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Method No. RRC-87-77 Date 11/30/

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TITLE:

GAS CHROMATOGRAPHIC DETERMINATION OF BENSULIDE AND BENSULIDE OXYGEN ANALOG IN SOIL

I. SCOPE

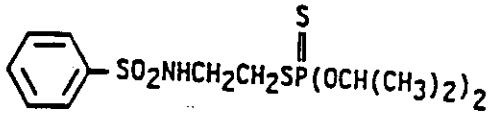
This method is intended for the determination of bensulide and its oxygen analog in soil. Bensulide is the active ingredient in BETASAN® and other selective herbicides manufactured by Stauffer Chemical Company. The method has been validated for concentrations of bensulide in soil between 0.05 and 5.0 ppm.

II. SUMMARY OF METHOD

Bensulide and its oxygen analog are extracted from soil with a methanol-water solution. The analytes are then extracted from the methanol-water solution into toluene. The toluene extract is analyzed for each analyte by using a capillary gas chromatograph equipped with a nitrogen-phosphorus detector.

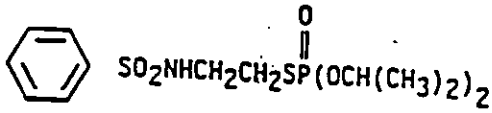
III. INTRODUCTION

Bensulide is S-(O,O-diisopropyl phosphorodithioate) ester of N-(2-mercapto-ethyl)benzenesulfonamide. The CAS (Chemical Abstracts Service) name is O,O-bis(1-methylethyl) S-[2-[(phenylsulfonyl)amino]ethyl]phosphorodithioate (9CI). Bensulide has structure I shown below:



I

Bensulide oxygen analog has structure II shown below:



II

IV. APPARATUS AND REAGENTS

A. Apparatus

1. Gas Chromatograph. Hewlett-Packard Model 5880A, equipped with capillary splitless inlet, Hewlett-Packard Model 7673A automatic sampler, nitrogen-phosphorus detector, and electronic integrator or data acquisition system.

2. Injection Port Insert. Splitless insert, 2 mm i.d. x 77 mm, Hewlett-Packard Part #18740-80220.

3. Chromatographic Column. Bonded, fused-silica capillary, 10 m megabore, 1.5 micron film thickness, cross-linked methyl silicone, J&W part #1251012.

4. Pipets. Serological, capacities of 1.0, 5.0 and 10.0 mL.

5. Bottles. Wide-mouth, 4 oz.

6. Bottles. Narrow-mouth 1 oz and 2 oz with poly-seal caps.

7. Syringes. 10, 100, and 500-microliter capacities, Hamilton 701N, 710N, 750N or equivalent.

8. Volumetric Flasks. 100 mL capacity.

9. Graduated Cylinder. 100 mL capacity.

10. Mechanical Shaker. Eberbach laboratory shaker or equivalent.

11. Centrifuge. International, Model K or equivalent, 3/4 hp with explosion-proof motor capable of 2100 rpm at average radius of 17.2 cm.

B. Reagents

1. Toluene. High purity, tested for the absence of interfering impurities.

2. Methanol. High purity, tested for the absence of interfering impurities.

3. Water. Deionized produced by Millipore Milli-Q or similar system.

4. Hydrochloric Acid. Reagent grade, 37%.

5. Extraction Solution. Methanol-water 60/40 v/v.

6. Bensulide Standard. Available from Stauffer Chemical Co., 1200 S. 47th St., Box No. 4023, Richmond, CA 94804-0023.

7. Calibration Solutions. Prepare a stock calibration solution in toluene by weighing 100 mg of bensulide standard into a 100-mL volumetric flask; dilute to the mark with toluene. This stock solution contains 1000 µg/mL of bensulide. Calibration matrix solutions of 1.0, 0.10 and 0.01 µg/mL are prepared by dilution of portions of the stock calibration solution with toluene extract obtained from extractions of untreated control (check) samples. Similarly, stock calibration solutions are prepared for bensulide oxygen analog.

8. Fortification Solution. Prepare a stock fortification solution by weighing 100 mg of bensulide standard into a 100-mL volumetric flask; dilute to volume with methanol. This stock solution contains 1000 µg/mL of bensulide. A fortification solution of 10 µg/mL is prepared by dilution of a portion of the stock calibration solution with methanol. Similarly, a stock calibration solution is prepared for bensulide oxygen analog.

V. PROCEDURE

A. Extraction

Prepare soil by mixing thoroughly. Weigh 50 g of soil into a 4-oz wide-mouth jar; add 50 mL of 60/40 methanol/water. Seal jar with aluminum foil and cap. Shake the jar on a mechanical shaker for one hour and centrifuge at 2000 rpm for 10 minutes. (Adding one drop of conc. HCl just prior to centrifuging helps to separate the contents when centrifuged.) Transfer a 10-mL aliquot of the extract to a 2-oz, narrow-mouth jar, add 10 mL toluene and 20 mL water, cap the jar tightly and shake it for 2 minutes. With a pipet, transfer the toluene phase into a dry 1-oz jar containing sodium sulfate.

B. Gas Chromatographic Conditions

Follow the manufacturer's instructions for operation of the gas chromatograph. Use these additional parameters for the analysis.

Inlet	splitless insert
Oven initial temperature	180°C
Initial time	0.5 min
Temperature programming rate	10°C/min
Oven final temperature	230°C
Oven final time	12 min
Injector temperature	230°C
Detector	280°C
Carrier gas	Helium
Carrier gas pressure	4 psi
Injection	3 µL
Quantitation	peak height (external standard)
Split valve off	0.5 seconds

Under the above conditions the elution time of bensulide oxygen analog is 6.82 minutes and bensulide is 8.33 minutes.

C. Calibration and Sample Analysis

The calibration solutions and sample extracts are injected into the gas chromatograph using the conditions given above. For calibration, the calibration solution that generates the peak area or height that is closest in size to that in the sample extract is chosen. Replicate injections of this solution are made until a constant calibration factor results (± 10%). The calibration solution is re-injected after every five sample extract injections. If the analyte response produced by the calibration solution changes during the analysis by more than ± 10%, the affected sample extracts are re-analyzed after calibration has been re-established.

VI. CALCULATIONS

A. Linear Response

When the detector response is linear (± 10%) over a range of calibration solution concentrations that includes the analyte concentration in solution, calculate the analyte concentration in the sample from the following formula:

$$P \text{ (analyte conc., ppm)} = R \times F$$

where R = response from injection of the sample solution, peak height or area units
F = analytical response factor.

The analytical response factor is calculated as follows:

$$F \text{ (electronic units)} = T/(C \times X)$$

where T = concentration of calibration solution, µg/mL
C = equivalent concentration of sample in injected solution g/mL
X = response from injection of calibration solution, peak height or area units.

Factors averaged from bracketing concentrations of calibration solutions, from calibration solutions injected before and after injection of sample solution, or both, may be used.

B. Curve-fitting for Non-linear Response

When the detector response is reproducible but non-linear, calculate the analytical results by the following equation:

P (analyte concentration in the sample, ppm) = Y/C

where Y = analyte concentration in the injected solution, µg/mL
C = equivalent concentration of sample in injected solution g/mL.

The analyte concentration in the injected solution is calculated from the power curve

Y (analyte concentration in the injected solution, µg/mL) = A(X x B)

where X = detector response, peak height or area units

A and B = constants determined from a curve fit program using calibration solution concentrations and responses.

VII. DISCUSSION

A. Recoveries/Accuracy

Fortified soil samples were prepared by the addition of the analytes to the untreated control samples. The samples were then analyzed by the method specified above. Recovery data are listed in Tables 1 and 2. At the fortification levels of 0.05, 1.0 and 5.0 ppm, the average recoveries of bensulide are 86, 88 and 83%, respectively. At the fortification levels of 0.05, 1.0 and 5.0 ppm, the average recoveries of bensulide oxygen analog are 68, 85 and 84%, respectively. Sample chromatograms are presented in Figures 1 and 2 for bensulide and the oxygen analog, respectively.

B. Method Precision

The precision of the method was determined by analysis of 10, 4, and 8 samples of soil fortified at 0.05, 1.0, and 5.0 ppm, respectively. The measured coefficients of variation (100 s/x) were 17.7%, 10.7% and 9.7%, respectively for bensulide and 13.7%, 6.4%, and 11.4%, respectively, for bensulide oxygen analog.

VIII. REFERENCES

1. Stauffer Chemical Company Laboratory Notebook No. WRC 10949, pp 1-43.

M13:37-77

IX. SAFETY PRECAUTIONS

A. Methanol

- Flammable
- Use in well-ventilated area
- Avoid breathing vapor
- Avoid contact with skin and eyes

B. Toluene

- Flammable
- Use in well-ventilated area
- Avoid breathing vapor
- Avoid contact with skin

C. Hydrochloric Acid

- Use in well-ventilated area
- Avoid breathing vapor
- Avoid contact with skin and eyes

D. Bensulide

- Harmful if swallowed or absorbed through the skin
- Avoid breathing mists
- Causes moderate eye irritation
- Do not get in eyes, on skin, or on clothing