Determination of Residues of 2-(*p-tert*-Butylphenoxy)cyclohexyl Propargyl Sulfite (Omite) in Peanuts, Cottonseed, and Corn

A gas chromatographic method is presented for the determination of 2-(*p-tert*-butylphenoxy)cyclohexyl propargyl sulfite (Omite) in peanuts, cottonseed, and corn. After extraction, lipid material is removed by acetonitrile–hexane partition steps. Further cleanup is accomplished by passing the extract through a Florisil column. An alumina column is then used for peanut extracts. Final determination is made with a gas chromatograph equipped with a sulfur-specific flame photometric detector. Recovery of Omite from the three crops averaged 95%. The limit of detection was 0.1 ppm.

Analytical methods for determining residues of 2-(*p-tert*-butylphenoxy)cyclohexyl propargyl sulfite (Omite, a registered trademark of Uniroyal, Inc.) in watery crops and peanuts have previously been reported (Devine and Sisken, 1972). However, cleanup of peanut extracts was insufficient when routinely analyzing a large number of samples. Buildup of oil in the inlet section of the gas chromatograph prevented analysis of more than several samples at a time before the response decreased to a nondetectable level. The glass insert and glass wool in the inlet part of the column then had to be changed to restore the original response. To correct this problem, modifications of the method were made and the resultant procedure is reported in this paper. Successful analysis of other oily crops such as cottonseed and corn (grain) was also performed with this method.

EXPERIMENTAL SECTION

Apparatus and Reagents. A Tracor MT-220 gas chromatograph with a glass insert and a sulfur-specific flame photometric detector (Brody and Chaney, 1966) was used for the analyses. A 6 ft × 3/16 in. i.d. glass column was packed with 2% SE-30 on 60–80 mesh Gas-Chrom Q. To prevent flame blowout due to the solvent, the hydrogen and oxygen–air gas lines entering the detector were reversed. Gas flows were optimized at the following: H_2 = 100 ml/min, O_2 = 40 ml/min, and air = 20 ml/min. The column temperature was 190° and the carrier gas (N_2) flow was 70 ml/min. The inlet temperature was 225° and the detector temperature was 180°. With these chromatographic conditions, Omite eluted in approximately 3 min.

All chemicals were reagent grade and solvents were Pesticide Grade (Fisher) or equivalent. The alumina was Fisher F-540, 80–200 mesh, and was used directly from the bottle. Upon heating, the alumina was found to contain approximately 3% moisture.

Procedure. A 20-g subsample of shelled peanuts, corn kernels, or cottonseed was blended for 1 min at fast speed in a Waring blendor. The ground sample was then extracted for 3 min with 200 ml of a 1:1 mixture of hexane and 2-propanol. The homogenate was filtered through a coarse-porosity fritted Büchner funnel (350 ml capacity) with the aid of a slight vacuum. The alcohol was then washed out of the extract with aqueous sodium chloride solution (Devine and Sisken, 1972).

The recovered hexane was dried with sodium sulfate and evaporated just to an oily residue on a rotary evaporator with a water bath maintained at 40°. The residue was quantitatively transferred to a 500-ml separatory funnel with a total of 50 ml of hexane. The hexane was then extracted with 3 × 50 ml of acetonitrile (previously saturated with hexane), shaking for 1 min each time.

The combined acetonitrile extracts were evaporated to an oily residue on a rotary evaporator at 40°. The residue was quantitatively transferred to a 125-ml separatory funnel with a total of 20 ml of hexane. The hexane was extracted with 3 × 20 ml of acetonitrile (previously saturated with hexane), again shaking for 1 min each time. The acetonitrile extracts were combined in a round-bottomed flask and evaporated just to dryness. A 20-ml portion of hexane was added to the flask and evaporation was again performed to ensure complete removal of acetonitrile.

The residue was dissolved in 10 ml of benzene and passed through a Florisil column (Devine and Sisken, 1972). The solvent used to elute Omite from the column, however, was changed to 150 ml of 3% acetone in hexane to ensure complete recovery of Omite from the column. Extracts of cottonseed and corn samples were then concentrated to an appropriate volume for analysis. Peanut extracts, however, generally needed additional cleanup and so were evaporated just to dryness and dissolved in 10 ml of benzene before passing through an alumina column.

An 11 mm i.d. chromatographic column was prepared by adding a plug of glass wool and 5 g of alumina. The column was rinsed with 50 ml of benzene and when the solvent reached the top of the column the concentrated peanut extract was added. Collection of the effluent was then started. Two 10-ml rinses of benzene were used to complete the transfer of the extract and when the solvent reached the top of the column 50 ml of additional benzene was added. The combined benzene eluates were concentrated to a suitable volume for analysis.

Aliquots of the final extract were injected into a gas chromatograph equipped with a flame photometric detector (394-nm filter). The area of the sample peak, determined by peak height × width at half peak height, was compared with a standard curve of Omite (plotting peak area vs. nanograms injected on log–log paper) to determine the amount of residue present.

RESULTS AND DISCUSSION

Changes from the original Omite method were made because of the nature of the samples. Two acetonitrile–hexane partition steps and a Florisil column were added to improve removal of oil from the extracts. Because of a lesser amount of oil, extracts from corn were passed through only one acetonitrile–hexane partition step, using the smaller volumes of 20 ml of hexane and 3 × 20 ml of acetonitrile. As with all column chromatography, proper elution of Omite from both Florisil and alumina should be checked before passing samples through.

The gas chromatographic conditions are stated only as a guide since column characteristics and detector response vary from lab to lab. The column was conditioned by alternately injecting Omite standard and an extract until the response stabilized. This generally occurred after two or three injections of extract. A standard injection was made after every third or fourth sample injection to ensure that the response remained stable. With a final volume of 2 ml and a 10-μl injection, the validated limit of detection was 0.1 ppm. An Omite standard peak equivalent to at least 0.05 ppm could, however, be detected. With the described modifications, a series of 15 peanut

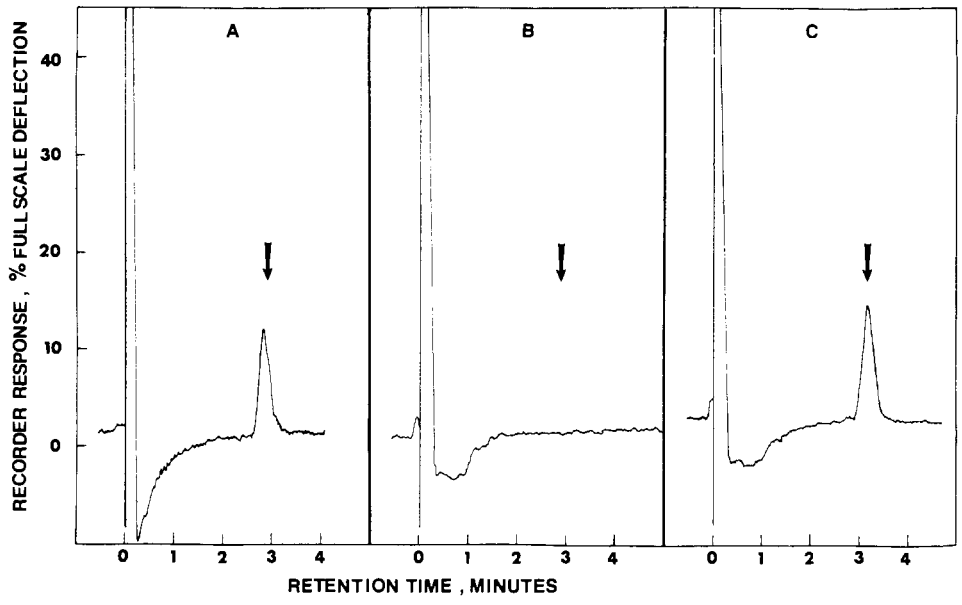

Figure 1. Typical chromatograms for determining Omite residues in peanuts: (A) Omite standard, 6 ng injected; (B) peanut, control, 84 mg injected, nondetectable residue; (C) peanut, control, fortified with 0.1 ppm of Omite, 76 mg injected, 83% Omite recovered.

Table I. Summary of Recovery Data for Omite

Crop	Fortification level, ppm	No. of recoveries	Range, %	Av recovery, %
Peanuts	1.0	3	85–109	97
	0.1	10	76–114	93
Cottonseed	1.0	2	93, 103	97
	0.1	4	84–108	98
Corn	1.0	1		100
	0.1	5	84–100	92

samples has been analyzed in 1 day without appreciable decrease in response.

Typical chromatograms for Omite analysis are shown in Figure 1. Treated samples were the same as the control sample. Electrometer sensitivity was 2×10^{-8} afs. Chromatograms of cottonseed and corn samples were similar, showing no interfering peaks.

To validate the method, known amounts of Omite were added to control samples prior to extraction. The fortified samples were then processed through the procedure to determine the recovery. Table I summarizes the recovery data obtained for Omite from the three crops. The average recovery of Omite was 95%. Since no detectable Omite residues were found in field-treated samples, the majority of the recoveries were run at the limit of detection.

A specificity study was performed with peanuts where all pesticides registered in 1972 were added to a control sample at their maximum tolerance level. Omite was added at the 0.1-ppm level and the samples were carried through the procedure. The control sample and control plus registered pesticides showed no apparent Omite residues, while a recovery of 110% was obtained from the control plus registered pesticides plus 0.1 ppm of Omite. Similar specificity studies were also performed with cottonseed and corn and the same results were obtained. Hence, there would be no interferences in peanuts, corn, or cottonseed from any of the pesticides registered for use.

LITERATURE CITED

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James M. Devine

Lake Ontario Environmental Laboratory
State University of New York
College of Arts and Science
Oswego, New York 13126

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