Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Pebulate

MRID #: 415568-06

Matrix: Soil

Analysis: GC/NPD

Stauffer Chemicals

STAUFFER CHEMICAL COMPANY
RICHMOND RESEARCH CENTER
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Method No RRC-85-97
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Supersedes
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TITLE

GAS CHROMATOGRAPHIC DETERMINATION OF PEBULATE IN SOIL

I. SCOPE

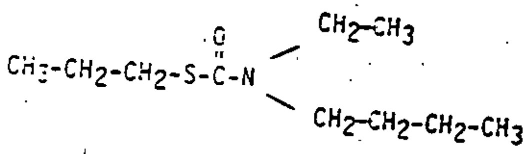
This method is intended for the determination of residues of pebulate in soil. The method has been validated at pebulate levels between 0.01 ppm and 1.0 ppm.

II. SUMMARY OF METHOD

A known quantity of sample is extracted with toluene, and the extract is analyzed for pebulate by capillary gas chromatography using nitrogen-phosphorus detection.

III. INTRODUCTION

Pebulate is the active ingredient in TILLAM® Selective Herbicide, and has the following chemical structure:



IV. APPARATUS AND REAGENTS

A. Apparatus

1. Gas Chromatograph. Hewlett-Packard Model 5880A, equipped with nitrogen-phosphorus detector and splitless capillary inlet. An equivalent chromatograph may be used.

2. Chromatographic Column. Fused-silica capillary, 12 m x 0.20 mm I.D., cross-linked methyl silicone, 0.33 micron film thickness. Hewlett-Packard 19091A Opt. 101 or equivalent.

3. Shaker. Reciprocating, Eberbach or equivalent.

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B. Reagents

1. Toluene. Nanograde® or equivalent.
2. Acetone. Nanograde® or equivalent.
3. Sodium Sulfate. Reagent grade.
4. Deionized Water. Produced by a Millipore Milli-Q or equivalent system.
5. Pebulate Standard. Available from Stauffer Chemical Co., 1200 S. 47th Street, Richmond, Ca 94804.
6. Calibration Solutions. Prepare a 1000 µg/mL stock solution by dissolving pebulate in toluene. Prepare calibration solutions of 0.01, 0.05, 0.1 and 1.0 µg/mL by diluting the stock solution with toluene.
7. Fortification Solutions. Prepare a 1000 µg/mL stock solution by dissolving pebulate in acetone. Prepare fortification solutions at other concentrations as required by diluting the stock solution with acetone.

V. PROCEDURE

A. Extraction

Place a 50-g sample of thoroughly mixed soil in an 8-ounce wide-mouth glass bottle; add 100 mL water and 50 mL toluene and cap the bottle with a PTFE - lined cap. Shake the bottle for two hours with a mechanical shaker and then centrifuge to separate the phases. Transfer a portion of the upper (toluene) phase to a 1-oz bottle that contains approximately 1 g sodium sulfate.

B. Determination of Soil Wet and Dry Weights

Transfer approximately 20 g of soil into a weighed aluminum pan. Determine and record the weight of the pan plus soil before and after drying at 105°C for 12 to 24 hours.

C. Gas Chromatographic Conditions

Use the following conditions with a Hewlett-Packard Model 5880A chromatograph:

Column initial temperature	90°C
Initial time	1.00 min

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Temperature programming rate	30 C/min
Column final temperature	130°C
Injector temperature	220°C
Detector temperature	300°C
Carrier gas	Helium
Carrier gas pressure	20 psi
Make-up gas flow (He total)	30 mL/min
Air flow	80 mL/min
Hydrogen flow	3.5 mL/min
Injection	2 µL splitless

Purge function activated at 0.5 min
Quantitation by on-line integrator or peak height

Under the above conditions the elution time of pebulate is approximately 3.6 min. The elution time depends on the length and condition of the column, and should be determined emperically by injection of a calibration solution.

D. Calibration and Sample Analysis

Inject the calibration solutions and sample extracts into the gas chromatograph using the conditions given above. For calibration, choose the calibration solution that generates the peak area or height that is closest in size to that in the sample extract. Make replicate injections of this solution until a constant calibration factor results (± 10%). Re-inject the calibration after every six sample extract injections. Dilute the sample if necessary to obtain a response within the calibration If the analyte response produced by the calibration solution during the analysis by more than ± 10%, re-analyze the sample extracts after calibration has been re-established.

VI. CALCULATIONS

A. Calibration Factors

Calculate a response factor, F, for each injection of a calibration solution as follows:

$$F \text{ (ng/area counts or ng/cm)} = \frac{C \times V}{H}$$

where C = concentration of calibration solution, ng/µL
V = volume of calibration solution injected, µL
H = peak area (counts) or height (cm)

B. Analyte in Sample

Calculate the concentration of the analyte in the original sample as follows:

$$\text{Residue (ppm) as wet weight} = \frac{F \times P}{V \times S}$$

F = calibration factor, ng/area counts or ng/cm
P = peak area (counts) or height (cm) from sample extract
V = volume of sample extract injected, µL
S = concentration of sample in extract injected, mg/µL

For convsersion of wet-weight residues to dry-weight residues use the following formula:

$$\text{Residue (ppm) as dry weight} = \text{Residue (ppm) as wet weight} \times \frac{W}{D}$$

where W = original weight of soil taken, g
D = weight of soil after drying, g

VII. DISCUSSION

A. Recoveries

Soil samples for recovery determinations were fortified at 0.01 to 1.0 ppm by addition of the appropriate amount of fortification solution to a weighed subsample of untreated soil prior to extraction. The mean recovery was 105% . Recovery data are summarized in Table I.

Figure 1 shows examples of chromatograms of calibration solution, and of extracts from untreated, fortified untreated, and treated soil samples.

B. Interferences

As shown in Figure 1, there were no significant interferences in the chromatograms from extracts of untreated soil.

VIII. REFERENCES

1. WRC Notebook No. 9993, pp 35 to 48.

IX. SAFETY PRECAUTIONS

A. Toluene and Acetone

- --Flammable
- --Vapors harmful
- --Avoid contact with skin and clothing
- --Use with proper ventilation; avoid breathing vapor

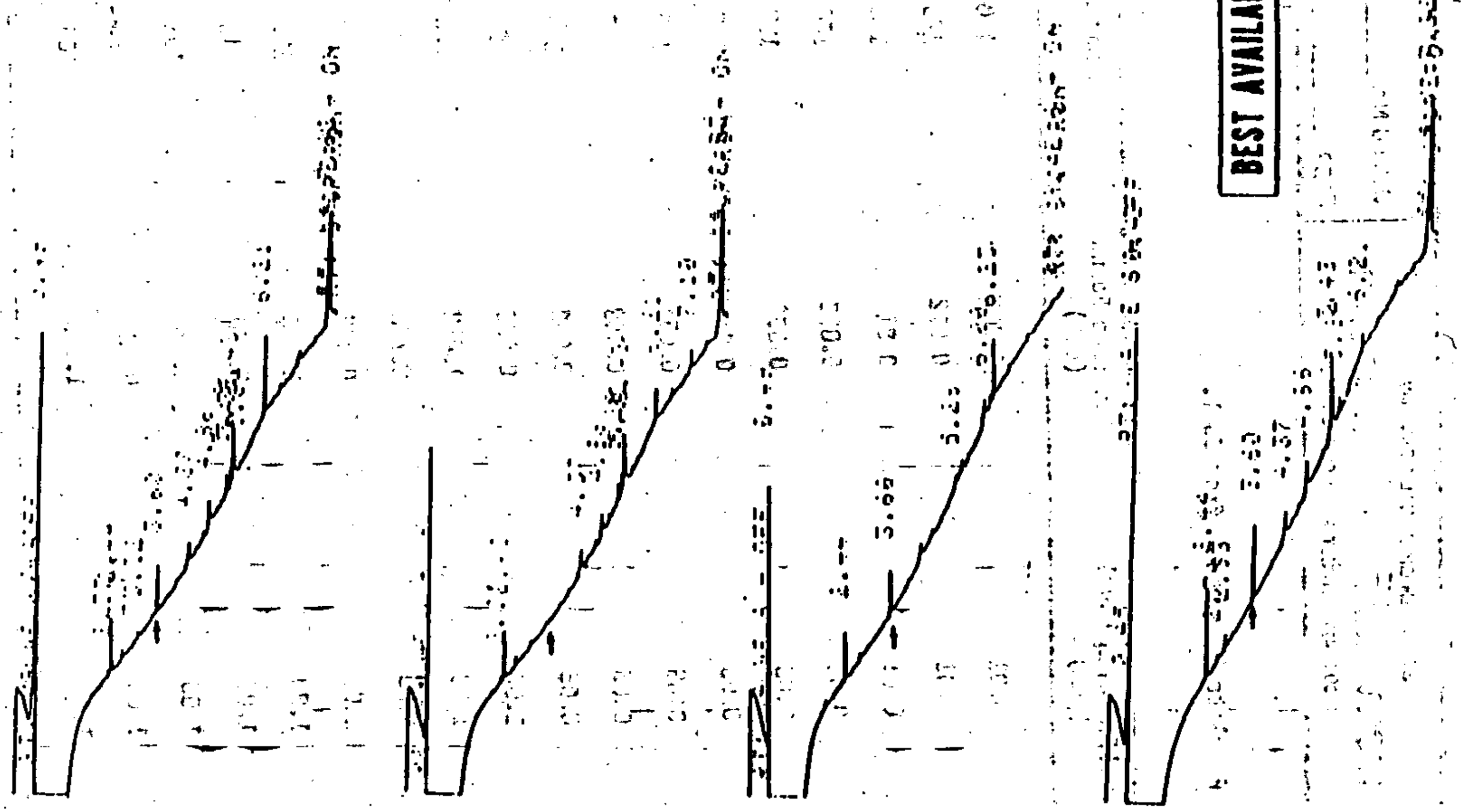
B. Pebulate

- --Avoid contact with skin and clothing

Table 1. Pebulate Recoveries from Soil.

Fortification Level (ppm)	Pebulate Found (ppm)	% Recovery
0.01	0.011	110
0.01	0.012	120
0.01	0.01	100
0.01	0.012	120
0.05	0.054	120
0.05	0.055	110
0.05	0.054	120
0.05	0.049	98
0.05	0.052	104
1.00	0.965	97
1.00	1.012	101
1.00	0.796	98
1.00	0.955	96
1.00	1.070	107
1.00	0.950	95
1.00	1.028	103
1.00	0.929	93
1.00	1.049	105

Figure 1. Typical Chromatograms of Pebulate in Soil



A. Calibration Solution, 0.01 µg/mL

B. Untreated Soil, 1 g/mL

C. Untreated Soil, 1 g/mL fortified with pebulate at 0.01 µg/g

D. Treated Soil, 1 g/mL