to make free water visible on the surface of the soil. This required about 80 ml. of water to 100 grams of soil.

Recovery of the EPTC after evaporation of the solvent to less than 0.5 ml. was 94% using the solvent Skelly F. This recovery was constant, but lower (91%) using Skelly B (hexane), a higher boiling fraction. Recovery from two soil types was determined with the results being shown in Table I.

The recoveries presented in Table I have been corrected for the loss of EPTC experienced upon reducing the solvent to 0.5 ml. Shorter distillation times have been used successfully, particularly with larger amounts of chemical. Essentially quantitative recoveries have been obtained using 1000 γ of EPTC and 100 grams of soil with distillation times of 1 to 2 hours.

A comparison of recoveries with the method used to those obtained by the procedure described previously (2, 4)

Table I. Recovery of EPTC from Soil as Determined by Gas Chromatography

Soil Type	Weight, Grams	EPTC, γ		Recovery, %
		Added	Recovered	
Muck	100	200	194	97 \pm 2
	100	100	96	96 \pm 2
Sandy Loam	100	200	190	95 \pm 3
	100	100	93	93 \pm 2

showed that this method gave at least equally good recoveries of EPTC from soil. In the older method, recoveries of 81% using 2000 γ of EPTC were obtained in this laboratory. These recoveries were obtained by placing the receiver in an ice bath to reduce losses; without this precaution recoveries were even lower.

The lower limit of sensitivity of this method is determined by the sensitivity of the detector system in the gas chromatograph. The thermal conductivity cell used in the instrument employed in this

study requires at least 10 γ . Assuming that the lowest practical volume after dilution is 300 ml. and a sample volume of 50 ml. used for injection, one could detect as little as 60 γ of EPTC in a sample. Since 200- to 300-gram samples of soil can be as easily extracted as 100 grams, the practical sensitivity would be of the order of 0.2 p.p.m. in the soil.

Conclusions

An analytical method for EPTC in soil has been developed employing gas

chromatographic techniques. This method proved to be faster than previously reported methods and gives an average recovery of 95 \pm 2% on soil samples. The limits of sensitivity of this method are determined by the limitations of the instrument used.

Literature Cited

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HERBICIDE TOXICITY

Mammalian Toxicity of Sesone Herbicide

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Sesone herbicide has proved eminently successful as a means of killing weed seedlings without harming most established plants. As it is converted in the animal body to 2,4-dichlorophenoxyacetic acid, its metabolic pathway, in all probability, is that taken by the acid. By stomach intubation the compound is moderately toxic for rats. The results of repeated oral feeding of rats and dogs are presented and the various criteria of effect are summarized. These data support the statement that rats are not injured by 200 p.p.m. in their diet and are slightly injured by 600 p.p.m. when fed during their 2-year life span. In the dog a dosage of 9 mg. per kg. per day fed by capsule 5 days a week for 1 year, approximately equivalent to 360 p.p.m. in the dry diet, was tolerated without ill effect.

IN 1950 King, Lambrech, and Finn (9) reported an effective new chemical, sodium 2,4-dichlorophenoxyethyl sulfate (Sesone herbicide), for use as a soil treatment. It has the unique property of not harming most established plants when sprayed or dusted directly on the foliage at concentrations that kill seedlings in the soil. This means that crops in the field being treated, or in adjacent fields, are not subject to injury by drift during application. Studies on the rate of disappearance of this herbicide from soil under greenhouse conditions indicate the time required ranges from 12 to 30 days with 1 to 10 pounds per acre.

Carroll (1) has shown that the material is hydrolyzed readily to biologically

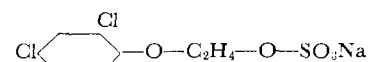
active 2,4-dichlorophenoxyethanol and sodium bisulfate in aqueous preparations at pH 3.0 to 4.0.

Vlitos (13) contends that the herbicidal activity of sodium 2,4-dichlorophenoxyethyl sulfate can be attributed to a reaction pathway involving either acid or enzymic hydrolysis to 2,4-dichlorophenoxyethanol followed by oxidation of the latter compound to 2,4-dichlorophenoxyacetic acid.

Sesone herbicide is being sold commercially as a pre-emergence treatment to prevent the growth of weeds on peanuts, bulb and corm crops, established strawberries and asparagus, and a large variety of nursery stock. It is also being distributed for use on 56 different varieties of home garden plants (4).

Physical Properties

Sodium 2,4-dichlorophenoxyethyl sulfate marketed under the names Sesone herbicide (Union Carbide Corp.) or Crag Herbicide 1 is a stable, nonvolatile,



white crystalline solid which melts at 170° C. It is soluble to the extent of 25% by weight in distilled water at 25° C. A 4% solution can be made in hard water containing as much as 260 p.p.m. of calcium carbonate. The preferred method of estimation (8) is based upon the observation that sodium alkyl sulfates form chloroform-soluble complexes with methylene blue chloride, which is