TITLE: DETERMINATION OF BUTYLATE RESIDUES IN CORN AND SOILS

I. SCOPE

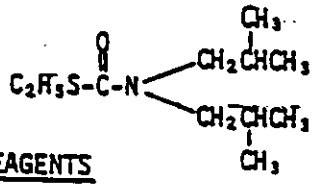
This method is intended for the determination of residues of butylate in soils and corn. The detection limit of the method is 0.05 ppm butylate. In soil, the method has been validated in the range of 0.01 to 5 ppm butylate.

II. SUMMARY

Butylate is separated from the crop or soil by either toluene extraction or steam distillation. The isolated butylate is determined by gas chromatography using a nitrogen-phosphorus flame ionization detector.

III. INTRODUCTION

Butylate is the active ingredient in SUTAN® a selective herbicide that effectively controls a variety of annual grasses, nutgrass and many broad-leaf weeds. Butylate is S-ethyl di-isobutylthiocarbamate Its chemical structure is:



IV. APPARATUS AND REAGENTS

A. Apparatus

1. Gas Chromatograph. Hewlett-Packard Model 5710A or equivalent equipped with a nitrogen-phosphorus flame ionization detector.

2. Gas Chromatographic Columns.

   a. 360 cm long by 2 mm i.d. glass containing 100/120 mesh Ultrabond protected by an oxygen trap in the carrier gas line.

   b. 180 cm long by 2 mm i.d. glass containing 10% OV-101 on 80/100 mesh Gas Chrom Q.

   c. 135 cm long by 2 mm i.d. glass containing 10% SP 2401 on 100/120 mesh Supelcoport.

3. Chromatography Tubes.

   Pyrex, 300 mm long by 11 mm i.d. constricted at the lower end to hold a Pyrex wool plug. An 80 mL pear-shaped solvent reservoir is attached to the other end.

4. Evaporator.

   Buchler Rotary Evapo-Mix or equivalent with $\frac{3}{4}$-16 connectors. Available from VWR, P.O. Box 3200 Rincon Annex, San Francisco, California 94119.

5. Centrifuge Tubes.

   40-50 mL, graduated, $\frac{3}{4}$-16, with Pyrex stoppers. Available from VWR, P.O. Box 3200 Rincon Annex, San Francisco, California 94119.

6. Steam Distillation Apparatus.

   See Figure 1. Includes: hot plate 6" x 6", 900 watts, 4-liter Erlenmeyer flask, adapter with joints 24/40 to 45/50, Friedrichs condenser modified as shown in Figure 1.

7. Waring Blender.

   One gallon and one pint capacities.

8. Syringe.

   10 µL Hamilton No. 701 or equivalent.

9. Filter Paper.

   Whatman No. 7.

10. Jars, Various

11. Mechanical Shaker.

    Variable speed, reciprocating. Available from VWR, P.O. Box 3200 Rincon Annex, San Francisco, California 94119.

B. Reagents

1. Toluene, Acetone. Pesticide grade or equivalent.

2. Sodium Sulfate, Sodium Chloride. Reagent grade, anhydrous.

3. Hydrochloric Acid. Conc., reagent grade.

4. Antifoam Agent. Available from Hodag Chemical Co., 7247 N. Central Park, Skokie, Illinois 60076.

5. Aluminum Oxide. Woelm, acid, activity grade 1, available from ICI Pharmaceuticals, Inc., Life Sciences Group, 26201 Miles Road, Cleveland, Ohio 44128.

6. Carbon. Activated, Darco Grade G-60; available from ICI United States, Inc., Specialty Chemicals Division, Wilmington, Delaware 19897.

7. Butylate Standards. 100, 10, 1, 0.5 and 0.05 µg/mL in toluene. Butylate is available from Stauffer Chemical Co., De Guigne Technical Center, 1200 S. 47th Street, Richmond, California 94804.

V. PROCEDURES.

A. Steam Distillation and Extraction

Weigh 100-200 g of crop sample or soil in a 1-gallon blender can, add 2-2.5 liters of water and blend for about 30 seconds. Transfer the macerate to a 4-liter, wide-mouth Erlenmeyer flask with the aid of an additional 500-600 mL of water. Add 10 mL of antifoam reagent and 200 g of sodium chloride. Connect the apparatus as shown in Figure 1 and collect about 400 mL of distillate in a 500 mL separatory funnel. Acidify the distillate with 5 drops of conc. HCl and extract the butylate twice with 5 mL portions of toluene by shaking the flask for about 30 seconds. The aqueous phase from the first extraction is transferred to a second 500 mL separatory funnel and extracted with the second 5 mL portion of toluene. Combine the toluene extracts in a 1-ounce, narrow-mouth bottle containing 2-5 grams of sodium sulfate and store for subsequent analysis on the gas chromatograph or for clean up.

B. Toluene Extraction

Weigh 50 g of chopped sample into 1 pint blender jar. Add 200 mL of toluene and blend the mixture for 3-5 minutes at medium speed. Filter the sample through Whatman No. 7 filter paper layered with anhydrous Na_2SO_4. Store the extract in a 4 oz. Polyseal-capped narrow-mouth bottle with about 5 g of Na_2SO_4.

For soils, weigh 50 g of sample in an 8-ounce, wide-mouth jar. Add 25 mL H_2O and 50 mL of toluene, seal the jar tightly and agitate it on a mechanical shaker for about one hour. Let the mixture stand until the supernate becomes clear.

C. Cleanup

A cleanup procedure is required only if interfering crop or soil extractives are present. Add 4 g of a mixture of aluminum oxide: carbon, 19:1 w/w to a chromatographic tube containing a Pyrex wool plug in the constricted end and top with 1 to 2 cm of sodium sulfate. Pour the toluene extract from 5 g of sample (5 mL of toluene soil extract or 20 mL of toluene crop extract) onto the column and apply slight pressure, enough to deliver 1 mL/min. Stop when the solvent reaches the top of the sodium sulfate layer. Pour an additional 5 mL of toluene through the column. Elute the butylate from the column into a centrifuge tube using 25 mL of toluene: acetone 95:5 v/v. Carefully remove the solvent via evaporation down to a final volume between 4 and 5 mL on a Buchler Rotary Evapo-Mix. Reduction to a final volume below 0.5 mL may cause loss of butylate and is to be avoided. Dilute to 5.0 mL with toluene.

D. Gas Chromatography

Analyze the extracts from A, B or C above by gas chromatography using the following conditions. The parameters listed are for a Hewlett-Packard model 5710A equipped with a nitrogen-phosphorus flame ionization detector and a SP 2401 column.

Inlet temperature:	180°C
Column temperature:	170°C
Detector temperature:	300°C
Nitrogen carrier gas:	30 mL/minute
Hydrogen:	3 mL/minute
Air:	50 mL/minute
Chart speed:	0.25 inch/minute
Quantitation:	peak height
Aliquot injected:	5 µL

The retention time of butylate under these conditions is about 2.4 minutes. Typical response: 7 centimeters peak height for 1 nanogram at 4X attenuation.

VI. CALCULATIONS

The level of butylate in the sample is calculated as follows:

$$ppm = \frac{N}{W}$$

Where N is nanograms of butylate found in the aliquot.
W is the weight of the sample in the aliquot injected in milligrams.

N is determined by comparing bracketed peak heights of standards with the sample peak height or from a standard curve.

VII. DISCUSSION

Typical recoveries of butylate from various crops and soils are shown in Table I.

Retention times of potentially interfering herbicides are shown in Table II.

Sample chromatograms are shown in Figures 2 - 6.

The detection limit of butylate with the conditions stated in the analytical method is about 0.05 ppm.

VIII. SAFETY

Toluene Acetone

Avoid skin contact

Avoid breathing vapors.

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TABLE II

Retention times - Ultrabond column

COMPOUND	TR, MINUTES
EPTC	1.8
Butylate	2.4
Vernolate	2.6
Randox	3.4
R-29148	4.0
R-25788	4.2
Avadex	> 8
Napropamide	> 8
Atrazine	> 8
Bladex	> 8