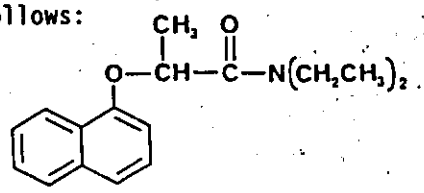
DETERMINATION OF NAPROPAMIDE RESIDUES IN SOIL BY CAPILLARY GAS CHROMATOGRAPHY

1 SUMMARY/INTRODUCTION

This method is intended for determining napropamide in soils at levels of 0.01 ppm to 5.0 ppm. Napropamide is the active ingredient in DEVRINOL® Selective Herbicide, manufactured by ICI Americas Inc. Its structure is as follows:



Napropamide is extracted directly from soil with water and toluene. The toluene extract is analyzed for napropamide by capillary gas chromatography.

2 MATERIALS/METHODS

2.1 Apparatus

2.1.1 Gas Chromatograph. Hewlett-Packard Model 5880A, equipped with capillary splitless inlet, Hewlett-Packard Model 3673A automatic sampler, nitrogen-phosphorus detector, and electronic integrator or data acquisition system. Any chromatograph giving equivalent performance may be used.

2.1.2 Injection Port Insert. Splitless insert, 2 mm i.d. by 77 mm, Hewlett-Packard Part No. 18740-80220.

2.1.3 Chromatographic Column. H.P. Ultra 2 (crosslinked 5 % phenylmethyl silicone), 12 m x 0.2 mm x 0.33 μm thickness, or equivalent.

2.1.4 Glass Bottles. Four-ounce, wide-mouth bottles with aluminum foil-lined caps.

2.1.5 Syringe. 10, 100, and 500 microliter capacities, Hamilton 701N, 710N, 750N, or equivalent.

2.1.6 Reciprocating Shaker. Eberbach Corporation, Model 6010, or equivalent.

2.1.7 Centrifuge. IEC International, Model C1582, or equivalent.

2.2 Reagents

2.2.1 Solvents. Toluene, Acetone, Nanograde®, or equivalent.

2.2.2 Napropamide. Analytical reference-standard napropamide. Available from ICI Americas Inc., 1200 South 47th Street, Box 4023, Richmond, CA 94804-0023, Attention: Environmental Sciences Department Manager.

2.2.3 Calibration and Fortification Solution. To prepare a 1000 µg/mL stock solution of napropamide, weigh to the 4th decimal place approximately 50 mg of primary standard of known purity into a 4-oz narrow-mouth bottle. Calculate the weight of solvent to add, based on the weight of primary standard taken, the purity of the primary standard, and the density of the solvent, as follows:

$$S = W \times P \times D \times \ell$$

where S = the weight of solvent to add (g),

W = the weight of primary standard taken (mg std),

P = the purity of the primary standard (mg a.i./mg std),

D = the density of the solvent (g/mL),

and ℓ = 1 = the required volume of solvent per mg of active ingredient (mL solvent/mg a.i.).

Add the calculated weight of the appropriate solvent to the bottle, close the bottle with a polyseal cap, and mix thoroughly to dissolve the primary standard. Use toluene (D = 0.867 g/mL) for calibration solutions, and acetone (D = 0.792 g/mL) for fortification solutions.

To prepare working calibration solutions, dilute the stock calibration solution by weight with toluene to give 1.0, 0.1, and 0.01 µg/mL solutions or other concentrations as required.

Dilute the stock fortification solution by weight with acetone to give a 10 µg/mL solution, or other concentrations as required.

2.3 Analytical Procedure

2.3.1 Extraction. Weigh 25 g of thoroughly-mixed soil sample into a 4-oz wide-mouth bottle. Add 25 mL of distilled water and 25 mL of toluene. Cap the bottle with an aluminum foil-lined lid and shake it on the reciprocating shaker for 2 hours. Centrifuge for 10 - 20 minutes at 2000 rpm to aid the separation of the phases. Remove the top (toluene) phase for analysis. Alternatively, use any convenient

weight of soil > 20 g, and extract with water and toluene in a soil:water:toluene w:v:v ratio of 1:1/2 - 1:1; confirm the validity of the extraction method by analysis of fortified control samples.

2.3.2 Fortification. Analyze unfortified and fortified control samples with each set of treated samples to demonstrate method recovery according to the Quality Assurance SOP. For example, for 25-g samples, weigh 25 g of untreated control soil into a 4-oz wide-mouth bottle. Add 0.025 mL of the 10 µg/mL acetone fortification solution to produce a fortification level of 0.01 ppm, or add 0.125 mL of the 1000 µg/mL acetone fortification solution to produce a fortification level of 5.0 ppm. Add 25 mL of water, 25 mL of toluene and extract as above. If a different weight of soil is analyzed, use that weight and adjust the volume or concentration of fortification solution to give the desired analyte concentration. Extract using the same volumes of water and toluene as for the treated samples.

2.4 Instrumentation

2.4.1 Operating Conditions. Follow the manufacturer's instructions for operation of the gas chromatograph and nitrogen-selective detector. Use these parameters for the analyses or other operating conditions that achieve equivalent sensitivity, reproducibility, and resolution.

Inlet	Splitless insert, purge activated at 0.5 min
Oven initial temperature	100° C
Initial time	1.0 min
Temperature programming rate	25° C/min
Oven final time	15 min
Oven final temperature	240° C
Injector temperature	220° C
Detector temperature	300° C
Carrier gas	Helium
Carrier gas pressure	23 psi
Carrier gas flow	2.4 mL/min through column, 78 mL/min vented
Injection size	1.5 µL

Quantitation — Peak height (external standard)

Under the above conditions the elution time of napropamide is 6.2 minutes. See Figure 1 for typical chromatograms.

2.4.2 Calibration. The gas chromatograph is calibrated using the analyte calibration solutions specified in section 2.2.3. Calibrate the instrument using either the 1.00 or 0.10 µg/mL calibration solution. Check for sensitivity by analyzing the 0.01 µg/mL analyte calibration solution. Check for response linearity by analyzing the 1.00, 0.10, and 0.01 µg/mL calibration solutions.

2.4.3 Analysis of Extracts. Inject the sample extracts using the same conditions used for calibration. The identity of the analyte peak in the sample chromatogram is assigned based upon the coincidence of retention times (within 0.03 minutes) with those of the calibration chromatograms. If the response of a peak identified as an analyte exceeds that of the highest calibration solution, dilute the sample extract until its response is within the calibrated range. Re-inject the calibration solution after every two to four sample injections and recalibrate as needed. Re-inject the calibration solution at completion of the sample analysis.

2.5 Interferences

No clean-up is required when this procedure is utilized as described. However, extractives from soil occasionally contribute peaks with retention times near that of napropamide. Satisfactory resolution can usually be achieved with appropriate oven temperature manipulations or column choice. Appendix A shows typical chromatograms. Analyze extracts of samples from untreated plots to demonstrate the absence of interferences from sample matrices, solvents, or labware. The chromatograms in Appendix A demonstrate resolution of napropamide from several other compounds. The retention time of napropamide under the conditions described is 6.2 minutes. R-25788, pebulate, fonofos oxon and fonofos analyzed under the same conditions have retention times of 2.5, 3.1, 4.3 and 4.7 minutes, respectively.

2.6 Confirmatory Techniques

Unexpected positive results, as in untreated control or pre-application samples, should be confirmed by other means, preferably by GC/MS, MSD, or use of a second capillary column of different polarity.

2.7 Calculations

2.7.1 Calibration Factors

F = the response factor for the analyte (ppm per electronic unit), calculated as follows:

$$F = \frac{C}{P \times S}$$

where C = the concentration of analyte in the calibration solution (µg/mL)

S = equivalent concentration of sample in injected extract (g/mL)

P = the peak area or height (electronic units) of the analyte peak in the chromatogram of the calibration solution.

2.7.2 Analyte in Sample. The concentration of napropamide in the original sample is calculated using external standard method as follows:

$$ppm = F \times R$$

where ppm = the amount of analyte in the soil in parts per million,

R = the peak height (electronic units) of the analyte peak in the chromatogram of the sample extract,

and F = the response factor for the analyte (ppm per electronic unit), calculated as described above.

Note for the above external standard calculations, equal volumes of both the extract and the calibration solutions are injected.

Averaged response factors obtained from injections of calibration solution before and after injection of sample extracts may be used for calculation of the analyte concentration in the sample.

3.3 Dry Weight Basis

This method determines the residues on an as-received basis. If it is desired to express the values on a dry-weight basis, compensation is necessary for water present in the sample. Percent moisture can be determined by drying a subsample at 105° C for 24 hours.

3.4 Safety Precautions

3.4.1 Toluene, Acetone. Flammable. Avoid contact with skin and clothing. Avoid breathing vapor; work in well ventilated area.

3.4.2 Napropamide. Avoid contact with skin and clothing. Work in well ventilated area. Wash with soap and water after any accidental contact.

4 CONCLUSIONS

The method is specific for the analysis of napropamide in soil. Only readily available laboratory equipment and reagents are required. The analysis can be completed by one person in an eight-hour period if an

adequately homogenized sample is available. Untreated and fortified untreated samples should be extracted and analyzed with each set of samples to demonstrate absence of interferences and adequate recovery. If determination of napropamide at a concentration other than 0.01 ppm to 5.0 ppm is required, suitably fortified samples must be analyzed to validate the method at that concentration.