Analytical Residue Method for Triallate and the Sodium Salt of 2,3,3-trichloroprop-2-ene Sulfonic Acid in Soil

Author: J. M. Allan

Scope

The analytical procedure given here determines residue levels of triallate [S-(2,3,3-trichloroallyl)diisopropyl-thiocarbamate] and 2,3,3-trichloroprop-2-ene sulfonic acid (the major metabolite of triallate) in soil.

Summary

The analytical method described here is for residue determinations of triallate and 2,3,3-trichloroprop-2-ene sulfonic acid (TCPSA) in soil. Soil is extracted with acetonitrile/water (distilled in glass) using a mechanical shaker, and filtered through a Buchner funnel. An aliquot of the extract is diluted with water and partitioned with isooctane (distilled in glass) to isolate triallate. The isooctane is eluted through a florisil cleanup column, concentrated and quantitated by capillary GC using a ^{63}Ni electron capture detector. The aqueous layer, containing TCPSA is partitioned with methylene chloride once as a cleanup, then a second time using a phase transfer catalyst. The second extract is evaporated, passed through a cation exchange column and derivatized with triethylorthoformate. The resulting ethyl sulfonate is quantitated by capillary GC using a ^{63}Ni ECD. A general method schematic is provided in Figure F1.

Limit of Validation

0.01 ppm each compound, based on 6.25 g aliquot of a 25 g (wet wt.) sample.

Apparatus and Equipment

250 mL polyallomer centrifuge bottle (Nalgene® Cat. No.: 3128-0250)

Buchner funnels, Fisher No. 10-362B

Mettler balance PC 4400 or equivalent

Oil bath or equivalent

Calab rotary evaporator

100 mL and 250 mL round bottom flasks, Fisher No. 10-067D and E

50 mL Kjeldahl shaped flask, Kontes No. K-294305

Whatman glass microfibre filters, 5.5 cm, Fisher No. 09-873E

Glass wool, Fisher No. 11-388

Graduated cylinders 10-1000 mL, Fisher No. 08-549-5B:C:D:E:G:H:I

100 mL volumetric flask, Fisher No. 10-210C

250 mL separatory funnels, Fisher No. 10-437-10C

Graduated mixing cylinders (250 mL) Fisher No. 08-566E

25 mL Kuderna-Danish receiver tubes

Pasteur pipettes 5-3/4" length, Fisher No. 13-678-6A

Pasteur pipettes 9" length, Fisher No. 13-678-6B

Serological pipettes from 1.0 through 10.0 mL, Fisher No. 13-676-28D:E:F:G

Glass chromatographic column: 1.2 x 22 cm (1.0 cm ID) topped with a 3 x 10 cm reservoir and fitted with a Teflon stopcock with a 1.5 cm delivery tip

Mechanical shaker, Kraft

Varian 3700 gas chromatograph equipped with electron capture detector, strip chart recorder, computer data system and Varian autosampler (or equivalent)

GC Column:

A. Triallate Analysis (Hazleton Laboratories)
6' x 2 mm glass column packed with 3% Dexil 300
on 100/120 mesh supecoport

B. TCPSA and Triallate Analysis
J & W Fused silica capillary column
Stationary phase: DB-5
Film Thickness: 0.25 µM
Column Dimensions: 15 M x 0.322 mM

Column Conditions

Column	A	B	
Analyte	Triallate	TCPSA	Triallate
Column temperature (Isothermal)	180°C	102°C	160°C
Injector temperature	300°C	200°C	200°C
Detector temperature	350°C	300°C	300°C
Attenuation/Range	128/1	128/1	64/1
Volume Injected	1 µL	3 µL	3 µL
Carrier gas	95/5 Argon/ Methane 33 mL/ min	He 2.5 mL/min	He 2.5 mL/min
Split ratio	None	50:1	50:1
Chart speed	0.64 cm/min	1.0 cm/min	1.0 cm/min
Quantification	External Standards, Peak Height		

Solvents, Reagents and Solutions

Deionized water

Isooctane, distilled in glass

Acetonitrile, distilled in glass

Methylene chloride. distilled in glass

Sodium sulfate (anhydrous) reagent grade, Fisher No. S-421

5% sodium sulfate solution

Florisil 60-100 mesh (chromatographic grade, Fisher No. F-100)

AG 50W-X8 ion exchange resin; 200-400 mesh, hydrogen form Bio-Rad No. 142-1451

Triethylorthoformate, Fluka Chemical Corp., No. 75530

Tetrabuthylammonium hydrogen sulfate, Aldrich No. 15-583-7

Fortification Solutions

Weigh to four significant figures 0.1 g of triallate (99.9%) into a 100 mL volumetric flask, and dilute to 100 mL with high purity acetone, mix well to insure complete dissolution. This stock solution contains 1000 µg/mL of triallate.

Weigh to four significant figures 0.1 g of 2,3,3-trichloro-prop-2-ene sulfonic acid sodium salt (99.9%) into a 100 mL volumetric flask, dissolve and dilute with deionized water to the mark. The stock solution contains 1000 µg/mL of TCPSA.

From the 1000 µg/mL stock solutions, prepare a 50.0 µg/mL solution by pipetting 5.0 mL of each (triallate and TCPSA) concentrate into a 100 mL volumetric flask and diluting to the mark with 60%/40% acetonitrile/water.

From the 50.0 µg/mL solution, subsequent dilutions using 60%/40% acetonitrile/water are made for fortification standards.

10.0 mL of 50 µg/mL diluted to 100 giving 5.0 µg/mL
5.0 mL of 50 µg/mL diluted to 100 giving 2.5 µg/mL
2.5 mL of 50 µg/mL diluted to 100 giving 1.25 µg/mL
10.0 mL of 5.0 µg/mL diluted to 100 giving 0.50 µg/mL
5.0 mL of 5.0 µg/mL diluted to 100 giving 0.25 µg/mL

Triallate Standards for ECD

Weigh to four significant figures 0.1 g of triallate (99.9%) into a 100 mL volumetric flask, dissolve and dilute with high purity isooctane to the mark. This concentrated solution contains 1000 µg/mL of triallate.

From the 1000 µg/mL concentrate, pipet 10 mL into a 100 mL volumetric flask and dilute to the mark with isooctane. This concentration is 100 µg/mL of triallate.

Prepare a 10.0 µg/mL solution of triallate by pipetting 10 mL of the 100 µg/mL solution into a volumetric and diluting with high purity isooctane to 100 mL.

Pipette 10 mL of the 10 µg/mL standard into another 100 mL volumetric, dilute with high purity isooctane and mix well. The concentration of this solution is 1.0 µg/mL of triallate.

Pipette 10 mL of the 1.0 µg/mL solution into another 100 mL volumetric, dilute with isooctane and mix well. This solution contains 0.10 µg/mL of triallate.

From the 10 µg/mL solution, pipette 5.0 mL into a 100 mL volumetric flask, dilute to the mark with high purity isooctane and mix well. This solution contains 0.5 µg/mL of triallate.

From 0.5 µg/mL and 0.1 µg/mL solutions, subsequent analytical dilutions are made as follows, using high purity isooctane (distilled in glass).

Milliliter	µg/mL Standard	Standard Dilution	Concentration µg/mL
7.0	0.50	100	0.035
6.0	0.50	100	0.030
5.0	0.50	100	0.025
4.0	0.50	100	0.020
3.0	0.50	100	0.015
10.0	0.10	100	0.010
5.0	0.10	100	0.005
10.0	0.025	100	0.0025

Note: After preparation, standards should be stored under refrigeration (4-6°C) in amber bottles.

Preparation of the Ethyl Ester of 2,3,3-Trichloroprop-2-ene Sulfonic Acid

Weigh 2.0 grams of TCPSA-Na^+ into a 50 mL beaker. Add 25 mL deionized water and stir until dissolved.

Prepare an AG-50W-X8 column by transferring 10 mL of previously water washed resin to 1.2 cm o.d. (1.0 cm ID) x 22 cm (with a 1.5 cm delivery tip) containing 5 mL deionized water and a glass wool plug. Allow the resin to settle and wash the column with 25 mL deionized water. Place the dissolved TCPSA-Na^+ on the column and allow to elute collecting the eluate, follow the sample with additional 25 mL deionized water and collect the sample and wash in a 250 mL round-bottom flask.

Evaporate the free acid to dryness using a rotary evaporator and a 40-50°C water bath.

To the dry residue add a magnetic stirring bar and 150 mL triethylorthoformate. Connect the 250 mL flask to a reflux condenser and a drying tube. Attach a variable transformer-controlled heating mantle supported by a magnetic stirring motor unit mounted on a "Lab Jack". Adjust the height of the heater/stirring assembly to firmly support the flask in contact with the reflux condenser.

Start the magnetic stirrer, turn on the cooling water and reflux for 1 hour.

Distill the excess triethylorthoformate and the ethyl ester under vacuum (b.p. 108-100°C, 0.5 mm) to give 1.76 g (98.5%) ester. The ester is a clear colorless oil.

Ethyl Sulfonate Standards for ECD

Weigh to four significant figures 0.1 g of the prepared ethyl sulfonate (98.5%) into a 100 mL volumetric flask, dissolve and dilute with isooctane (distilled in glass) to the mark. This concentrated solution contains 1000 µg/mL of TCPSA-Ethyl ester.

From the 1000 µg/mL concentrate, pipet 10 mL into a 100 mL volumetric flask and dilute to the mark with isooctane (distilled in glass). This concentration is 100 µg/mL of TCPSA-ethyl ester.

Prepare a 10.0 µg/mL solution of ester by pipetting 10 mL of the 100 µg/mL solution into a volumetric and diluting with isooctane (distilled in glass) to 100 mL.

Pipette 10.0 mL of the 10 µg/mL standard into another 100 mL volumetric, dilute with isooctane (distilled in glass) and mix well. This solution contains 1.00 µg/mL.

Prepare a 0.50 µg/mL solution of ester by pipetting 5.0 mL of the 10.0 µg/mL solution into a volumetric and diluting with isooctane (distilled in glass) to 100 mL.

Prepare a 0.10 µg/mL solution by pipetting 10.0 mL of the 1.00 µg/mL solution into a 100 mL volumetric and diluting with isooctane.

From the 0.50 and 0.10 µg/mL solutions, subsequent analytical dilutions are made as follows, using isooctane (distilled in glass).

Milliliter	µg/mL Standard	Dilution Volume	Concentration µg/mL
7.0	0.50	100	0.035
6.0	0.50	100	0.030
5.0	0.50	100	0.025
4.0	0.50	100	0.020
3.0	0.50	100	0.015
10.0	0.10	100	0.010
5.0	0.10	100	0.005
10.0	0.025	100	0.0025
5.0	0.025	100	0.00125

Store all standards in brown bottles under refrigeration.

Procedure

Weigh 25.0 grams of soil into a 250 mL centrifuge bottle. Fortifications must be made at this stage.* Add 150 mL 80%/20% acetonitrile/water and shake for 15 minutes on a mechanical shaker. Decant the extract through a Buchner funnel fitted with a prerinsed Whatman filter. Collect the extract in a 250 mL round-bottom flask. Complete the transfer by rinsing the sample bottle and filter cake twice with 20 mL acetonitrile/water. Transfer the extract to a 250 mL graduated mixing cylinder and adjust the volume to 200 mL with acetonitrile/water.

* For example, a 0.01 ppm fortification to a 25 gram sample is made by pipetting 1.0 mL of the 0.25 µg/mL triallate/TCPSA in fortification solution into the centrifuge bottle.

Partition

Combine a 50 mL aliquot of extract with 150 mL 5% sodium sulfate solution and 50 mL isooctane in a 250 mL separatory funnel. Shake the separatory funnel for 5 minutes on a mechanical shaker and allow 15 minutes for phase separation. Collect the lower aqueous portion in a 250 mL Erlenmeyer and retain for later TCPSA partitioning. Deliver the isooctane layer directly into the Florisil® column as described below.

Triallate Florisil Cleanup

Apply a small plug of glass wool into the base of a glass chromatographic column. Add about 30 mL of isooctane to the empty column and slowly add 5.0 g of Florisil® (as received from supplier) allowing the adsorbent to wet thoroughly as it settles. Add 4 cm of granular sodium sulfate to the top of the column then drain to the sodium sulfate level.

Deliver the isooctane layer in the separatory funnel directly onto the column and begin elution. Allow the sample to completely enter the column and discard the eluate. Do not allow the column to go dry. Elute the column with an additional 65 mL of isooctane, collecting the eluate in a 100 mL round-bottom flask. Evaporate the samples just to dryness on a rotary evaporator using a room temperature water bath. Adjust the final sample volume to 5.0 mL with isooctane. The sample is ready for GC-ECD analysis.

Triallate Quantification

Sample quantification is based on the peak height of the sample compared to a calibration curve obtained on external standards across the range of expected concentrations. Appropriate sample dilutions must be made in order to keep the triallate concentration within the range of the standards used for quanitification by GC/ECD. Correction must then be applied to account for the total dilution of the sample injected and the percent moisture of the soil.

TCPSA Analysis Partition

To the aqueous layer retained from the triallate partition step, add 3 drops of concentrated H_2SO_4 and transfer back to the 250 mL separatory funnel. Add 50 mL of methylene chloride and shake for 2 minutes. Allow the layers to separate and discard the methylene chloride layer. To the aqueous layer in the separatory funnel add 2.0 grams of tetrabutylammonium hydrogen sulfate (a phase transfer catalyst) and 50 mL of methylene chloride. Shake the separatory funnel for 5 minutes on a mechanical shaker. Allow the two layers to separate for 15 minutes. Drain the methylene chloride solution into a 100 mL round-bottom flask. Evaporate the methylene chloride to dryness using a rotary evaporator keeping the round-bottom flask immersed in a room temperature water bath.

Preparation of AG-50W-X8

Divide a 1 lb bottle of resin in half and wash each half 3 times with 500 mL deionized water. Store under deionized water until used.

Column Chromatography

Prepare an AG 50W-X8 column by transferring 10 cc of washed (200-400 mesh; hydrogen form) resin to a 1.2 cm x 22 cm column containing a glass wool plug and 5 cm deionized water. Allow the resin to settle and wash the column with 10 mL deionized water. Place a 50 mL Kjeldahl shaped flask under

the delivery tip of the column. Dissolve the evaporated residue in 7.5 mL deionized water, transfer to the column with a disposable pipet and begin collection. Allow the sample to enter the column and follow with 2 x 5 mL deionized water flask washes using the same disposable pipet and allowing each wash to completely enter the column before applying the next wash. Elute the column with an additional 10 mL of deionized water added directly to the column. Connect the sample flask to a rotary evaporator, partially immerse in an ice bath and begin operation. Adjust water bath heaters to reach 55°-60°C over the course of evaporation. Alternatively, the samples may be blown to drynesss with N_2 in a 40°C water bath overnight, then rotovaped to final dryness in a 60°C water bath (about 10 min). After evaporation cool the flask to room temperature and stopper to protect from moisture. The sample is ready for derivatization.

Derivatization

To the Kjeldahl flask containing the evaporated residue, add 1 mL of triethylorthoformate and swirl to coat the sides of the flask. Stopper the flask firmly with a glass stopper and place in a 100°C oil bath for 1 hour. After the heating period, remove the flask and allow to cool to room temperature. Remove the stopper, pipet 9.0 mL of isooctane into the flask and mix well. The sample is now ready for GC-ECD analysis.

Quantification

Sample quantification is based on the peak height of the sample compared to a calibration curve obtained on external standards across the range of expected concentrations. Appropriate sample dilutions must be made in order to keep the concentration within the range of the standards used for quantification by GC/ECD (additional dilutions made with isooctane). Correction must then be applied to account for the total dilution of the sample injected and percent moisture of the soil. No correction is made for the small difference in molecular weight between the sodium salt of TCPSA (MW=247.46) and the ethyl sulfonate (MW=253.53).

FIGURE F1

SCHEMATIC OUTLINE OF METHODOLOGY
FOR
TRIALLATE AND TCPSA

25 Grams Sample

Extract with 200 mL of 80/20% Acetonitrile/Water

50 mL Aliquot Diluted with 150 mL 5% Na_2SO_4

Partitioned with Isooctane

Triallate	TCPSA
↓	↓
Isooctane Layer	H_2O Layer
↓	↓
Florisil Column	Partition with $MeCl_2$ (discard)
↓	↓
Concentrate	Repartition Aqueous with $MeCl_2$ & TBAHS
↓	↓
Quantitation GLC ^{63}Ni Detector	Evaporate $MeCl_2$
	↓
	AG-50 Column
	↓
	Evaporate
	↓
	Derivatization with TEOF
	↓
	Quantitation GLC ^{63}Ni Detector