Determination of Oxadiazon Residues in Soils

Introduction:

This method is appropriate for the determination of oxadiazon and its metabolites in soils. The procedure allows the simultaneous determination of parent oxadiazon and three soil metabolites. The metabolites are identified as the methoxy (RP17272), the phenolic (RP25496), and the carboxylic (RP26449). See Figure 1 for compound structures. See Figures 2a and 2b for representative chromatograms showing response to a standard containing each of the residue components and their relative retention times, and an untreated control soil.

Briefly, 100 g of soil is extracted with 200 ml of 1:1-acetone:water by 30 minutes of mechanical shaking. The container is centrifuged and 100 ml of supernatant solution is partitioned with methylene chloride to transfer the residue to a volatile solvent. The solvent is evaporated and the residue methylated with diazomethane. The methylation is necessary for satisfactory chromatography of the phenolic and carboxylic metabolites. The methylation solution is evaporated and the residue dissolved in toluene for injection into a gas chromatograph. Detection is based on capillary column chromatography with an N/P detector in the nitrogen mode. See Table I for instrument parameters.

Reagents:

a. Acetone, reagent grade.
b. Phosphoric Acid Gr, 85%, EM Science, or equivalent.
c. Methylene chloride, reagent grade.
d. Sodium sulfate, anhydrous granular, Mallinckrodt AR grade
e. Diazomethane reagent (see next section for preparation).
f. Toluene, reagent grade.
g. Distilled, or de-ionized water.
h. Potassium hydroxide, reagent grade.
i. Ethyl ether, anhydrous reagent grade.
j. N-Methyl-N'-nitro-N-nitrosoguanidine (Sigma Chemical Co., St. Louis, MO).

Preparation of Diazomethane:

1. Dissolve 5.0 g potassium hydroxide in 5.0 ml de-ionized water. Chill in a wet ice bath.

2. Add 55 ml ethyl ether. Carry out the remaining steps with the reaction flask remaining in the ice bath.

3. SLOWLY add 3.3 g N-methyl-N'-nitro-N-Nitrosoguanidine in small portions to the ether, swirling after each addition.

4. Decant the ether. Store in a freezer until needed.

NOTE: Reaction must be carried out under a hood. N-methyl-N'-nitro-N-nitrosoguanidine and diazomethane are extremely toxic and appropriate precautions should be taken during preparation and use.

Standards and Spiking Solutions:

a. Weigh 0.100 g of oxadiazon and the methoxy and carboxylic metabolites into a 100-ml volumetric flask, dilute to the mark with toluene and shake until solution is complete. The phenolic metabolite is weighed and diluted separately because it becomes methoxy upon being methylated.

b. Withdraw a 2-ml aliquot with a pipet and dilute to 100-ml with toluene in a second volumetric flask. This solution contains 20 µg/ml each of oxadiazon and metabolites.

c. Remove 20 ml of stock solution (b) and dilute to 100 ml as above. The standard solution now contains 4.0 µg/ml each of oxadiazon and metabolites.

d. By a similar procedure, prepare standard solutions containing 2.0, 1.0, 0.50 and 0.25 µg/ml of oxadiazon and each metabolite. Any similar series of concentrations of standards is satisfactory.

e. Store solution in a freezer at -15°C and return to room temperature only during use. These solution are stable for several months when stored and used in this manner.

NOTE: Part of the mixed standard of oxadiazon and the two metabolites described in part (a) above is removed and methylated before further dilution. The 2 ml aliquot described in (b) is removed from this methylated portion and dilutions made as described to obtain standards. Dilutions of the unmethylated solution are made

to obtain appropriate concentrations for use in spiking soil samples for recovery data.

Procedure:

1. Air dry the soil by spreading the sample in a thin layer on non-absorbent paper on the laboratory bench. Pass soil through a no. 8 U.S. standard sieve to remove stones and detritus.

2. Mix well and weigh 100 g of soil into a 250 ml screw cap plastic bottle.

3. Spike untreated control samples at this point for the determination of recoveries.

4. Add 200 ml 1:1-acetone:water to each bottle and screw cap on tightly.

5. Shake the bottle end to end on a reciprocating shaker for 30 minutes.

6. Centrifuge at 2500 rpm for 5 minutes.

7. Decant 100 ml of the supernatant liquid into 250 ml separatory funnel.

8. Add 1 ml phosphoric Acid. Swirl to mix.

9. Extract the residue by shaking for 30 seconds with 50 ml of methylene chloride. Drain the methylene chloride (bottom) layer through a bed of about 150 g of anhydrous granular sodium sulfate contained in a 10 cm funnel plugged with cotton into a 250 ml Erlenmeyer flask.

10. Add 25 ml acetone to the aqueous layer, swirl to mix, and extract with 50 ml of fresh methylene chloride. Drain the bottom layer through the sodium sulfate into the same flask as before.

11. Repeat step 10. Wash the sodium sulfate with an additional 25 ml methylene chloride and allow to drain into the same flask.

12. Evaporate the methylene chloride to dryness by setting the flask in a 40°C warm water bath and purging with a gentle stream of air.

13. Methylate the residue by adding 4 ml of diazomethane reagent and allowing to stand at room temperature for 15 minutes with

occasional swirling.

14. Evaporate to dryness with air in a warm water bath as before.

15. Dissolve the residue in an appropriate volume of toluene for injection into the gas chromatograph.

Quantification:

Construct three calibration curves by plotting the peak height for each of the three analyses against the concentration of the respective analytes in the injected standard solutions. The concentration of each analyte in soil can be determined from the peak heights for the analytes in the sample chromatogram and from the slopes and intercepts of their respective calibration curves.

$$\text{ppm analyte in soil} = \frac{Y \times D}{\frac{W}{2} \times R}$$

Where Y = µg/ml analyte in injected sample from the calibration curve.

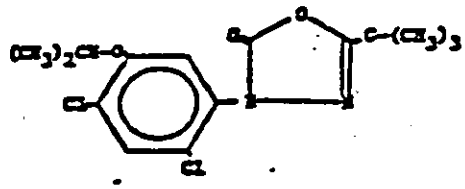
D = ml final dilution for injection

W = weight (g) of soil sample

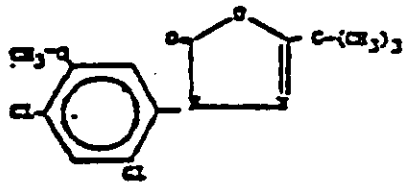
W/2 = half of the extract that was analyzed (100g of soil was extracted with 200 ml solution but only 100 ml solution was analyzed/sample)

R = percent recovery of analyte from fortified sample

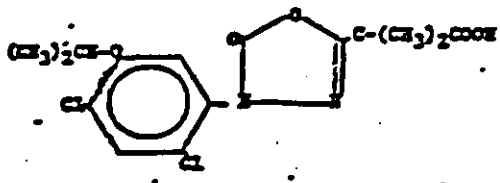
FIGURE I
Structural Formulae for Oxadiazon and its Soil Metabolites



(RP 17623) OXADIAZON

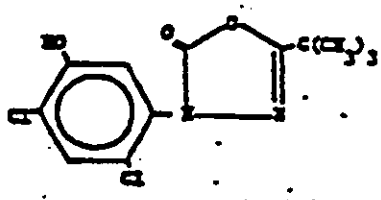


RP 17272
METHOXY METABOLITE



CARBOXYLIC ACID METABOLITE

RP 26449



PHENOLIC METABOLITE

RP 25496

See P183 for revisions

TABLE I
Experimental Chromatographic Conditions for the Carlo Erba HRGC 5300 Gas Chromatograph

Equipped with:	SL416 Splitless control module MFC500 Multifunction controller EL480 Electrometer control module NPD-40 Detector SP4100 Spectra Physics computing integrator one unit of peak height = 0.94 µV at 60HZ
Column:	Fused silica capillary column, 15 meter x 0.25 mm. DB-17 liquid phase, film thickness 0.25 µm
Carrier Gas:	Helium at 1.0 kg/cm^2 (flow of 55 ml/min)
Temperature Program:	Initial at 140°C for 1 min. 20°C/min to 200°C, hold 4 min 25°C/min to 225°C, hold 9 min Cool to 140°C and equilibrate for 1 min before next injection
Injection Volume:	2 µl
Attenuation:	Electrometer as required (may vary with instrument performance and residue level)
Injection Temperature:	200°C
Detector Temperature:	300°C
Injection Mode:	Splitless for 30 sec. after then split 10:1-vent:column