CHEVRON CHEMICAL COMPANY
ORTHO AGRICULTURAL CHEMICALS DIVISION
DEVELOPMENT RESEARCH DEPARTMENT
RICHMOND, CALIFORNIA

DETERMINATION OF NALED
AND DDVP RESIDUES IN CROPS
METHOD RM-3G-4

FILE NO.: 740.01/DIBROM
DATE: May 15, 1985

INTRODUCTION

Naled (Phosphoric acid 1,2-dibromo-2,2-dichloroethyl dimethyl ester) is an insecticide which is rapidly converted by crops to DDVP (Dichlorvos; Phosphoric acid 2,2-dichloroethenyl dimethyl ester). This method determines both naled and DDVP by gas chromatography after extraction from crops and cleanup by solvent partitioning. This revision of RM-3G-3 describes modifications to the cleanup steps and updates instrument conditions.

REAGENTS

Acetone - pesticide residue analyzed.

Acetonitrile - Omnisolv. Other grades and even certain lots of this brand have been found to convert naled to DDVP. The acetonitrile should be checked by fortifying a 50-ml aliquot with 1.0 mL of a 10 µg/ml solution of naled in acetone, adding 1 mL of the dipropylphthalate solution below, rotary vacuum evaporating the acetonitrile, adding 5 mL of hexane, and determining the extent of decomposition of naled to DDVP by the GC conditions described below.

DDVP - analytical standard. Stock solution prepared in hexane. Reference standards prepared by dilution with hexane. Fortifying solutions prepared by dilution with acetone.

Dipropylphthalate - Eastman Kodak. Prepare a 1% solution in hexane.

Hexane - Residue analyzed.

Hydrochloric Acid - Reagent grade. Concentrated.

Naled - analytical standard. Stock solution prepared in methanol. Reference standards prepared by dilution with hexane. Fortifying solutions prepared by dilution with acetone.

Sodium Sulfate - anhydrous, granular, AR. Acetone-washed and air-dried. Prepare a saturated aqueous solution.

APPARATUS

Centrifuge - Equipped to hold 500-mL or larger centrifuge bottles.

Omni-Mixer equipped with an adaptor and shaft for quart Mason jars.

Hobart Food Chopper or similar blender.

Rotary vacuum evaporators with a maximum water bath temperature of 30 degrees.

Gas Chromatograph

Hewlett-Packard 5890 equipped with NP detector and automatic sampler and 3392A recording integrator or equivalent.

Column: 10m x 530µ 50% phenylmethylsilicone wide bore capillary

Column Oven Temperatures:
Initial: 125° with no hold
Rate: 25°/min
Final: 210° and hold for 0 to 5 min depending upon late eluters in the crop extracts.

Detector Temperature: 250°
Injection Port Temperature: 150°
Carrier Gas: Helium at 20 mL/min
Detector Makeup Gas: Helium at 10 mL/min
Air: 80 mL/min
Hydrogen: 3 mL/min
Injection size: 1-2 µL
Retention Times: DDVP 1.06 min (Fig. 1)
Naled 2.93 min (Fig. 2)

Alternate Gas Chromatograph

Varian 6000 equipped with electron capture detector and 3390 recording integrator.

Column: 30m x 250µ DB-1 from J & W Scientific

Column Oven Temperatures:
Initial: 100°, hold for 3 min
Rate: 25°/min
Final: 250° and hold for 1 min

Detector Temperature: 300°
Injection Port Temperature: 150°
Carrier Gas: Helium at 1.3 mL/min with an injection port split ratio of 20:1
Detector Makeup Gas: Nitrogen at 30 mL/min
Injection size: 1 µL
Retention Times: DDVP 5.4 min (Fig. 3)
Naled 8.5 min (Fig. 3)

EXTRACTION

Note: Samples must be extracted within 24 hours of receipt.

Macerate the frozen tissue in a Hobart food chopper and weigh exactly 100 grams into a quart Mason jar. Immediately add 5 mL of concentrated hydrochloric acid and stir until all of the sample is acidified. (Two control samples to be used for recovery purposes should be fortified with 1.0 mL of a 10.0 µg/mL acetone solution of either naled or DDVP at this point in the procedure.) Add 50 grams of anhydrous sodium sulfate and stir. Add 75 mL of saturated sodium sulfate and again stir. Add 400 mL of hexane and blend the mixture on an Omni-mixer for 10 minutes. Transfer to a centrifuge bottle and centrifuge at 1500 rpm for 10 to 20 minutes. Decant the hexane extract through anhydrous sodium sulfate into either an amber bottle for storage or into a 1000-mL graduate cylinder. Transfer the remaining solid residue into the original Mason jar. Rinse the centrifuge bottle with an additional 400 mL of hexane, add the rinse to the Mason jar, and blend for 10 minutes. Filter this extract into the same container with the first extract. If the extracts are not to be immediately analyzed, store them in the presence of anhydrous sodium sulfate at -20°C.

CLEANUP *

Measure the total volume of extract and transfer half to a 500-mL separatory funnel. Extract three times with 25 mL acetonitrile and combine the acetonitrile extracts in a 250-mL separatory funnel. Wash the acetonitrile with 50 mL of hexane and discard the hexane wash. Transfer the acetonitrile to a 500-mL round bottom flask, add 1 mL of 1% dipropylphthalate in hexane and evaporate the acetonitrile to near dryness on a rotary vacuum evaporator. Add 10-mL of acetonitrile and 50 mL deionized water and carefully evaporate the acetonitrile on the rotary vacuum evaporator. If the aqueous solution is not clear, then filter through a fast filtering paper. Transfer the aqueous solution to a 250-mL separatory funnel and extract with three 50-mL portions of hexane. Filter the extracts through anhydrous sodium sulfate into a 250-mL round bottom flask. Add 1 mL 1% dipropylphthalate in hexane and evaporate the combined filtrate just to dryness on the rotary vacuum evaporator. Dissolve the residue in exactly 5.0 mL of hexane and transfer to an amber vial for storage at 4°C until time of analysis.

MEASUREMENT

Transfer 500 µL of the solutions to be measured to amber vials for use on the autosampler. Load the sample tray in the following order: DDVP standard, naled standard, DDVP standard, naled standard, sample, DDVP standard, sample, naled standard, etc. alternating samples and standards. The standard vials contain 1.0 µg/mL of naled or DDVP in hexane. The integrator is programmed to measure peak height (or area).

CALCULATIONS

$$\text{PPM (naled or DDVP)} = \frac{\text{Peak Height (sample)} \times 1.0\ \mu g/mL \times 2 \times \text{Dilution Factor}}{\text{Mean Peak Height Std.} \times \text{sample weight (g)}}$$

LIMIT OF DETECTION

The limit of detection is 0.01 ppm for both naled and DDVP.

NOTES

1. Naled is thermally labile and so the injection port temperature is maintained as low as is practically possible. Naled decomposes to DDVP and under the conditions stated the naled standard will give a DDVP peak which has less than 10% of the peak height of the naled peak. This is equivalent to less than 5% decomposition of naled, which is considered acceptable.

2. The linearity of the instrument should be determined daily with separate DDVP and naled standards of 0.1, 0.6, 0.8, 1.0, and 1.2 µg/mL. The relative standard deviation of the response factor for each chemical should 5% or less for the 0.6 to 1.2 µg/mL range and 10% or less for the 0.1 to 1.2 µg/mL range. If necessary sample extracts should be diluted to bring the concentration of naled and DDVP within range of linearity established.

3. The relative standard deviation for the 1.0 µg/mL reference standards injected with the samples should be less than 7%.

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METHOD **RM-3G-4 ADDENDUM**

FILE NO.: 740.01/DIBROM
DATE: SEPTEMBER 11, 1987

Alternate Gas Chromatography Condition:

Column: 30m x 530 µ 50% phenylmethylsilicone wide bore capillary (1 µ thickness)

Oven Temperatures:

Initial: 125°C with no hold

Rate: 15°C/min

Final: 210°C and hold for 3 min

Detector Temperature: 275°C

Injector Temperature: 150°C

Carrier Gas: Helium at 20 ml/min

Detector Makeup Gas: Helium at 10 ml/min

Air: 80 ml/min

Injection Size: 1-2 µl

Retention Times: DDVP 2.33 min (Figure 4)
Naled 5.68 min (Figure 5)

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