METHOD OUTLINE

RESIDUE DETERMINATION METHOD: GRM 94.15

Independent Laboratory Validation of Method GRM 94.15 -
Determination of Residues of *cis*- and *trans*-3-Chloroallyl Alcohol in Water by
Capillary Gas Chromatography with Mass Selective Detection

Pipet 40.0 mL of control water samples into a series of labeled 2-oz bottles.

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Use some of the samples as controls and fortify the remaining samples by adding 1.0-mL aliquots of the appropriate spiking solutions in acetone to obtain concentrations ranging from 0.10 to 5.0 ng/mL. A reagent blank, containing no water sample, should be carried through the method with the samples.

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Add 10 µL of 1-propanol, 15 g of sodium chloride, 15 mL of MTBE and seal the bottle with a PTFE-lined cap.

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

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Centrifuge the bottle for 3 minutes at 1000 rpm.

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Place a silica gel SPE column on vacuum manifold box.

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

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

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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.

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Transfer the MTBE layer of the sample solution 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.

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Add 15 mL of MTBE to the sample jar, shake for 5 minutes. Centrifuge the bottle for 3 minutes at 1000 rpm. Again, transfer the MTBE layer of the sample solution to the reservoir and pull the sample through the column at a flow rate of approximately 2 mL/min.

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METHOD OUTLINE (continued)

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 with the MTBE in the vial.

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Quantitatively transfer the MTBE in the 45-mL vial to a 50-mL Erlenmeyer flask. Rinse the vial with approximately 2 mL of MTBE and add to the flask.

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Add approximately 3 mL of hexane and approximately 0.1 g of anhydrous sodium sulfate to the flask.

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Attach a Snyder column to the flask.

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Heat the flask on a hot plate (a sand bath was used on a hot plate) to a steady boil.

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Allow the sample to concentrate to near dryness.

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

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

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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.

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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.

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Add approximately 0.1 g of anhydrous sodium sulfate.

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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.

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Transfer 1.0 mL of each of the calibration standards to 8-mL vials, then derivatize.

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Heat the samples and calibration standards in an aluminum block heater at 70 °C for 15 minutes.

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METHOD OUTLINE (continued)

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

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Add approximately 1 mL of 0.1 N hydrochloric acid and vortex each vial for 5 seconds.

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Centrifuge the vial for 5 minutes at 2500 rpm.

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

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Analyze the samples and calibration standards by capillary gas chromatography with mass spectrometry.

ANALYTICAL RESULTS

Calculations

Calibration standards were analyzed with each sample set. Power regression equations were generated for each analyte using the log of the concentrations of the calibration standards versus the log of the respective peak area responses. The least squares coefficient of determination (r^2 value) of each power regression equation was 0.99 or greater. Concentrations of the analytes in the final solutions were determined by substituting the peak area responses into the applicable power regression equation as shown below:

$$\text{ng/mL} = \left[\frac{(\text{m/z 136 CAIBC peak area})}{\text{constant}}\right] \wedge (1/\text{exponent})$$

where the exponent is the coefficient and the constant is the inverse log of the Y-intercept generated from the power regression equation.

For example, using the *trans*-CAAL data from Figure 2, 8 and 10.

trans-CAAL conc. ng/mL =

$$\left[\frac{(\text{m/z 136 } \textit{trans}\text{-CAIBC peak area (sample)} - \text{peak area (control)})}{\text{constant}}\right] \wedge (1/\text{exponent})$$

$$\textit{trans}\text{-CAAL conc. ng/mL} = \left[\frac{(1904 - 0)}{5611.4}\right] \wedge (1/1.3254)$$

trans-CAAL conc. ng/mL = 0.4424 ng/mL

Percent recovery was calculated using the equation shown below:

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

$$\text{Recovery} = \frac{0.4424 \text{ ng/mL}}{0.5000 \text{ ng/mL}} \times 100$$

Recovery = 88%

Statistics

The mean recovery was calculated for each analyte by dividing the sum of the percent recoveries of each analyte by the number of samples in the set.

The standard deviation(s) was calculated for each analyte by summing the squares of the individual deviations from the mean, dividing by the number of degrees of freedom, and extracting the square root of the quotient.

Summary of Key Dates

Sample Identification	Extracted	Analyzed
CAAL-009-1-RB	03-13-96	03-15-96
CAAL-009-2-CT	03-13-96	03-15-96
CAAL-009-3-CT	03-13-96	03-15-96
CAAL-009-4-S1	03-13-96	03-15-96
CAAL-009-5-S2	03-13-96	03-15-96
CAAL-009-6-S3	03-13-96	03-15-96
CAAL-009-7-S4	03-13-96	03-15-96