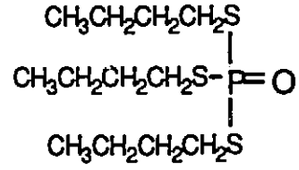
INTRODUCTION

A method for the quantitative extraction and simultaneous detection by GC for residues of DEF and DBDS from a California soil has been developed at PTRL-West. The method utilizes GC with FP detection in the sulfur mode with a DB-225 column for separation.

DEF has the following chemical and physical properties:

Chemical Name: S,S,S-tributyl phophorotrithioate

Chemical Structure:



Empirical Formula: $C_{12}H_{27}S_3PO$

Molecular Wt.: 314.5

Appearance: Colorless to pale yellow clear liquid Boiling point: 105°C @ 0.3mm Hg

Vapor Pressure: 1.7×10^{-6} mm Hg @ 20°C

Solubility : Soluble in aliphatic, aromatic, chlorinated hydrocarbons and alcohol solvents.
Water: 2.3ppm @ 20°C.

Stability: Relatively stable to acids and heat. Hydrolyzes slowly under alkaline conditions.

MATERIALS AND METHODS

DESCRIPTION OF METHOD:

DEF and DBDS are extracted from soil with 5% acetone in hexane. The soil extract is reduced to approximately 5 ml being careful not to let the flask go to dryness. These reduced extracts are resuspended to 10 ml in the original acetone hexane mixture and passed through a florisil Sep-Pak. The Sep-Pak is then rinsed with an additional 5 ml of extraction mixture. The final extract is reduced to 1 ml and analyzed by GC with FP detection in sulfur mode.

EQUIPMENT:

Nalgene polypropylene bottles, 250-ml
Centrifuge and centrifuge rotor capable of accepting 250 ml bottles
Vacuum filter flasks, 250 ml
Sintered glass filter funnels, medium porosity
Glass funnels
Round bottomed flasks, 500 ml
Graduated cylinders, 100 ml
Wrist action shaker
Graduated centrifuge tubes, 30 or 50 ml and 15 ml
Rotary vacuum evaporator with water bath, bath temperature 35°C
Injection syringe with Luer-Lock connection, 10 ml
Injection syringe, 10 µl
Gas chromatograph with FP detector in Sulfur mode, Hewlett Packard 5840A
Integrator

REAGENTS :

Acetone, for residue analysis
Hexane, for residue analysis
Extraction mixture: 5% acetone in hexane
Sodium sulfate, reagent grade
DEF and DBDS standard solutions: 1000 µg/ml each in hexane
^{14}C-DEF and ^{14}C-DBDS supplied by Mobay
Glass wool
Florisil Sep-Paks (Waters Assoc.)

SOILS:

The method was validated for two soils; Sandy Loam Soil (Mobay #371), and Silty Loam Soil (Mobay #307) both supplied by Mobay. Characteristics of these soils are presented in Appendix C.

ANALYTICAL PROCEDURE:

Soil samples of 100 grams each were weighed into 250-ml Nalgene polypropylene bottles. 100 ml of extraction solvent (5% acetone in hexane) were added to the soil. The bottles were shaken on a wrist action shaker for 10 min and centrifuged for 5 min at 3000 rpm to pellet the soil. The supernatant was filtered through medium porosity filter funnels into 250-ml suction flasks. The funnels were rinsed with 5 ml of the extraction solvent. The soil was extracted twice more with 50 ml of the extraction mixture following the above procedure. The filtered supernatant was transfered to a 500-ml round bottomed flasks by passing the liquid through a glass funnel with a glasswool plug containing 25 gm of anhydrous sodium sulfate. The sodium sulfate bed was then rinsed with 10 ml of the extraction solvent. The filtered and dried soil extract was reduced by rotoevaporation to approximately 5 ml. [Note: It is important at this point in the procedure not let the flask go to dryness. DBDS is fairly volatile and is readily lost if the flask goes dry.] The remaining solution is transfered to a 15-ml graduated centrifuge tube. The flask was rinsed with the extraction mixture and the final volume of the solution was adjusted to 10 ml. The solution was pulled up into a 10-ml syringe and then passed through a florisil Sep-Pak into a 30 or 50-ml graduated centrifuge tube. The 50-ml graduated centrifuge tube, syringe and Sep-Pak were rinsed with 5 ml of the extraction solvent mixture to remove any remaining DEF

and DBDS. The final solution was reduced under N_2 to 1 ml and transfered to an appropriate vial for GC analysis.

GC ANALYSIS:

Two microliters of the final solution were injected onto a gas chromatograph with an FP detector in sulfur mode. Standards ranging from 0.005 ppm to 1.5 ppm equivalents in soil are injected between every two samples. A 15-meter DB-225 column with a 1µm thick liquid phase is used for separation. A typical chromatogram of DEF and DBDS is shown in Figure 1. The following GC conditions resulted in retention times of approximately 5.2 min for DBDS and 11.1 min for DEF.

Instrument: Hewlett Packard 5840
Column: Fused silica DB-225 15 M x 0.53 mm id with 1µm film thickness (J&W Scientific)
Injector Temp: 250° C
Oven: 50° C for 2 min.
50° C to 220° C at 20° C/min
220° C for 12 min
Detector: 280° C
Carrier Gas: He at 19.4 ml/min (~ 7 psi)
Makeup gas: None
Combustion Gases: H_2 100 ml/min
Air 110 ml/min
O_2 28 ml/min
Attenuation: 1
Injection volume: 2-µl

EVALUATION:

Quantitative evaluation is performed with integrated areas of standard and sample solutions. Equal volumes of the sample and standard solutions are injected. Since FPD is a non-linear detector in the sulfur mode, a log/log plot is made with each set of standards consisting of at least 4 points ranging from 0.005 ppm equivalents to 1.5 ppm equivalents. It is not desirable to inject standards greater than 1.5 ppm equivalents as the response

deviates from an exponential reponse. All samples should be diluted if the final concentration of the extract is determined to be greater than 1.5 ppm.

RECOVERIES:

Recoveries were determined on two different soil types; sandy and silty loam soils (see appendix C). Soils were fortified as described by the protocol for PRTL project No. 147W in Appendix A. The lowest determined concentration in soil was 0.01 mg/kg soil.

CALCULATION OF RESIDUES:

All standards for standard curve generation are on a ppm equivalent in soil basis. Quantitation of total residue in soil is based directly on the standard curve generated over the course of GC analysis of the samples. Cricket-Graph ™ was used to generate a standard curve fitted to the functional form $Y = AX^B$, where Y (average area) is predicted by values of X (Concentration) with initial values for parameter of A and B determined by the computor program. After the curve has been fitted, the concentration of DEF and DBDS is generated using the formula:

$$\mu g/g = \left(\frac{\text{Area}}{A}\right)^{1/B}$$

After the concentration of each component is determined, the concentration of DBDS is determined in DEF equivalents by the following formula:

ppm DBDS as DEF equivalents = ppm DBDS x (1.76)

where 1.76 is the ratio of the molecular weights of DEF and DBDS. The DBDS concentrations shown in Tables I and II have not been calculated as DEF equivalents.