Analysis of Zolone Insecticide—Acaricide on Grapes

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Phosalone (S-[(6-chloro-2-oxo-3-benzoxazolinyl)methyl] 0,0-diethyl phosphorodithioate, Zolone® insecticide-acaricide) is acheiving importance for control of insects and mites resistant to many other organophosphorus pesticides. It is particularly useful, from a practical standpoint, for the control of resistant insects and mites on grapes, because of its low phytotoxicity and mammalian toxicity.

General analytical methods for organophosphorus pesticides have been adapted to include determination of Zolone in kale, by charcoal column cleanup and gas-liquid chromatographic (GLC) determination using a KCl thermionic detector (1), and in river water by gas chromatographic determination using a phosphorus flame photometric detector (2). In addition an analytical method is available for Zolone residues in various crops which utilizes florosil column cleanup and GLC determination using an electron capture detector (3).

We report here an analytical procedure involving modifications designed to overcome problems encountered in the extraction and detection steps when the electron capture method was employed. The method, for Zolone residues in grapes, involves extraction of the crop with chloroform, cleanup of the extract on a florisil column, and determination by a tritium electron capture GLC system modified to prevent condensation of Zolone and coextractives of similar low volatility in the detector cell. Acceptable recoveries (80-96%) are demonstrated at the 1.0 and 0.1 ppm fortification levels; the latter value approaches the limit of detectability. In addition, the response of Zolone standards to the sulfur and halide microcoulometric GLC detectors is included as possible alternates for specific determination.

Equipment

1. Hobart Food Cutter, Model 8141
2. Waring Laboratory Blendor, 1/5 horsepower, with one quart capacity stainless steel cups.

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3. Rotary Vacuum Evaporator, Borg.
4. Adsorption Column, 24 mm O.D. glass, 25 cm length, with drip tip and 250 ml liquid reservoir, custom built.
5. Gas-liquid chromatograph, Varian Aerograph, Model 204, with 4 1/2 foot x 3 mm glass column packed with 10% (w/w) OV-1 on Chromosorb G, Hi Performance, A/W, DMCS treated, 80/100 mesh; and electron capture detector assembly modified as described below.

Materials

1. Solvents redistilled: Chloroform, benzene, and ethyl acetate.
2. Hyflo Super Cel, Fisher Scientific.
3. Florisil, 60/100 mesh, Floridin Co., used as supplied.
4. Sodium Sulfate, anhydrous, low nitrogen, Mallinckrodt.
5. Chromosorb G, Hi-Performance, A/W, DMCS, 80/100 mesh, Varian Aerograph.
6. Silicone OV-1, Applied Science.

Method

Extraction. Chop a 100 gram sample of frozen grapes with a Hobart Food Cutter with dry ice added, until it is of mushy consistency, i.e., 3-5 minutes. Transfer the contents to a one quart capacity blender cup and add 200 ml chloroform previously cooled to -20°. Macerate for 2 minutes at low and high speeds on a Waring Laboratory Blendor. Prepare a Buchner funnel with a mat of Hyflo Super Cel. Filter the contents of the blender cup with vacuum, and wash thoroughly with an additional 100 ml of cold chloroform.

Cleanup. Evaporate one quarter of the final volume of the chloroform extract just to dryness in a 200 ml round bottom flask, with a rotary vacuum evaporator and warm water bath. Place a small glass wool plug in the bottom of an adsorption column, and fill to 4 inches (20 grams) with florisil, with light tapping on the column. Without disturbing the florisil, add 1 inch of anhydrous sodium sulfate followed by a small plug of glass wool. Prewash the column with 100 ml of benzene. Before the level of the benzene disappears into the top glass wool plug, rinse the flask containing the sample with 10 ml of benzene, and add to the top of the column. Rinse with 2 more 10 ml portions of benzene, and then add a total of 50 ml benzene in small portions to the top of the column to assure that the sample is completely within the florisil material. Discard the total benzene forerun* and change receiver to a 500 ml round bottom flask. Elute the sample with 200 ml 5% ethyl acetate-benzene mixture, and collect until column runs dry.

*At least one sample should be checked for premature elution of Zolone, indicating a much too inactive florisil.

Analysis. Evaporate the eluted ethyl acetate-benzene mixture just to dryness by vacuum (25" Hg) in a 60°C water bath with a rotary vacuum evaporator. Quantitatively transfer the contents of the flask to a small graduated tube by repeated rinsings with small portions of benzene. Adjust the final volume to a predetermined value, e.g. 10 ml, corresponding to the sensitivity range desired in the GLC analysis.

Prior to analysis by GLC, inject microgram amounts of Zolone standard until reproducible responses are obtained. The ideal column oven temperature for Zolone analysis was found to be 245°C. Since the temperature of a tritium foil detector should not exceed a maximum of 225°C for any extended period of time and in order to reduce condensation and/or adsorption of Zolone in the column-to-detector stainless steel transfer tube, some changes were required in the detector oven compartment. These changes, which involve attaching the detector directly to the exit end of the column, are illustrated in Figure 1.

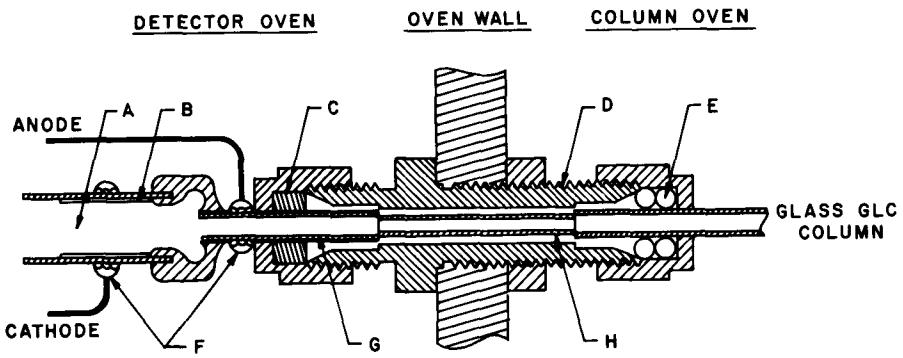

Figure 1. Detector assembly modification

A. Kovar Cell
B. Tritium foil
C. Silicone rubber septum
D. 1/8" Swagelok 316 bulkhead union
E. 1/8" Silicone "O" rings
F. Small alligator clips
G. Teflon insulated kovar inlet tube
H. 2 mm O.D. glass tube

Results and Discussion

The utility of electron capture GLC for determination of phosophorodithioate insecticides has been demonstrated previously (4). The necessity of pre-conditioning the column to such compounds, by injecting large amounts of the compound to be analyzed and the crop extract, has been pointed out (5,6). Column conditioning in this way has the drawback of successively de-

creasing the sensitivity of the tritium electron capture detector due to condensation since the detector is operated at sub-column temperature. In the Varian Aerograph Model 204 used in this work, this condensation problem is most acute since there is a six inch transfer line maintained at detector temperature, between column and detector. Our early attempts at using the Varian Aerograph 204 for Zolone analysis led to a nonreproducible response and considerable peak tailing, particularly when small amounts of Zolone standard were injected. Injecting large amounts of Zolone to "condition" the system led to better reproducibility, but no relief from the tailing problem. Attaching the detector directly to the exit end of the column proved successful in reducing to a great extent these two undesirable characteristics.

Table 1 shows the recoveries obtained for different samples of Thompson Seedless grapes fortified with Zolone at the 1.0 and 0.1 ppm levels. The samples were selected to represent grapes in the various stages of maturity in the 48 day period following a typical time of application of the pesticide. The use of chloroform as an extraction solvent was based on its water-immiscibility, low tendency for emulsion formation, and excellent solvent properties for the pesticide.

The concentration curve for the modified electron capture detector used in the analysis is shown in Figure 2. Peak areas were determined with a Lietz planimeter. Detector response was approximately linear in the region 0.1 to 2 ng. At the lower value, this corresponds to a sensitivity of 0.05 ppm. In practice the operable sensitivity may vary with the individual sample, although, in our study the 0.05 ppm level of sensitivity was always obtainable.

TABLE 1

RECOVERY OF ZOLONE ON GRAPES

Sample	Fortification	% Recovery
1	0.1 ppm	84%
	1.0	96
2	0.1	85
	1.0	90
3	0.1	88
	1.0	90
4	0.1	80
	1.0	94
5	0.1	84
	1.0	96

Mean recovery, 0.1 ppm: 84.2%; average mean deviation: 1.8%
Mean recovery, 1.0 ppm: 93.2%; average mean deviation: 2.6%

Other detectors, besides electron capture and those previously reported (1,2), could conceivably be used for GLC determination of Zolone. The concentration curves obtained using the Dohrmann microcoulometric detector in both the halide and sulfur modes are shown in Figures 3 and 4. The specificity offered by these detection systems was not needed in the present work, since major interferences were not encountered; the modified electron capture detector, with its greater sensitivity and ease of operation, was found to be entirely suitable.

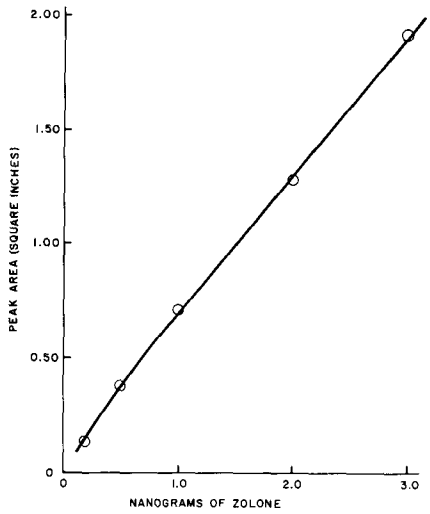

Figure 2. Concentration curve of Zolone, electron capture detector

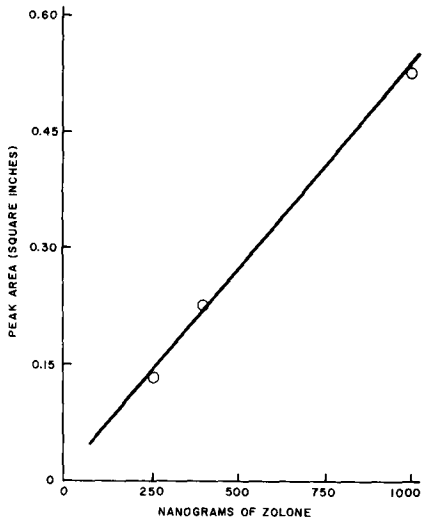

Figure 3. Concentration curve of Zolone, Dohrman microcoulometric detector-halide mode

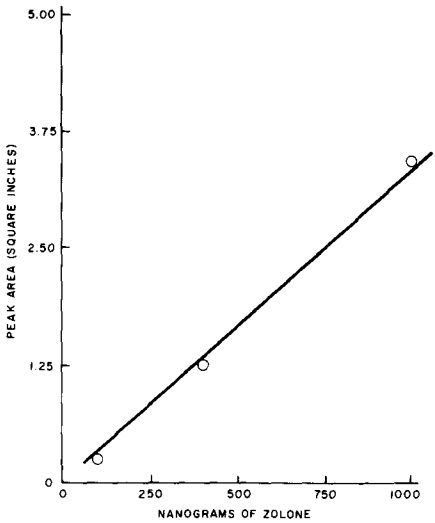

Figure 4. Concentration curve of Zolone, Dohrmann microcoulometric detector-sulfur mode

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