DESCRIPTION OF ANALYTICAL METHOD

Method Identification Number: DowElanco residue analytical method GRM 94.11

Title of Method: Determination of Residues of 1,2-Dichloropropane, *cis*- and *trans*-1,3-Dichloropropene, and Trichloronitromethane in Water by Purge and Trap Extraction, Capillary Gas Chromatography and Mass Selective Detection

Scope of Method: This method is applicable for the quantitative determination of 1,2-dichloropropane, *cis*- and *trans*-1,3-dichloropropene, and trichloronitromethane residues at a validation level of 0.05 ng/mL.

Identification of test substance used: Name: 1,2-dichloropropane

AGR Number:	AGR277102	% Purity:	99.2%
Analytical Report No.:	FA&PC 950058	Report Date:	21 JUL 1995

Identification of test substance used: Name: *cis*-1,3-dichloropropene

TSN Number:	TSN100275	% Purity:	98.9%
Analytical Report No.:	94-230549	Report Date:	31 AUG 1995

Identification of test substance used: Name: *trans*-1,3-dichloropropene

TSN Number:	TSN100276	% Purity:	97.8%
Analytical Report No.:	94-230549	Report Date:	31 AUG 1995

Identification of test substance used: Name: trichloronitromethane

TSN Number:	TSN100245	% Purity:	98.9%
Analytical Report No.:	FA&PC 953047	Report Date:	26 FEB 96

Identification of internal standard used: Name: 2-bromo-1-chloropropane

Lot Number:	00102CKMN	% Purity:	95%
Reference:	Aldrich	Expiration Date:	16 MAY 1995

METHOD OUTLINE

RESIDUE METHOD: GRM 94.11

Independent Laboratory Validation of Method GRM 94.11 - Determination of Residues of 1,2-Dichlororopane and *cis*- and *trans*-1,3-Dichloropropene, and Trichloronitromethane in Water by Purge and Trap Extraction, Capillary Gas Chromatography and Mass Selective Detection

Depending on the anticipated analyte concentration, set the Purge and Trap operating conditions.

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Carry out the initial calibration by baking out the trap at approximately 185 °C and the GC oven temperature to 220 °C for 10 minutes

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Perform calibration check by using 0.100 ng/mL standard (low level)

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Generate calibration curve by analyzing 25 mL volumes of standards at each concentration from lowest to highest concentration

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Analyze a blank with 25 mL of water and 5 µL of the 2.5 µg/mL internal standard

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Analyze standards at desired levels (in 25 mL of water) the same as for blank sample

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Analyze 25 mL of control water and fortifications at desired levels and analyze as blank sample

Calculations: Calibration standards were run with the sample set. Equations were generated for each analyte by plotting the log of the equivalent concentration in ng/mL on the x-axis and the log of the quantitation ratio on the y-axis. The quantitation ratios were determined to four significant figures on a Texas Instruments TI-36X Solar hand calculator. Logs were generated on the hand calculator and used to 4 significant figures. The quantitation ratio is defined as the peak area of the quantitation ion divided by the peak area of the internal standard ion. The quantitation ion for 1,2 dichloropropane is *m/z* 63, for *cis*-1,3-dichloropropene is *m/z* 75, for *trans*-1,3-dichloropropene is *m/z* 75, and for trichloronitromethane is 119. For the internal standard 2-bromo-1-chloropropane the monitored ion is *m/z* 77. An equation obtained by least squares fit of the standard injection data of the following form was generated using the Nelson Analytical Series Model 4400X Chromatography Data System:

$$\text{LOG Quantitation Ratio} = B0 + B1\ (\text{LOG Concentration in ng/mL})$$

Therefore: $\text{ng/mL} = (\text{quantitation ratio/inverse LOG } B0)^{1/B1}$
(done using hand calculator)

All calculations were done with figures truncated, as shown in the tables.

Statistical Methods: 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 (SD) 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. It was calculated using the program on a Texas Instruments TI-36X Solar hand calculator.

FULL DESCRIPTION OF ANALYTICAL INSTRUMENTATION USED

Instrument:	Hewlett-Packard Model 5890 Series II gas chromatograph LSC 2000 Purge and Trap
Detector:	Hewlett-Packard 5970B mass selective detector in selected ion monitoring (SIM) mode
Analytical Column:	Supelco Vocol Capillary column (30 m x 0.25 mm i.d. and 1.4 µm thickness)
Column Temperature:	35 °C, hold 1 minute, to 140 °C at 11 °C per minute, set manually to 210 °C at end of run for 5 minutes, then reset to 35 °C.
Injector Temperature:	200 °C
Interface Temperature:	230 °C
Carrier Gas:	Helium
Head Pressure:	28 kPa
Linear Velocity:	approximately 40 cm/second at 260 °C oven temperature
Electron Multiplier:	2600 (tune voltage + 200)
Dwell time:	100 msec
Ions Monitored:	

2-bromo-1-chloropropane -	*m/z* 77 (internal standard)
1,2-dichloropropane -	*m/z* 63 (quantitation), *m/z* 76 (confirmation)
cis-1,3-dichloropropene -	*m/z* 75 (quantitation), *m/z* 112 (confirmation)
trans-1,3-dichloropropene -	*m/z* 75 (quantitation), *m/z* 112 (confirmation)
trichloronitromethane -	*m/z* 119 (quantitation), *m/z* 82 (confirmation)

Retention times:	2-bromo-1-chloropropane -	approximately 9.6 minutes
	cis-1,3-dichloropropene -	approximately 8.7 minutes
	trans-1,3-dichloropropene -	approximately 9.3 minutes
	1,2-dichloropropane -	approximately 7.8 minutes
	trichloronitromethane -	approximately 9.5 minutes

Instrument:	Tekmar LSC 2000 with needle sparge and Supelco VOCARB 3000 (K) Trap
Injection Mode:	split (20-1)
Splitter Flow:	20 mL/min.
Purge Flow:	40 mL/ min.
Desorb Flow:	20.2 mL/min.
Transfer Line Temp.:	140 °C
Valve Temp.:	140 °C