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# Determination of Residues of *cis*- and *trans*-3-Chloroallyl Alcohol in Soil by Capillary Gas Chromatography with Mass Selective Detection

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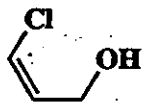
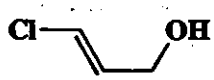
## A. Scope

This method is applicable for the quantitation of residues of the 1,3-dichloropropene metabolites, *cis*- and *trans*-3-chloroallyl alcohol (CAAL) in soil. The method was validated over the concentration range 0.42 ng/g to 2.1 µg/g with a limit of quantitation of 0.42 ng/g.




*cis*-3-Chloroallyl Alcohol
CAS 4643-05-4




*trans*-3-Chloroallyl Alcohol
CAS 4643-06-5

## B. Principle

CAAL residues in soil are extracted with 0.01 N hydrochloric acid and the acid extract is purified by passing through an ion-exchange solid phase extraction (SPE) column. CAAL residues are partitioned from the acid extract into methyl-*t*-butyl ether (MTBE). The MTBE is dried and purified by passing over anhydrous magnesium sulfate and through a silica gel SPE column. Hexane is added and the sample is concentrated using a Snyder distillation column. The sample is further concentrated under nitrogen and brought to a final volume of 1 mL with hexane. CAAL residues in hexane are derivatized with isobutyl chloroformate in the presence of pyridine to their corresponding *cis*- and *trans*-3-chloroallyl isobutyl carbonates (CAIBC) and analyzed by capillary gas chromatography with mass selective detection (GC/MSD). Soils indicating levels of CAAL above approximately 40 ng/g are diluted 100-fold with hexane and reanalyzed.

C. Safety Precautions

1. Each analyst must be acquainted with the potential hazards of the reagents, products, and solvents used in this method before commencing laboratory work. SOURCES OF INFORMATION INCLUDE: MATERIAL SAFETY DATA SHEETS; LITERATURE, AND OTHER RELATED DATA. Safety information on non-DowElanco products should be obtained from the container label or from the supplier. Disposal of reagents, reactants, and solvents must be in compliance with local, state, and federal laws and regulations.

2. Acetone, hexane, methanol, MTBE and 1-propanol are flammable and should be used in well-ventilated areas away from ignition sources.

3. *cis*- and *trans*-3-Chloroallyl alcohol are corrosive and lachrymators. It is imperative that proper eye and personal protection equipment be used when handling these compounds. Handling of neat material should be carried out in a fume hood.

4. Isobutyl chloroformate is highly toxic, irritating to eyes, respiratory system and skin. It is imperative that proper eye and personal protection equipment be used when handling this reagent. Handling of neat material should be carried out in a fume hood.

D. Equipment (Note N.1.)

1. Automatic sampler, Model 7673, Hewlett-Packard, Wilmington, DE 19808.

2. Balance, analytical, Model AE200, Mettler Instrument Corporation, Hightstown, NJ 08520.

3. Balance, pan, Model BB2440, Mettler Instrument Corporation.

4. Centrifuge, with rotor to accomodate 8-mL vials, Model Centra-8, International Equipment Company, Needham Heights, MA 02194.

5. Centrifuge, with rotor to accomodate 2-oz bottles, Model CU-5000, International Equipment Company.

6. Evaporator, N-Evap, Model 111, Organomation Associates, Inc., South Berlin, MA 01549.

7. Gas chromatograph, Model 5890 Series II, Hewlett-Packard.

8. Heater, dry bath incubator, catalog number 11-718-2, Fisher Scientific, Pittsburgh, PA 15219.

9. Heater, dry bath incubator (aluminum) heating block, catalog number 11-718-16, Fisher Scientific.

10. Hot plate, Thermolyne extra-capacity hotplate, catalog number 11-496-5A, Fisher Scientific.

11. Mass selective detector, Model 5971A, Hewlett-Packard, Palo Alto, CA 94304.

12. Mass selective detector data system, Model G1034B, Hewlett-Packard.

13. Shaker, variable speed reciprocating with box carrier, Model 6000, Eberbach Corporation, Ann Arbor, MI 48106.

14. Ultrasonic bath, Model 1200, Branson Cleaning Equipment Company, Shelton, CT 06484.

15. Vacuum manifold box, Model spe-21, J.T. Baker, Inc., Phillipsburg, NJ 08865.

16. Vial crimper, catalog number 8710-0979, Hewlett-Packard, Wilmington, DE 19808.

17. Vortex mixer, Model G-560, Scientific Industries, Inc., Bohemia, NY 11716.

18. Water purification system, Model Milli-Q UV Plus, Millipore Corporation, Milford, MA 01757.

E. Glassware and Materials (Note N.1.)

1. Bottle, 2 oz, round, wide-mouth, clear, with PTFE-lined screw caps, catalog number 03-320-11C, Fisher Scientific, Pittsburgh, PA 15219.

2. Column, capillary gas chromatography, Durabond-17 liquid phase, 20 m x 0.18 mm i.d., 0.3 µm film thickness, catalog number 121-1723, J&W Scientific, Folsom, CA 95630.

3. Column, silica gel SPE, catalog number 7086-07, J.T. Baker, Inc.

4. Column, strong anion-exchange (quaternary amine) SPE, catalog number 7091-03, J.T. Baker, Inc.

5. Column adapter, PTFE, catalog number 120-1100, Jones Chromatography, Inc., Lakewood, CO 80228.

6. Column inlet liner, deactivated, catalog number 5181-3315, Hewlett-Packard.

7. Column reservoir, 25 mL, catalog number 71213-1011,Varian Sample Preparation Products, Harbor City, CA 90710.

8. Erlenmeyer flask, 50 mL, 19/22 joint, catalog number 296510-0050, Kontes, Vineland, NJ 08360.

9. Filter, charcoal, catalog number 7972, Chrompack, Inc., Raritan, NJ 08869. (Note N.2.)

10. Filter, moisture, catalog number 7971, Chrompack, Inc. (Note N.2.)

11. Filter, oxygen, catalog number 7970, Chrompack, Inc. (Note N.2.)

12. Gas, helium, 99.995% purity, Airco, Murray Hill, NJ 07974.

13. Gas, nitrogen, 99.99% purity, Airco.

14. Microdispenser, 10 µL and 25 µL, Drummond Dialamatic Microdispenser, catalog numbers 300210 and 300225, Drummond Scientific Company, Broomall, PA 19008.

15. Microdispenser replacement bore, 10 µL and 25 µL, catalog numbers 300210G and 300225G, Drummond Scientific Company.

16. Micro Snyder distilling column, 19/22 joint, catalog number 569001-0319, Kontes.

17. Prefilter, glass fiber Acrodisc, catalog number 09-730-195, Fisher Scientific.

18. Syringe, 100 and 500 µL capacity, catalog numbers 80600 and 80800, Hamilton Co., Reno, NV89520.

19. Vial, 8 mL, with PTFE-lined screw cap, catalog number B7800-3, National Scientific Company, Lawrenceville, GA 30243.

20. Vial, 45 mL, with PTFE-lined screw cap, catalog number 60958A-11, Kimble Glass, Vineland, NJ 08360.

21. Vial, autosampler, 2 mL, catalog number C4011-1, National Scientific Company.

22. Vial seal, catalog number C4011-1A, National Scientific Company.

F. Reagents and Chemicals (Note N.1.)

1. Reagents

a. Acetone, Optima grade, catalog number A929-4, Fisher Scientific, Pittsburgh, PA 15219.

b. Hexane, Optima grade, catalog number H303-4, Fisher Scientific.

c. Hydrochloric acid, 0.1 N, ACS reagent grade, certified concentration, catalog number SA54-4, Fisher Scientific.

d. Isobutyl chloroformate, 98%, catalog number 17798-9, Aldrich Chemical Company, Milwaukee, WI 53233.

e. Magnesium sulfate (anhydrous), Certified, catalog number M65-500, Fisher Scientific.

f. Methanol, HPLC grade, catalog number A452-4, Fisher Scientific.

g. Methyl-*t*-butyl ether, HPLC grade, catalog number E127-4, Fisher Scientific.

h. 1-Propanol, 99.5+%, HPLC grade, catalog number 29,328-8, Aldrich Chemical Company.

i. Pyridine, HPLC grade, catalog number 27040-7, Aldrich Chemical Company.

j. Sodium chloride, ACS reagent grade, catalog number S271-1, Fisher Scientific.

k. Sodium sulfate (anhydrous), certified ACS grade, catalog number S421-500, Fisher Scientific.

k. Standards

(1) *cis*-3-Chloroallyl alcohol

The *cis*-CAAL standard, AGR164303, Lot Number GHC 0083-27, with a purity of 95.1% was used in this study (1).

(2) *trans*-3-Chloroallyl alcohol

The *trans*-CAAL standard, AGR159855, Lot Number GHC-2-12-119, with a purity of 94.8% was used in this study (2).

Obtain from Test Substance Coordinator, DowElanco, Indianapolis, IN 46268-1053.

2. Prepared Solutions

a. 0.01 N Hydrochloric acid solution

Pipet 100 mL of 0.1 N hydrochloric acid into a 1000-mL volumetric flask and dilute to volume with deionized water.

G. Preparation of Standards

All solutions prepared in Section G should be stored in amber bottles and sealed with PTFE-lined caps.

1. Preparation of *cis*- and *trans*-CAAL Stock Solutions

*cis*- and *trans*-CAAL are volatile liquids and pose some difficulty in weighing to a specific value. The following procedure is meant as a guideline to stress that the analyte be accurately weighed and recorded to four significant figures. Based upon an average density of 1.17 g/mL (3), a 100-µL syringe was used to deliver 86 µL of *cis*- or *trans*-CAAL in the preparation of stock solutions.

a. Tare a 100-mL volumetric flask and scintered glass stopper. Deliver 86 µL of *cis*-CAAL to the flask and stopper the flask. Weigh and record the amount of *cis*-CAAL in the flask. Dilute to volume with acetone to obtain a 1000 µg/mL stock solution.

b. Tare a 100-mL volumetric flask and scintered glass stopper. Deliver 86 µL of *trans*-CAAL to the flask and stopper the flask. Weigh and record the amount of *trans*-CAAL in the flask. Dilute to volume with acetone to obtain a 1000 µg/mL stock solution.

2. Preparation of *cis*- and *trans*-CAAL Spiking Solutions

a. Transfer 1.0 mL of each of the stock solutions in Sections G.1.a. and G.1.b. to a 100-mL volumetric flask and bring to volume with acetone to obtain an initial solution of 10.0 µg/mL for each *cis*- and *trans*-CAAL. This solution is used for preparation of spiking solutions.

b. Solutions for spiking soil samples are prepared by diluting the initial solution from Section G.2.a. with acetone as follows:

| Aliquot of 10.0 µg/mL Soln. | Final Soln. Volume | Spiking Soln. Final Conc. | Equivalent Sample Conc.[a] |
|---|---|---|---|
| mL | mL | ng/mL | ng/g |
| 0.100 | 250 | 4.00 | 0.400 |
| 0.100 | 100 | 10.0 | 1.00 |
| 0.500 | 250 | 20.0 | 2.00 |
| 1.00 | 250 | 40.0 | 4.00 |
| 1.00 | 100 | 100. | 10.00 |
| 2.00 | 100 | 200. | 20.00 |

[a] The equivalent sample concentration is based on fortifying a 10-g soil sample with 1.0 mL of spiking solution.

c. Fortification of soils at levels above 20 ng/g are performed by adding the appropriate aliquot of the 10.0 µg/mL solution from Step G.2.a. directly to the soil as follows:

| Aliquot of 10.0 µg/mL | Equivalent Sample Conc.[a] |
|---|---|
| mL | ng/g |
| 0.100 | 100.0 |
| 0.500 | 500.0 |
| 2.00 | 2000.0 |

[a] The equivalent sample concentration is based on fortifying a 10-g soil sample with the appropriate aliquot of the 10.0 µg/mL solution.

3. Preparation of *cis*- and *trans*-CAAL Calibration Solutions

a. Transfer 1.0 mL of each of the stock solutions in Sections G.1.a. and G.1.b. to a 100-mL volumetric flask and bring to volume with hexane to obtain an initial solution of 10.0 µg/mL for each *cis*- and *trans*-CAAL. This solution is used for preparation of calibration solutions.

b. Solutions for calibration are prepared by diluting the initial solution from Section G.3.a. with hexane as follows:

| Aliquot of 10.0 µg/mL Soln. | Final Soln. Volume | Soln. Final Conc. | Equivalent Sample Conc.[a] |
|---|---|---|---|
| mL | mL | ng/mL | ng/g |
| 0.050 | 250 | 2.00 | 0.20 |
| 0.100 | 250 | 4.00 | 0.40 |
| 0.500 | 250 | 20.0 | 2.0 |
| 1.00 | 100 | 100. | 10.0 |
| 2.00 | 100 | 200. | 20.0 |
| 4.00 | 100 | 400. | 40.0 |

[a] The equivalent sample concentration is based on the concentration of a 10-g soil extract to a final volume of 1.0 mL.

c. Calibration standards are prepared for capillary gas chromatography/mass spectrometry as described in Steps I.1.z. through I.1.ff.

H. Gas Chromatography/Mass Spectrometry

1. Column

Install the splitless column inlet liner (Section E.6.) and the capillary column (Section E.2.) in the split/splitless injection port of the GC/MSD following the manufacturer's recommended procedure.

2. Typical Operating Conditions

| | |
|---|---|
| Instrumentation: | Hewlett-Packard Model 5890 (II) Gas Chromatograph<br>Hewlett-Packard Model 5971A Mass Selective Detector<br>Hewlett-Packard Model G1034B Data System Software |
| Column: | J&W Scientific fused silica capillary<br>Durabond-17 liquid phase<br>20 m x 0.18 mm i.d.<br>0.3 μm film thickness |
| Temperatures: | |
| Column | 65 °C for 1.0 min<br>65 °C to 150 °C at 5 °C/min, 0 min hold at 150 °C<br>150 °C to 260 °C at 20 °C/min, 0 min hold at 260 °C |
| Injector<br>Interface | 230 °C<br>280 °C |
| Carrier Gas: | helium |
| Head Pressure<br>Linear Velocity | approximately 100 kPa<br>approximately 40 cm/sec at an oven temperature of 130 °C |
| Injection Mode: | splitless |
| Purge Delay<br>Splitter Flow<br>Septum Purge | 0.7 min<br>50 mL/min<br>1.0 mL/min |
| Injection Volume: | 2 μL |
| Detector: | electron impact ionization with selected ion monitoring |
| Calibration Program<br>Electron Multiplier | maximum sensitivity autotune (Note N.3.)<br>approximately 1412 volts (tune voltage plus 200) |
| Ions Monitored: | |
| *cis*-CAIBC | *m/z* 136 (quantitation) and *m/z* 75 (confirmation) |
| *trans*-CAIBC | *m/z* 136 (quantitation) and *m/z* 75 (confirmation) |
| Dwell Time | 100 msec |

Mass spectra of *cis*- and *trans*-CAIBC are shown in Figures 1 and 2, respectively. The nominal *m/z* 136 quantitation ion results from loss of 2-methyl-2-propene (mass 56). Both the quantitation and the nominal *m/z* 75 confirmation ions retain the chlorine functionality of CAAL.

3. Calibration Curves

Typical calibration curves for the determination of *cis*- and *trans*-CAAL in soil are shown in Figures 3 and 4, respectively.

4. Typical Chromatograms

Typical chromatograms of a standard, control sample, and a 0.42 ng/g recovery sample for *cis*- and *trans*-CAAL in soil are shown in Figures 5-10.

I. Determination of Recovery of *cis*- and *trans*-CAAL from Soil

1. Preparation of Recovery Samples

a. Weigh 10.0 g of control soil into a series of 45-mL glass vials.

b. For preparing fortified samples, use some of the samples as controls and fortify the remaining samples by adding the specified aliquots of the appropriate spiking solutions (Section G.2.b. and G.2.c.) in acetone to obtain concentrations ranging from 0.40 to 2000 ng/g. A reagent blank containing no soil should be carried through the method with the samples. To minimize the potential for cross contamination, equipment used to process samples and reusable glassware should be thoroughly rinsed with 0.01 N hydrochloric acid followed by acetone and allowed to dry prior to use.

c. Add 15.0 mL of 0.01 N hydrochloric acid to each sample vial and seal with a PTFE-lined cap.

d. Vortex the samples briefly and sonicate for 10-15 seconds.

e. Shake the samples for a minimum of 30 minutes on a reciprocating shaker at approximately 180 excursions/minute.

f. Centrifuge each sample for 10 minutes at 2500 rpm.

g. Carefully decant each extract to a clean 45-mL vial.

h. Extract each sample a second time by repeating Steps I.1.c., d. and f. Combine the extracts by decanting to the vial in Step I.1.g.

i. The samples are then purified using the following ion-exchange SPE procedure (Note N.4.):

(1) Place an ion-exchange SPE column (Section E.4.) on the vacuum manifold box.

(2) Attach a prefilter (Section E.17.) to the top of the column using an SPE column adapter (Section E.5.).

(3) Attach a 25-mL reservoir (Section E.7.) to the prefilter.

(4) Rinse the reservoir, prefilter and SPE column with approximately 5 mL of methanol. (Do not allow the column bed to dry.)

(5) Condition the SPE column with approximately 5 mL of deionized water. (Do not allow the column bed to dry.)

(6) Transfer the sample solution from Step I.1.h. to the reservoir and, with the aid of vacuum, pull the sample through the column at a flow rate of approximately 2 mL/min. Collect the eluent in a 45-mL vial.

(7) Rinse the sample vial with 3 mL of deionized water and transfer the rinse to the reservoir after the original sample load has completely passed through the column. With the aid of vacuum, pull the rinse through the column at a flow rate of approximately 2 mL/min. Collect and combine the eluents in the 45-mL vial from Step I.1.i.(6).

(8) Repeat Step I.1.i.(7) with a second 3 mL rinse of the sample vial, allow the first rinse to pass through the column before adding the second rinse to the reservoir. With the aid of vacuum, pull the rinse through the column. Collect and combine the eluents in the 45-mL vial from Step I.1.i.(6).

j. Transfer the combined eluents to a 2-oz glass bottle. Rinse the 45-mL vial with approximately 2 mL of deionized water and add to the bottle.

k. Add 10 µL 1-propanol, approximately 15 g of sodium chloride, 15 mL of MTBE and seal the bottle with a PTFE-lined cap. (The addition of 1-propanol is critical to reduce evaporative losses of CAAL.)

l. Shake the sample for 15 minutes on a reciprocating shaker at approximately 180 excursions/minute.

m. Centrifuge the bottle for 3 minutes at 1000 rpm.

n. The samples are then dried and purified using the following silica gel SPE procedure (Note N.4.):

(1) Place a silica gel SPE column (Section E.3.) on the vacuum manifold box.

(2) Add approximately 2 g of magnesium sulfate (anhydrous) to the SPE column.

(3) Attach a 25-mL reservoir to the top of the column using an SPE column adapter.

(4) Wash the SPE column by adding approximately 10 mL of MTBE to the reservoir and, with the aid of vacuum, pull the MTBE through the column. Discard the column wash.

(5) Transfer the MTBE layer (top layer) of the sample solution from Step I.1.m. to the reservoir and, with the aid of vacuum, pull the sample through the column at a flow rate of approximately 2 mL/min. Collect the MTBE in a 45-mL vial.

(6) Add 15 mL of MTBE to the sample bottle, shake for 5 minutes and repeat Steps I.1.m. and I.1.n.(5).

(7) After the two MTBE extracts have passed through the column, add approximately 5 mL of MTBE to the reservoir and, with the aid of vacuum, pull the MTBE through the column at a flow rate of approximately 2 mL/min. Collect and combine the eluents in the 45-mL vial from Step I.1.n.(5).

o. Quantitatively transfer the MTBE in the 45-mL vial to a 50-mL Erlenmeyer flask (Section E.8.). Rinse the 45-mL vial with approximately 2 mL of MTBE and add to flask.

p. Add approximately 3 mL of hexane and approximately 0.1 g of sodium sulfate (anhydrous) to the flask. (The sodium sulfate eliminates the need for boiling chips.)

q. Attach a Snyder column (Section E.16.) to the flask.

r. In a fume hood, heat the flask on a hot plate (Section D.9.) to a steady boil.

s. Allow the sample to concentrate to near dryness. Significant loss of CAAL will occur if the flask goes to dryness.

t. Remove the flask from the hot plate, add approximately 1 mL of hexane to the flask through the top of the Snyder column and allow the flask to equilibrate to ambient temperature.

u. Remove the Snyder column from the flask and quantitatively transfer the sample to an 8-mL vial. Rinse the flask twice with 1 mL MTBE, transferring each rinse to the 8-mL vial.

v. Concentrate the sample at ambient temperature on an N-Evap evaporator under a gentle flow of nitrogen to a volume of approximately 0.5 mL. Do not allow the volume to go significantly below 0.5 mL or loss of CAAL will occur.

w. Adjust the volume to 1.0 mL with hexane by visual comparison to two 8-mL vials containing a measured volume of 1.0 mL hexane.

x. Add approximately 0.1 g of anhydrous sodium sulfate.

y. Add 25 µL of pyridine and 25 µL of isobutyl chloroformate, seal the vial with a PTFE-lined cap, and vortex and sonicate the samples for 5 seconds.

z. Transfer 1.0 mL of each of the calibration standards in Section G.3.b. to 8-mL vials and derivatize following Step I.1.y.

aa. Heat the samples and standards in an aluminum block (Section D.7. and D.8.) at 70 °C for 15 minutes.

bb. Remove the vials from the aluminum block and allow the derivatized samples and standards to cool to ambient temperature.

cc. Add 1.0 mL of 0.1 N hydrochloric acid and vortex each vial for 5 seconds.

dd. Centrifuge the vials for 5 minutes at 2500 rpm.

ee. Transfer the top hexane layer to a 2-mL autosampler vial and seal the vial with a cap and crimper.

ff. Analyze the samples and calibration standards by GC/MSD as described in Section H.

gg. Samples showing levels of CAAL above approximately 40 ng/g are diluted 100-fold as follows:

(1) Transfer 100 µL of the derivatized sample from Step I.1.gg. to a 10-mL volumetric flask and dilute to mark with hexane.

(2) Transfer approximately 1 mL of the diluted sample to a 2-mL autosampler vial and seal the vial with a cap and crimper. (No rederivatization is required.)

(3) Reanalyze the sample by GC/MSD as described in Section H.

2. Calculation of Percent Recovery

a. Determine the *m/z* 75 and 136 response areas for both *cis*- and *trans*-CAIBC in the calibration standards.

b. For each standard, calculate the *cis*- and *trans*-CAAL confirmation ratios. The average confirmation ratio for all calibration standards will be used to confirm the presence of the respective CAAL in the soil samples.

For example, using the data for *cis*-CAIBC from Figure 5:

$$\text{Confirmation Ratio} = \frac{\text{peak area of quantitation ion}}{\text{peak area of confirmation ion}}$$

$$\text{Confirmation Ratio} = \frac{\text{peak area at } m/z \text{ 136}}{\text{peak area at } m/z \text{ 75}}$$

$$\text{Confirmation Ratio} = \frac{1225}{3952}$$

$$\text{Confirmation Ratio} = 0.3100$$

Positive confirmation of the presence of *cis*- or *trans*-CAAL is indicated when the confirmation ratio for the samples is in the range of ±20% of the average found for the standards.

c. Prepare *cis*- and *trans*-CAAL standard curves by plotting the equivalent soil sample concentration (ng/g) on the abscissa (x-axis) and the *cis*- and *trans*-CAIBC *m/z* 136 peak area on the ordinate (y-axis) as shown in Figures 3 and 4, respectively. Using regression analysis, determine the equation for the curve with respect to the abscissa.

For example, using power regression (4) with the *trans*-CAAL data from Figure 4:

$$Y = \text{constant} \times X^{(\text{exponent})}$$

$$X = \left(\frac{Y}{\text{constant}}\right)^{1/\text{exponent}}$$

$$\underset{(ng/g)}{\textit{trans}\text{-CAAL Conc.}} = \left(\frac{\textit{trans}\text{-CAIBC peak area}}{\text{constant}}\right)^{1/\text{exponent}}$$

$$\underset{(ng/g)}{\textit{trans}\text{-CAAL Conc.}} = \left(\frac{\textit{trans}\text{-CAIBC peak area}}{3225.7}\right)^{1/1.0220}$$

d. Determine the net concentration in each recovery sample by first subtracting the average *cis*- and *trans*-CAIBC *m/z* 136 peak area in the control sample from that of the recovery sample. Substitute *m/z* 136 the peak area obtained into the above equation and solve for the concentration.

For example, using the *trans*-CAAL data from Figures 9 and 10:

$$\underset{(ng/g)}{\textit{trans}\text{-CAAL Conc.}} = \left(\frac{\text{net } \textit{trans}\text{-CAIBC peak area}}{3225.7}\right)^{1/1.0220}$$

$$\underset{(ng/g)}{\textit{trans}\text{-CAAL Conc.}} = \left(\frac{1235 - 0}{3225.7}\right)^{1/1.0220}$$

$$\textit{trans}\text{-CAAL Conc.} = 0.3909 \text{ ng/g}$$

e. Determine the percent recovery by dividing the net concentration of each recovery sample by the theoretical concentration added.

$$\text{Recovery} = \frac{\text{Concentration Found}}{\text{Concentration Added}} \times 100\%$$

$$\text{Recovery} = \frac{0.3909 \text{ ng/g}}{0.4156 \text{ ng/g}} \times 100\%$$

$$\text{Recovery} = 94\%$$

The average recovery of all the recovery samples in a given sample set can be used to correct individual sample results for method efficiency.

J. Determination of *cis*- and *trans*-CAAL in Soil

1. Prepare reagent blank, control, recovery, and treated samples as described in Section I.1.

2. Prepare standard calibration curves for *cis*- and *trans*-CAAL and determine the percentage recoveries as described in Section I.2.

3. Determine the concentration of *cis*- and *trans*-CAAL in each treated sample by substituting the *cis*- and *trans*-CAIBC *m/z* 136 peak area obtained into the respective equations for the standard calibration curve, and calculate the uncorrected residue result.

   For example, using the *cis*-CAAL data from Figures 3 and 7, the uncorrected concentration is calculated as follows:

$$\underset{\text{(ng/g)}}{\textit{cis}\text{-CAAL Conc.}} = \left(\frac{\textit{cis}\text{-CAIBC peak area}}{3162.7}\right)^{1/1.0237}$$

$$\underset{\text{(ng/g)}}{\textit{cis}\text{-CAAL Conc.}} = \left(\frac{1130}{3162.7}\right)^{1/1.0237}$$

$$\textit{cis}\text{-CAAL Conc.} = 0.3659 \text{ ng/g}$$

4. To correct for method recovery, the following procedure is used:

   a. Determine the *cis*-CAAC concentrations in the soil samples as described in Section J.3. Calculate the average percent recovery from recovery samples in the set (Table I.).

   b. Determine the corrected analyte concentration in the soil samples as follows:

$$\underset{\text{(corrected ng/g)}}{\textit{cis}\text{-CAAL Conc.}} = \underset{\text{(ng/g)}}{\textit{cis}\text{-CAAL Conc.}} \times \frac{100}{\%\text{ Recovery}}$$

$$\underset{\text{(corrected ng/g)}}{\textit{cis}\text{-CAAL Conc.}} = 0.3659 \text{ ng/g} \times \frac{100}{86}$$

$$\underset{\text{(corrected)}}{\textit{cis}\text{-CAAL Conc.}} = 0.4255 \text{ ng/g}$$

K. Determination of Soil Moisture

1. Weigh 10.00 g of soil in an aluminum or glass container.

2. Place the sample in an oven at approximately 130 °C and allow to dry for a minimum of 16 hours.

3. Remove the sample from the oven, place in a desiccator until the sample has cooled to ambient temperature, and then re-weigh.

4. Calculate the percent moisture on a dry weight basis as follows:

$$\text{Percent Moisture} = \frac{\text{soil moisture weight (g)}}{\text{dehydrated soil weight (g)}} \times 100$$

$$= \frac{\left(\begin{matrix}\text{soil weight} \\ \text{before drying}\end{matrix} - \begin{matrix}\text{soil weight} \\ \text{after drying}\end{matrix}\right)}{\begin{matrix}\text{soil weight} \\ \text{after drying}\end{matrix}} \times 100$$

L. Determination of Corrected *cis*- and *trans*-CAAL in Soil

1. Determine the *cis*- and *trans*-CAAL concentration in the soil samples as described in Section J.
2. Determine the soil moisture as described in Section K.
3. Determine the corrected *cis*- and *trans*-CAAL concentrations in soil samples as follows:

$$\begin{matrix}\text{CAAL} \\ \text{Corrected Conc. (ng/g)}\end{matrix} = \left(\begin{matrix}\text{CAAL} \\ \text{Conc. (ng/g)}\end{matrix}\right)\left(\frac{100}{\%\ \text{Recovery}}\right)\left(1 + \frac{\%\ \text{Moisture}}{100}\right)$$