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Determination of D-048 [1-(2-Butynyl)-1-(*p-tert*-butylphenoxy)-2-butyl Sulfite] in Cottonseed

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A gas chromatographic method is described for the determination of D-048 [1-(2-butynyl)-1-(*p-tert*-butylphenoxy)-2-butyl sulfite] residues in cottonseed, cottonseed meal, and cottonseed oil. After extraction and cleanup by acetonitrile partition and Florisil column chromatography, D-048 is identified using a flame photometric detector in the sulfur mode. Recovery of D-048 averaged 91 ± 9% from the various cottonseed samples fortified at levels ranging from 0.1 to 1.0 ppm. The method is sensitive to 0.2 ppm for cottonseed oil and 0.1 ppm for cottonseed and cottonseed meal.

D-048 [1 - (2 - butynyl)-1-(*p-tert*-butylphenoxy)-2-butyl sulfite] is a new insecticide being developed for use on cotton. It is a nonsystemic, selective acaricide, effective against motile stages of phytophagus mites (Uniroyal Bulletin, 1970). To obtain necessary residue data, an analytical method was needed to determine D-048 in cottonseed, cottonseed meal, and cottonseed oil. The method, employing a flame photometric detector, is described in this report.

MATERIALS

Apparatus. A Tracor MT-220 gas chromatograph, equipped with a flame photometric detector in the sulfur mode (394-nm filter), was employed for the analysis. The gas chromatographic column was 4 ft × 3 mm i.d., glass, packed with 11% DC-200 (2.5 MCS) on 60–80 mesh Gas Chrom Q previously coated with 0.01% Versamid 900.

Reagents. All solvents were reagent grade. No additional purification was necessary. Sodium sulfate was reagent grade, anhydrous. Florisil (Fisher F-100), 60–100 mesh, was heated overnight at 130° and cooled in a desiccator before use. Addition of 2% moisture was needed to deactivate the Florisil for proper elution.

ANALYTICAL PROCEDURE

Sample Preparation and Extraction. Cottonseed and cottonseed meal were chopped in a Wiley Mill equipped with a 2-mm sieve. No preparation was necessary for the oil.

A 50-g sample of ground cottonseed was extracted with 200 ml of hexane and 50 g of sodium sulfate for 3 min in a Waring blender. Due to a greater amount of lint, some cottonseed samples may need a larger volume of solvent for adequate extraction. The homogenate was filtered through a coarse porosity fritted Buchner funnel using vacuum. The volume of recovered solvent was measured and the extract was quantitatively transferred to a 300-ml round-bottomed flask. The hexane was removed on a rotary vacuum evaporator at 40° and the oil was transferred to a 500-ml separatory funnel with a total of 40 ml of hexane. The extract was then processed through the acetonitrile partition and Florisil cleanup steps.

A 10-g sample of cottonseed oil was transferred to a 500-ml separatory funnel with a total of 40 ml of hexane. The mixture was then processed through the acetonitrile partition and Florisil cleanup steps.

A 50-g subsample of cottonseed meal was blended with 200 ml of acetonitrile for 3 min in a Waring blender. The homogenate was filtered through a coarse porosity fritted Buchner funnel using vacuum. A 100-ml aliquot of the filtrate was passed through 50 g of sodium sulfate. The sodium sulfate was then rinsed with two 20-ml aliquots of acetonitrile. The acetonitrile was removed on a rotary vacuum evaporator at 40°. The residue was taken up in acetone for analysis.

Acetonitrile Partition Step. The hexane–oil mixture was extracted with two 100-ml portions of acetonitrile (previously saturated with hexane), shaking for 1 min each time. The combined acetonitrile extracts were evaporated just to dryness on a rotary vacuum evaporator at 40°. The residue was taken up in 10 ml of benzene and processed through the Florisil column.

Table I. Summary of D-048 Recoveries from Cottonseed and Products

Fortification, ppm	% Recovery		
	Cottonseed	Oil	Meal
1.0	94	76	99
0.5	80	86	98
0.2	85	100	90
	100	108	80
	85	96	
0.1	85		96
Average:	88	93	93

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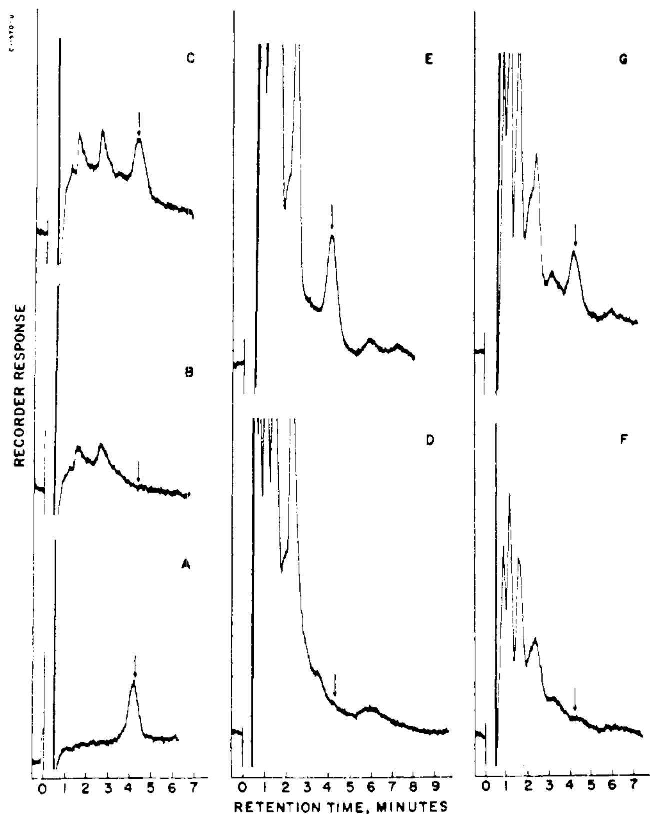

Figure 1. Representative chromatograms from analyses for D-048 residues in cottonseed, cottonseed oil, and cottonseed meal. A, standard D-048, 20-ng injection; B, control cottonseed meal, 250-mg injection; C, cottonseed meal fortified with 0.1 ppm of D-048, 250-mg injection; D, control cottonseed, 350-mg injection; E, cottonseed fortified with 0.1 ppm of D-048, 325-mg injection; F, control cottonseed oil, 100-mg injection; and G, cottonseed oil fortified with 0.2 ppm of D-048, 100-mg injection.

Florisil Column Cleanup. A 11 × 250 mm chromatographic column was prepared by adding a plug of glass wool and 10 g of Florisil. The column was rinsed with 30 ml of benzene and the wash was discarded. The concentrated extract was added with three 5-ml rinses of benzene. When the last of the rinses reached the top of the column, an additional 100 ml of benzene were added. The combined benzene eluates were evaporated just to dryness and the residue was taken up in an appropriate amount of acetone for analysis.

Gas Chromatographic Analysis. The following conditions were used for gas chromatographic analysis. Temperature: inlet, 225°; oven, 180°; detector, 160°; gases: nitrogen (carrier), 120 ml/min; hydrogen, 150 ml/min; oxygen, 20 ml/min; air, 20 ml/min. Optimum response for D-048 was given by these gas flows. With these chromatographic conditions, D-048 eluted in approximately 4 min.

An aliquot of the final extract was injected into a gas chromatograph equipped with a flame photometric detector in the sulfur mode. For optimum sensitivity, 1.0 ml was the final volume and 10 μl were injected. Peak area, determined by peak height × width at half peak height, was compared to a standard curve of D-048 to calculate the amount of residue present. As little as 10 ng of D-048 could be detected when the column was properly conditioned with periodic injections of 100–500 μg of D-048.

RESULTS AND DISCUSSION

No cleanup was necessary for the analysis of commercially prepared cottonseed meal, since the meal had already been extracted and pressed to remove the oil. The acetonitrile partition step is a modification of the method suggested by Mills (1959). The volumes were increased to handle a corresponding increase in the weight of oil. Only two extractions with acetonitrile were found necessary to quantitatively remove D-048 from a hexane–oil mixture. To ensure complete recoveries, proper elution of D-048 from the Florisil column should be checked for each group of samples.

The method was applied to field-treated samples and no detectable residues were found in any of the samples analyzed. Cottonseed meal and oil from field-treated samples were also found to contain no detectable residues.

Table I presents a summary of recovery data of D-048 from cottonseed and products. D-048 was added as a dilute acetone solution to the sample before addition of solvent and extraction. Recoveries averaged 91 ± 9%. Fortification levels ranged from 0.1 to 1.0 ppm. Chromatograms of control and fortified samples are presented in Figure 1. A chromatogram of 20 ng of D-048 is also shown. Electrometer sensitivity was 8×10^{-11} afs and the peak height of the 20-ng standard was 15% FSD. The limit of detection is 0.2 ppm for cottonseed oil and 0.1 ppm for cottonseed and meal.

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