Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Cloransulam-Meth

MRID #: 442315-03

Matrix: Water

Analysis: GC/MS

This method is provided to you by the Environmental Protection Agency's (EPA) Environmental Chemistry Laboratory (ECL). This method *is not* an EPA method but one which was submitted to EPA by the pesticide manufacturer to support product registration. EPA recognizes that the methods may be of some utility to state, tribal, and local authorities, but makes no claim of validity by posting these methods. Although the Agency reviews *all* Environmental Chemistry Methods submitted in support of pesticide registration, the ECL evaluates only about 30% of the currently available methods. Most methods perform satisfactorily but some, particularly the older methods, have deficiencies. Moreover, the print quality of the methods varies considerably because the methods originate from different sources. Therefore, the methods offered represent the best available copies.

If you have difficulties in downloading the method, or further questions concerning the methods, you may contact Elizabeth Flynt at 228-688-2410 or via e-mail at flynt.elizabeth@epa.gov.

DESCRIPTION OF ANALYTICAL METHOD

Method Identification Number: DowElanco residue analytical method GRM 96.04

Title of Method: Determination of Residues of Cloransulam-methyl and Cloransulam in Water by Capillary Gas Chromatography with Mass Selective Detection

Scope of Method: This method is applicable for the quantitative determination of residues of cloransulam-methyl, [*N*-(2-carbomethoxy-6-chlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo-[1,5-c]-pyrimidine-2- sulfonamide] and cloransulam, [*N*-(2-carboxy-6-chlorophenyl)-5-ethoxy-7-fluoro-[1,2,4]triazolo[1,5-c]-pyrimidine-2- sulfonamide] in water over the concentration range of 0.10-2.0 ng/mL, with a validated limit of quantitation of 0.10 ng/mL.

Identification of analytical standard used: Name: cloransulam

AGR Number:	TSN100609	% Purity:	99%
Analytical Report No.:	FA&PC 940389	Report Date:	24 FEB 1995

Identification of analytical standard used: Name: cloransulam-methyl

TSN Number:	AGR293572	% Purity:	99.2%
Analytical Report No.:	FA&PC 963036	Report Date:	26 APR 1996

Identification of analytical standard used: Name: *N*-methyl-cloransulam-methyl

TSN Number:	TSN100070	% Purity:	>96%
Analytical Report No.:	FA&PC 945137	Report Date:	10 JUN 1994

Identification of analytical standard used: Name: *N*-ethyl-cloransulam-methyl

TSN Number:	TSN100102	% Purity:	>97%
Analytical Report No.:	FA&PC 945138	Report Date:	10 JUN 1994

Identification of analytical standard used: Name: *N*-ethyl-cloransulam-ethyl

TSN Number:	TSN100099	% Purity:	>99%
Analytical Report No.:	FA&PC 950119	Report Date:	16 MAY 1995

METHOD OUTLINE

RESIDUE METHOD: GRM 96.04

Independent Laboratory Validation of GRM 96.04 - Determination of Residues of Cloransulam-methyl and Cloransulam in Water by Capillary Gas Chromatography with Mass Selective Detection

Pipet 100 mL of water into a series of 4-oz glass bottles.

↓

Use unfortified samples as controls. For fortified samples, add 1.0 mL of the appropriate spiking solutions in acetone to obtain concentrations ranging from 0.10 to 2.0 ng/mL. A reagent blank, containing no water sample, is carried through the method with the samples.

↓

Add 1.0 mL of 2.0 N hydrochloric acid to each sample bottle and seal with a PTFE-lined cap. Shake the bottles briefly to mix.

↓

Concentrate and purify the samples using the following C_{18} SPE procedure

--Place a C_{18} SPE column on the vacuum manifold box.

--Rinse the SPE column with 5 mL of acetonitrile. (Do not allow the column bed to dry.)

--Condition the SPE column with 5 mL of 0.01 N hydrochloric acid solution. (Do not allow the column bed to dry.)

--Attach a 70-mL reservoir to the top of the column using an SPE column adapter. Fill the reservoir with the sample solution. With the aid of vacuum, pull the sample through the column at a flow rate of approximately 2 mL/min. Add the remaining sample solution to the reservoir when a sufficient volume of sample has passed through the column.

--After the entire sample has passed through the column, add 15 mL of the 20% acetonitrile in 0.01 N hydrochloric acid solution to the reservoir. With the aid of vacuum, pull the solution through the column at a flow rate of approximately 2 mL/min.

--Remove the reservoir and column adapter. Allow the column to dry under vacuum for 30 minutes.

METHOD OUTLINE (CONT.)

–Elute the cloransulam-methyl and cloransulam with 5.0 mL of acetonitrile, collecting the eluate in an 8-mL vial. Discard the SPE column.

↓

Evaporate the sample to dryness by placing the vial in an N-Evap evaporator, with a nitrogen flow of approximately 20 mL/min and a water bath temperature of 50 °C.

↓

Allow the vial to cool and add 1 mL of acetone.

↓

Add 25 µL of triethylamine (TEA) to the vial and seal with a PTFE-lined cap. Vortex the vial briefly to mix.

↓

Add 100 µL of the triethyloxonium tetrafluoroborate (TEOTFB) solution to the vial and seal with a PTFE-lined cap. Vortex the vial briefly, and shake the vial for 20 minutes on a reciprocating shaker at approximately 180 excursions/minute.

↓

Repeat. Add 25 µL of TEA to the vial and seal with a PTFE-lined cap. Vortex the vial briefly to mix, and add 200 µL of the TEOTFB solution to the vial and seal with a PTFE-lined cap. Vortex the vial briefly, and shake the vial for 20 minutes on a reciprocating shaker at approximately 180 excursions/minute.

↓

Evaporate the sample to dryness by placing the vial in an N-Evap evaporator, with a nitrogen flow of approximately 20 mL/min and a water bath temperature of 50 °C.

↓

Allow the vial to cool and add 2.5 mL of 20% MTBE in hexane and 3 mL of 0.1 M potassium bicarbonate solution. Seal the vial with a PTFE-lined cap.

↓

Shake the vial for 3 minutes on a reciprocating shaker at approximately 180 excursions/minute.

↓

Centrifuge the vial at 2500 rpm for 2 minutes.

METHOD OUTLINE (CONT.)

Using a disposable Pasteur pipet, transfer the top organic layer to a clean 8-mL vial.

↓

Extract the aqueous solution with a second 2.5 mL of 20% MTBE in hexane, shake the vial for 3 minutes on a reciprocating shaker at approximately 180 excursions/minute, centrifuge the vial at 2500 rpm for 2 minutes and using a disposable Pasteur pipet, transfer the top organic layer to the appropriate 8-mL vial.

↓

Purify the samples using the following silica gel SPE:
--Place a silica gel SPE column on the vacuum manifold box.
--Rinse the SPE column with 5 mL of toluene.
--Condition the reservoir and SPE column with 5 mL of hexane. (Do not allow the column bed to dry.)
--Transfer the sample solution to the SPE column. With the aid of vacuum, pull the sample through the column at a flow rate of approximately 2 mL/min.
--Rinse the sample vial with 2.5 mL of 20% MTBE in hexane and transfer the rinse to the SPE column. With the aid of vacuum, pull the rinse through the column at a flow rate of approximately 2 mL/min.
--Elute the SPE column with 10 mL of 5% acetone in toluene. Collect the eluate in a 12-mL vial.

↓

Evaporate the sample to dryness by placing the vial in an N-Evap evaporator, with a nitrogen flow of approximately 20 mL/min and a water bath temperature of 50 °C.

↓

Allow the vial to cool and add 0.5 mL of toluene containing the internal standard.

↓

Vortex and sonicate the vial briefly, and centrifuge at 2500 rpm for 5 minutes.

↓

Transfer the sample to a 2-mL autosampler vial and seal with a cap and crimper.

↓

Analyze the samples by capillary gas chromatography with mass selective detection.

ANALYTICAL

Calculations

The calibration standards were injected and the peak areas were determined for the *m/z* 212 and *m/z* 180 ions for the *N*-ethyl-cloransulam-methyl, *m/z* 226 and *m/z* 180 ions for the *N*-ethyl-cloransulam-ethyl and for the *m/z* 198 ion for the *N*-methyl-cloransulam-methyl internal standard.

For each calibration standard, a confirmation ratio was calculated. The average confirmation ratio for the cloransulam-methyl and cloransulam calibration standards was used to verify the presence of cloransulam-methyl and cloransulam in water samples.

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

$$\text{Cloransulam-methyl Confirmation Ratio} = \frac{\text{peak area at } m/z\ 212}{\text{peak area at } m/z\ 180}$$

$$\text{Cloransulam Confirmation Ratio} = \frac{\text{peak area at } m/z\ 226}{\text{peak area at } m/z\ 180}$$

For example, using the data for cloransulam-methyl from Figure 5:

$$\text{Cloransulam-methyl Confirmation Ratio} = \frac{53}{124}$$

$$\text{Cloransulam-methyl Confirmation Ratio} = 0.427$$

Positive confirmation of cloransulam-methyl and cloransulam was indicated when the confirmation ratio for the samples was in the range of ±20% of the average found for the standards.

For each standard, the cloransulam-methyl and cloransulam quantitation ratios were calculated.

$$\text{Quantitation Ratio} = \frac{\text{peak area of quantitation ion}}{\text{peak area of internal standard ion}}$$

$$\text{Cloransulam-methyl Quantitation Ratio} = \frac{\text{peak area at } m/z \text{ 212}}{\text{peak area at } m/z \text{ 198}}$$

$$\text{Cloransulam Quantitation Ratio} = \frac{\text{peak area at } m/z \text{ 226}}{\text{peak area at } m/z \text{ 198}}$$

For example, using the data for cloransulam-methyl from Figure 5:

$$\text{Cloransulam-methyl Quantitation Ratio} = \frac{53}{1207}$$

$$\text{Cloransulam-methyl Quantitation Ratio} = 0.044$$

Separate standard curves for cloransulam-methyl and cloransulam were prepared by plotting the equivalent concentration on the abscissa (x-axis) and the respective quantitation ratio on the ordinate (y-axis) as shown in Figures 1 and 2. Using power regression analysis (2), the equation for the curve with respect to the abscissa was determined. The least squares coefficient of determination (r^2 value) of each power regression equation was 0.995 or greater. Concentrations of the analytes in the final solutions were determined by substituting the peak area responses into the power regression equation as shown below:

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

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

For example, using the cloransulam-methyl data from Figure 5:

$$\text{Cloransulam-methyl Conc. (ng/mL)} = \left[\frac{\text{Cloransulam-methyl Quantitation ratio}}{\text{constant}}\right]^{1/\text{exponent}}$$

$$\text{Cloransulam-methyl Conc. (ng/mL)} = \left[\frac{\text{Cloransulam-methyl Quantitation ratio}}{0.6953}\right]^{1/1.2034}$$

The net concentration of cloransulam-methyl and cloransulam in each recovery sample was determined by first subtracting the average quantitation ratios in the control sample from the respective ratios of each recovery sample. The net quantitation ratio obtained was substituted into the appropriate equation above to determine the concentration.

For example, using the cloransulam-methyl data from Figures 1, 4, and 5:

$$\text{Cloransulam-methyl Conc. (ng/mL)} = \left[\frac{\text{Cloransulam-methyl Quantitation ratio}}{0.6953}\right]^{1/1.2034}$$

$$\text{Cloransulam-methyl Conc. (ng/mL)} = \left[\frac{0.044 - 0.000}{0.6953}\right]^{1/1.2034}$$

$$\text{Cloransulam-methyl} = 0.101 \text{ ng/mL}$$

The percent recovery was determined by dividing the net concentration of each recovery sample by the theoretical concentration added.

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

For example, using the cloransulam-methyl data from Figure 5:

$$\text{Recovery} = \frac{0.101 \text{ ng/mL}}{0.100 \text{ ng/mL}} \times 100\%$$

$$\text{Recovery} = 101\%$$

Statistical Treatment of Data

Statistical treatment of data included the calculation of the means, standard deviations, and least squares correlation coefficients.

Summary of Key Dates

Sample Identification	Sample Description	Extracted	Analyzed
BB	Reagent Blank	01-Oct-96	01-Oct-96
18848401-C1	Pond Water Control	01-Oct-96	01-Oct-96
18848401-C2	Pond Water Control	01-Oct-96	01-Oct-96
18848401-FC1	Fortified Pond Water Control	01-Oct-96	01-Oct-96
18848401-FC2	Fortified Pond Water Control	01-Oct-96	01-Oct-96
18848401-FC3	Fortified Pond Water Control	01-Oct-96	01-Oct-96
18848401-FC4	Fortified Pond Water Control	01-Oct-96	01-Oct-96

RESULTS AND DISCUSSION

Representative Calibration Curves

Typical calibration curves used to determine the concentration of cloransulam-methyl and cloransulam in water are shown in Figures 1 and 2, respectively. Each curve ranges from an equivalent water sample concentration of 0.05 to 2.5 ng/mL. The correlation coefficient of each curve was greater than 0.995.

Representative Chromatograms

Eight representative chromatograms from the independent laboratory validation study are shown in Figures 3-10. The chromatograms include a standard, a control sample, and a 0.10 ng/mL limit of quantitation (LOQ) and 0.20 ng/mL (2x LOQ) recovery samples for cloransulam-methyl and cloransulam in water.

Analytical Recovery Data

Recoveries obtained during the independent lab validation are summarized in Tables I-II. Recoveries averaged 109 ±6% for cloransulam-methyl and 100 ±15% for cloransulam in water. Each recovery was within the EPA acceptable range of 70-120%.

CONCLUSIONS

Method GRM 96.04, "Determination of Residues of Cloransulam-methyl and Cloransulam in Water by Capillary Gas Chromatography with Mass Selective Detection," has been demonstrated

to be suitable for use in the analysis of water for the determination of residues of cloransulam-methyl and cloransulam with a validated LOQ of 0.10 ng/mL. All recoveries obtained for fortified samples of water were within the EPA acceptable range of 70-120%.

Method GRM 96.04 has been successfully validated by an independent laboratory.

ARCHIVING

All raw data and the original of the final report are filed in the DowElanco testing facility archives, Indianapolis, Indiana.

REFERENCES

1. Duebelbeis, D. O.; Thomas, A. D. "Determination of Residues of Cloransulam-methyl and Cloransulam in Water by Capillary Gas Chromatography with Mass Selective Detection", GRM 96.04, 1996, unpublished method of DowElanco.

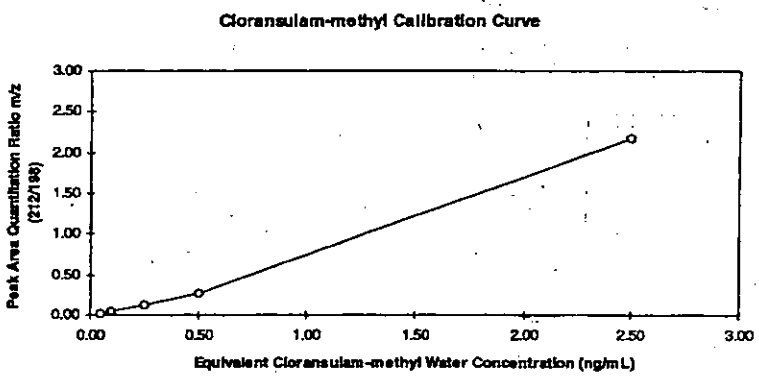
2. *HP-41C/41 CV Standard Applications Handbook*, Hewlett-Packard Publication No. 00041-90402, 1982, pp. 42-48.

Table I. Recovery of Cloransulam-methyl from Water

Sample Number	Date of Analysis	Cloransulam-methyl, ng/mL		Percent Recovery
		Added	Found	
Reagent Blank	01-Oct-1996	0.000	0.0000	–
18848401-C1	01-Oct-1996	0.000	0.0000	–
18848401-C2	01-Oct-1996	0.000	0.0000	–
18848401-FC1	01-Oct-1996	0.100	0.101	101
18848401-FC2	01-Oct-1996	0.100	0.114	114
18848401-FC3	01-Oct-1996	0.200	0.220	110
18848401-FC4	01-Oct-1996	0.200	0.220	110
			$\bar{x}$ =	109
			s =	6
			n =	4

Table II. Recovery of Cloransulam from Water

Sample Number	Date of Analysis	Cloransulam, ng/mL Added	Cloransulam, ng/mL Found	Percent Recovery
Reagent Blank	01-Oct-1996	0.000	0.0000	–
18848401-C1	01-Oct-1996	0.000	0.0000	–
18848401-C2	01-Oct-1996	0.000	0.0000	–
18848401-FC1	01-Oct-1996	0.100	0.085	85
18848401-FC2	01-Oct-1996	0.100	0.120	120
18848401-FC3	01-Oct-1996	0.200	0.195	97
18848401-FC4	01-Oct-1996	0.200	0.198	99
			$\bar{x}$ =	100
			s =	15
			n =	4

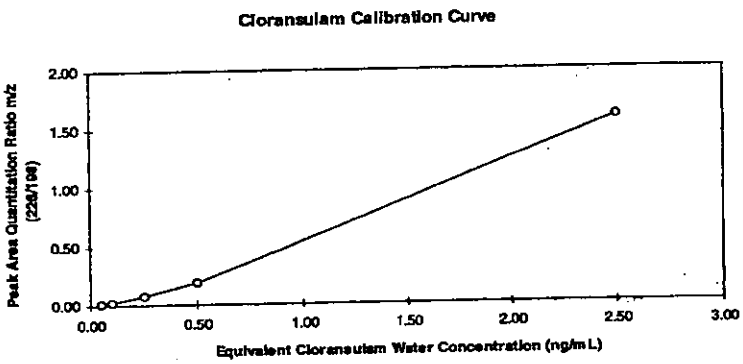


Cloransulam-methyl Equivalent Conc. ng/mL	Cloransulam-methyl Quantitation Ratio *m/z* (212/198)
0.050	0.0181
0.10	0.0487
0.25	0.1279
0.50	0.2783
2.5	2.1765

Power Regression Equation: $X = \left[\frac{Y}{0.6953}\right]^{1/1.2034}$

Coefficient of Determination (r^2): 0.9982

Figure 1. Typical Calibration Curve for the Determination of Cloransulam-methyl in Water

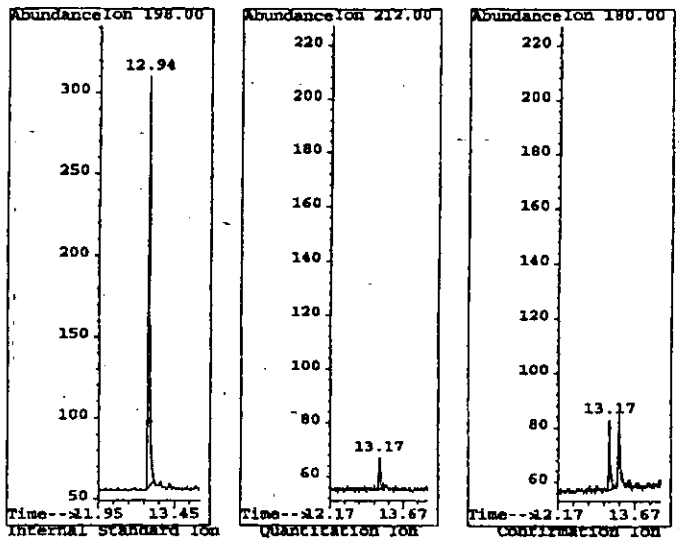


Cloransulam Equivalent Conc. ng/mL	Cloransulam Quantitation Ratio *m/z* (226/198)
0.050	0.0127
0.10	0.0218
0.25	0.0753
0.50	0.1913
2.5	1.5840

Power Regression Equation: $X = \left[\frac{Y}{0.4662}\right]^{1/1.2624}$

Coefficient of Determination (r^2): 0.9956

Figure 2. Typical Calibration Curve for the Determination of Cloransulam in Water



Data File : 0301015.D
ALS Bottle : 3
Data Path : C:\HPCHEM\1\DATA\100196\
Instrument : GC S/N 2950A25792
Method : DEB565

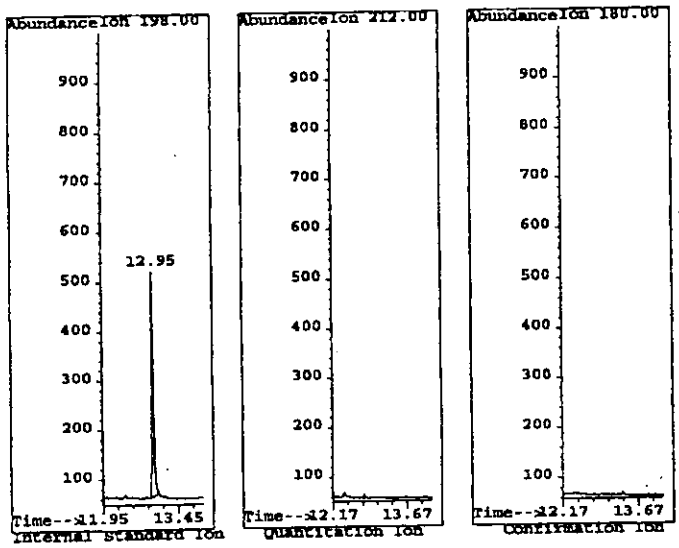
Acquisition: 1 Oct 96
Operator : D. E. Barnekow
Integration: 10/02/96
Integrator : David E. Barnekow

Sample Name: STD 20.0 ng/mL G.4.C.2
Sample Info: RES96059

Compound	Ion	Retention Time	Peak Area
Internal Standard	198	12.94	595
Cloransulam-methyl	212	13.17	29
	180	13.17	67

Quantitation Ratio: 0.0487
Cloransulam-methyl Equiv. Water Concentration: 0.10 ng/mL
Confirmation Ratio: 0.43
Average Standard Confirmation Ratio: 0.41

Figure 3. Typical Chromatogram of a 20-ng/mL Standard, Equivalent to 0.10 ng/mL Cloransulam-methyl in Water



Data File : 0801008.D
ALS Bottle : 8
Data Path : C:\HPCHEM\1\DATA\100196\
Instrument : GC S/N 2950A25792
Method : DEB565

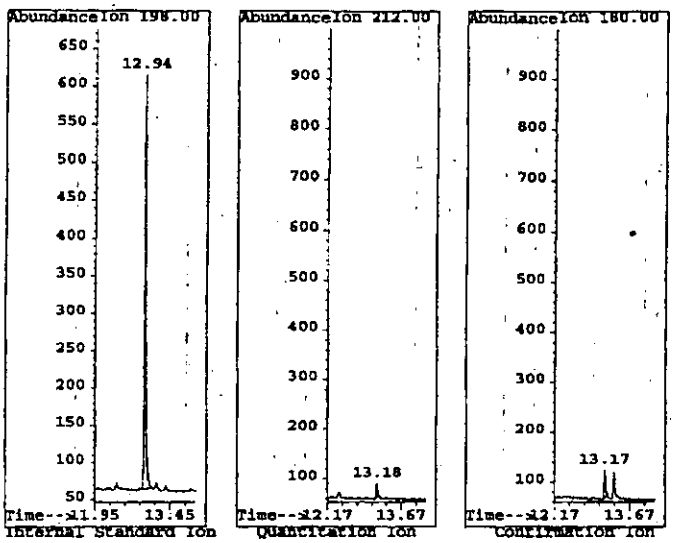
Acquisition: 1 Oct 96
Operator : D. E. Barnekow
Integration: 10/02/96
Integrator : David E. Barnekow

Sample Name: IVL Trial 3; Control Water (C1)
Sample Info: RES96059 - Water #18848401

Compound	Ion	Retention Time	Peak Area
Internal Standard	198	12.95	1072
Cloransulam-methyl	212	Not Found	Not Found
	180	Not Found	Not Found

Quantitation Ratio: 0.000
Cloransulam-methyl Concentration: 0.000 ng/mL
Average Standard Confirmation Ratio: 0.41

Figure 4. Typical Chromatogram of a Control Pond Water Sample for the Determination of Cloransulam-methyl



Data File : 1001010.D
ALS Bottle : 10
Data Path : C:\HPCHEM\1\DATA\100196\
Instrument : GC B/N 2950A25792
Method : DEB565

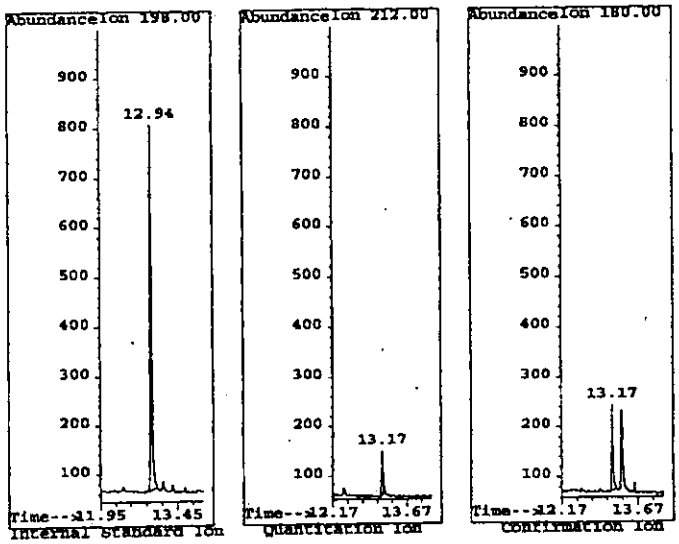
Acquisition: 1 Oct 96
Operator : D. E. Barnekow
Integration: 10/02/96
Integrator : David E. Barnekow

Sample Name: IVL Trial 3; Fortified Water (PC1)
Sample Info: RES96059 - Water #18848401 (0.10ng/mL)

Compound	Ion	Retention Time	Peak Area
Internal Standard	198	12.94	1207
Cloransulam-methyl	212	13.18	53
	180	13.17	124

Quantitation Ratio: 0.044
Cloransulam-methyl Concentration: 0.101 ng/mL
Recovery: 101%
Confirmation Ratio: 0.43
Average Standard Confirmation Ratio: 0.41

Figure 5. Typical Chromatogram of a Control Pond Water Sample Fortified with 0.10 ng/mL Cloransulam-methyl



Data File : 1201012.D
ALS Bottle : 12
Data Path : C:\HPCHEM\1\DATA\100196\
Instrument : GC S/N 2950A25792
Method : DEB565

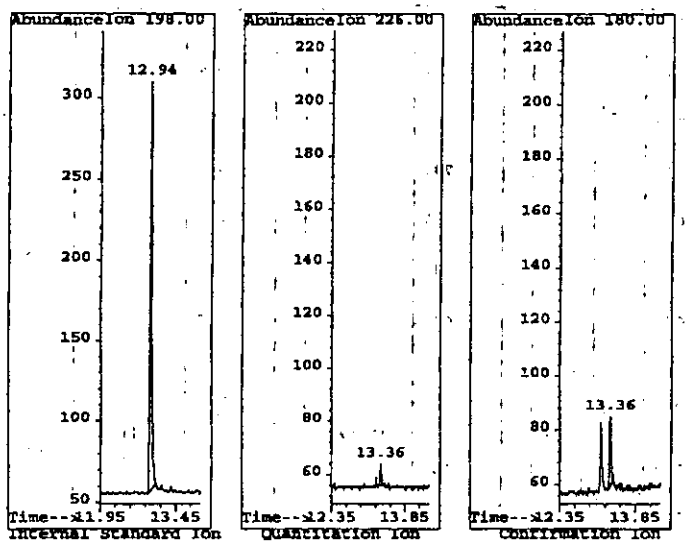
Acquisition: 1 Oct 96
Operator : D. E. Barnekow
Integration: 10/02/96
Integrator : David E. Barnekow

Sample Name: IVL Trial 3; Fortified Water (FC3)
Sample Info: RES96059 - Water #18848401 (0.20ng/mL)

Compound	Ion	Retention Time	Peak Area
Internal Standard	198	12.94	1523
Cloransulam-methyl	212	13.17	171
	180	13.17	378

Quantitation Ratio: 0.112
Cloransulam-methyl Concentration: 0.220 ng/mL
Recovery: 110%
Confirmation Ratio: 0.45
Average Standard Confirmation Ratio: 0.41

Figure 6. Typical Chromatogram of a Control Pond Water Sample Fortified with 0.20 ng/mL Cloransulam-methyl



Data File : 0301015.D
ALS Bottle : 3
Data Path : C:\HPCHEM\1\DATA\100196\
Instrument : GC S/N 2950A25792
Method : DEB565

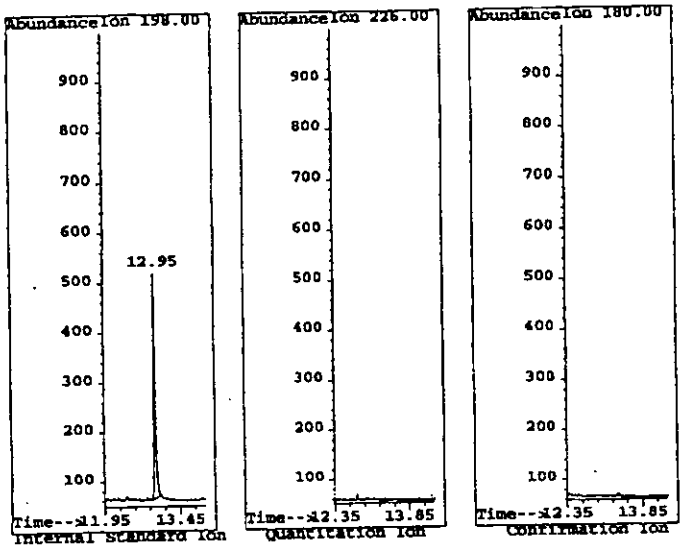
Acquisition: 1 Oct 96
Operator : D. E. Barnekow
Integration: 10/02/96
Integrator : David E. Barnekow

Sample Name: STD 20.0 ng/mL G.4.C.2
Sample Info: RES96059

Compound	Ion	Retention Time	Peak Area
Internal Standard	198	12.94	595
Cloransulam	226	13.36	13
	180	13.36	58

Quantitation Ratio: 0.022
Cloransulam Equiv. Water Concentration: 0.10 ng/mL
Confirmation Ratio: 0.22
Average Standard Confirmation Ratio: 0.25

Figure 7. Typical Chromatogram of a 20-ng/mL Standard, Equivalent to 0.10 ng/mL Cloransulam in Water



Data File : 0801008.D
ALS Bottle : 8
Data Path : C:\HPCHEM\1\DATA\100196\
Instrument : GC S/N 2950A25792
Method : DEB565

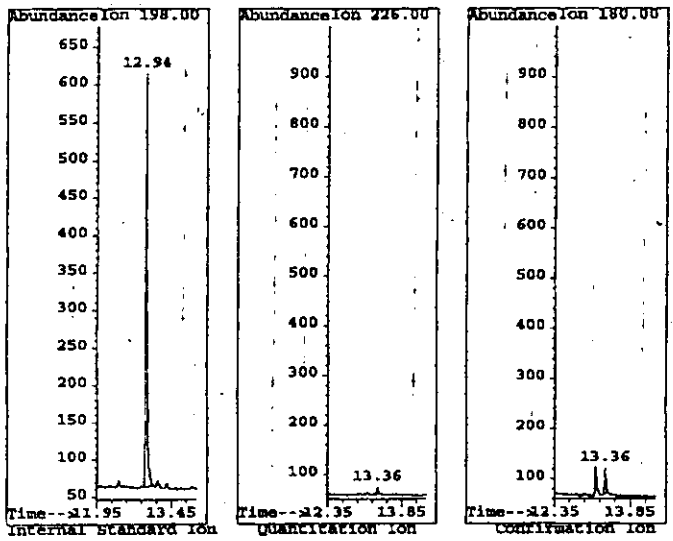
Acquisition: 1 Oct 96
Operator : D. E. Barnekow
Integration: 10/02/96
Integrator : David E. Barnekow

Sample Name: IVL Trial 3; Control Water (C1)
Sample Info: RES96059 - Water #18848401

Compound	Ion	Retention Time	Peak Area
Internal Standard	198	12.95	1072
Cloransulam	226	Not Found	Not Found
	180	Not Found	Not Found

Quantitation Ratio: 0.000
Cloransulam Concentration: 0.000 ng/mL
Average Standard Confirmation Ratio: 0.25

Figure 8. Typical Chromatogram of a Control Pond Water Sample for the Determination of Cloransulam



Data File : 1001010.D
ALS Bottle : 10
Data Path : C:\HPCHEM\1\DATA\100196\
Instrument : GC S/N 2950A25792
Method : DEB565

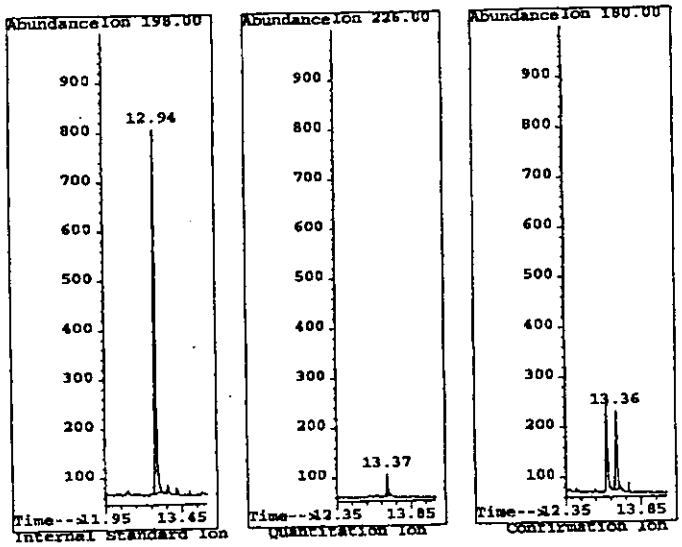
Acquisition: 1 Oct 96
Operator : D. E. Barnekow
Integration: 10/02/96
Integrator : David E. Barnekow

Sample Name: IVL Trial 3; Fortified Water (FC1)
Sample Info: RES96059 - Water #18848401 (0.10ng/mL)

Compound	Ion	Retention Time	Peak Area
Internal Standard	198	12.94	1207
Cloransulam	226	13.36	25
	180	13.36	100

Quantitation Ratio: 0.021
Cloransulam Concentration: 0.085 ng/mL
Recovery: 85%
Confirmation Ratio: 0.25
Average Standard Confirmation Ratio: 0.25

Figure 9. Typical Chromatogram of a Control Pond Water Sample Fortified with 0.10 ng/mL Cloransulam



Data File : 1201012.D
ALS Bottle : 12
Data Path : C:\HPCHEM\1\DATA\100196\
Instrument : GC S/N 2950A25792
Method : DRB565

Acquisition: 1 Oct 96
Operator : D. E. Barnekow
Integration: 10/02/96
Integrator : David E. Barnekow

Sample Name: IVL Trial 3; Fortified Water (FC3)
Sample Info: RES96059 - Water #18848401 (0.20mg/mL)

Compound	Ion	Retention Time	Peak Area
Internal Standard	198	12.94	1523
Cloransulam	226	13.37	90
	180	13.36	360

Quantitation Ratio: 0.059
Cloransulam Concentration: 0.195 ng/mL
Recovery: 97%
Confirmation Ratio: 0.25
Average Standard Confirmation Ratio: 0.25

Figure 10. Typical Chromatogram of a Control Pond Water Sample Fortified with 0.20 ng/mL Cloransulam

APPENDIX A

Tolerance Enforcement Form

DOWELANCO
(DowElanco Confidential)

Tolerance Enforcement Methods
Independent Laboratory Confirmation
(EPA Ref. - PR Notice 96-1; Supersedes PR Notice 88-5)

The information presented here will be reported to the Environmental Protection Agency (EPA) as the results of a successful confirmatory method trial by an independent laboratory.

1. CONFIRMING LABORATORY

Yes, this laboratory does follow generally accepted laboratory procedures which comply with Good Laboratory Practices (GLP) regulations required by EPA for residue chemistry studies.

Lab Manager: G. R. Oliver
Signature: _____ Date: 12/13/96
Name of Organization: DowElanco, Environmental Fate and Residue Chemistry
Address: 9330 Zionsville Road
City, State, Zip Code: Indianapolis, Indiana 46268
Analyst: David E. Barnekow
Signature: _____ Date: Dec 13, 1996
Telephone: (317) 337-3505

2. DESCRIPTION OF ANALYTICAL METHOD

Method Identification Number: DowElanco residue analytical method GRM 96.04

Title of Method: Determination of Residues of Cloransulam-methyl and Cloransulam in Water by Capillary Gas Chromatography with Mass Selective Detection

Scope of Method: This method is applicable for the quantitative determination of residues of cloransulam-methyl, [*N*-(2-carbomethoxy-6-chlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo-[1,5-c]-pyrimidine-2- sulfonamide] and cloransulam, [*N*-(2-carboxy-6-chlorophenyl)-5-ethoxy-7-fluoro-[1,2,4]triazolo[1,5-c]-pyrimidine-2- sulfonamide] in water over the concentration range of 0.10-2.0 ng/mL, with a validated limit of quantitation of 0.10 ng/mL.

Identification of analytical standard used: Name: cloransulam
AGR Number: TSN100609
% Purity: 99%
Analytical Report No.: FA&PC 940389
Report Date: 24 FEB 1995

Identification of analytical standard used: Name: cloransulam-methyl
TSN Number: AGR293572
% Purity: 99.2%
Analytical Report No.: FA&PC 963036
Report Date: 26 APR 1996

Identification of analytical standard used: Name: *N*-methyl-cloransulam-methyl
TSN Number: TSN100070
% Purity: >96%
Analytical Report No.: FA&PC 945137
Report Date: 10 JUN 1994

Identification of analytical standard used: Name: *N*-ethyl-cloransulam-methyl
TSN Number: TSN100102
% Purity: >97%
Analytical Report No.: FA&PC 945138
Report Date: 10 JUN 1994

Identification of analytical standard used: Name: *N*-ethyl-cloransulam-ethyl
TSN Number: TSN100099
% Purity: >99%
Analytical Report No.: FA&PC 950119
Report Date: 16 MAY 1995

3. ANALYTICAL RESULTS

Substrate: Pond Water
Identification Number of the CONTROL sample: Pond Water (SN 18848401)

SAMPLE RESULTS - CONTROL

Calculated analytical results of control sample

(1): Pond Water 0.0000 ng/mL for both cloransulam-methyl and cloransulam

SAMPLE RESULTS - CLORANSULAM-METHYL FORTIFIED AT (1x) LIMIT OF QUANTITATION LEVEL

Amount found and calculated % recovery

(1): Pond Water amount found = 0.101 and 0.114 ng/mL; calculated % recovery = 101% and 114%

SAMPLE RESULTS - CLORANSULAM-METHYL FORTIFIED AT (2x) LIMIT OF QUANTITATION LEVEL

Amount found and calculated % recovery

(1): Pond Water amount found = 0.220 and 0.220 ng/mL; calculated % recovery = 110% and 110%

SAMPLE RESULTS - CLORANSULAM FORTIFIED AT (1x) LIMIT OF QUANTITATION LEVEL

Amount found and calculated % recovery

(1): Pond Water amount found = 0.085 and 0.120 ng/mL; calculated % recovery = 85% and 120%

SAMPLE RESULTS - CLORANSULAM FORTIFIED AT (2x) LIMIT OF QUANTITATION LEVEL

Amount found and calculated % recovery

(1): Pond Water amount found = 0.195 and 0.198 ng/mL; calculated % recovery = 97% and 99%

AVERAGE CALCULATED % RECOVERY FOR FORTIFIED CONTROL WATER SAMPLES: Cloransulam-methyl - 109 ±6%; Cloransulam - 100 ±15%

4. FULL DESCRIPTION OF ANALYTICAL INSTRUMENTATION USED

Instrumentation	Hewlett-Packard Model 5890 Series II Gas Chromatograph/Model 5972 Mass Selective Detector, Autosampler Model HP 7673 GC/SFC Injector, HP ChemStation G1034B Ver B.02.03

Column	DB-5, 0.18 mm id x 10 m, 0.4-µm film thickness, J & W Scientific, Serial No. 5868915A
Oven Temperature	Hold at 120 °C for 1.0 min, then 120 °C to 325 °C at 15 C/min, hold for 1 min
Injector Temperature	270 °C
Transfer Line Temperature	300 °C
Carrier Gas	helium
Carrier Gas Linear Velocity	approximately 40 cm/sec
Head Pressure	50 kPa
Injection Mode	splitless
Injection Liner	deactivated, double taper
Injector Purge Delay	0.7 min
Split Flow	60 mL/min
Septum Purge	1.0 mL/min
Injection Volume	3 µL
Detector Mode	Electron impact, selected ion monitoring
Calibration Program	Maximum sensitivity autotune
Electron Multiplier Voltage	1541 volts (tune voltage plus 200)
Ions Monitored	
N-Methyl-cloransulam-methyl	*m/z* 198 (internal standard)
N-Ethyl-cloransulam-methyl	*m/z* 212 (quantitation), *m/z* 180 (confirmation)
N-Ethyl-cloransulam-ethyl	*m/z* 226 (quantitation), *m/z* 180 (confirmation)
Dwell Time	100 msec

5. DESCRIPTION OF ANY PROBLEMS ENCOUNTERED IN CONFIRMING THIS METHOD

Section/Step/Operation:

(1): No problems were encountered while validating this method.

6. IDENTIFICATION OF CRITICAL STEPS i.e., STEPS WHERE LITTLE VARIATION IS ALLOWED OR DIRECTIONS MUST BE FOLLOWED PRECISELY

(1): No critical steps were identified while validating this method.