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April 16, 2001

MEMORANDUM

SUBJECT: Acetamiprid Method Evaluation - Report No. ECM 0172W1
DP Barcode: D 263960

FROM: Aubry E. Dupuy, Jr., Branch Chief Aubry E. Dupuy Jr.
BEAD/Environmental Chemistry Laboratory

TO: Mah Shamim, Chief
Environmental Fate and Effects Division
Environmental Risk Branch IV

THRU: Hardip Singh, Senior
Gatekeeper Team/IO
Environmental Fate and Effects Division

The EFED/Environmental Fate and Effects Division has requested an Environmental Chemistry Method Evaluation (ECME) on the determination of Acetamiprid in water using the Nisso Chemical method, "Analytical Method for the Determination of Avcetamiprid in Water".

The attached method evaluation report includes three parts:

Part I: Summary and Conclusions

In this section any problems encountered with the method and how they were handled are discussed. ECL's opinion of how well the method performed is also performed.

Part II: Analytical Results

In this section the individual results of each sample at each spiking level for each matrix are listed. The relative standard deviation (RSD) for each spiking level is also presented here.

Part II: Experimental Details

In this section any modification(s) that were made to this method, instrumental parameters, spiking levels, explanation of instrument calibration, representative sample and standard chromatograms and

standard curves are listed and/or discussed.

If there are any questions regarding this report, please contact Christian Byrne at (228)-688-3213 or me at (228)-688-3212.

Attachments

cc: Dr. Christian Byrne, QA Officer
BEAD/Environmental Chemistry Laboratory

Environmental Chemistry Method Validation Report Number ECM 0172W1

Acetamiprid in Water

Environmental Chemistry Laboratory
Biological and Economic Analysis Division

April 13, 2001

Prepared by: Christian Byrne, _____
ECL Chemist Signature

Reviewed by: Elizabeth Flynt, _____
ECL QA Coordinator Signature

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PART I

Summary and Conclusions

We have completed the Environmental Chemistry Method Evaluation (ECME) for Acetamiprid in water. The method appears to be suitable for the detection of Acetamiprid at levels at or greater than 0.10 µg/L [0.10 ppb (parts-per-billion): 100 ppt (parts-per trillion)]. The method used for the ECME is entitled - **Analytical Method for the Determination of Acetamiprid in Water**. The performing laboratory was Nisso Chemical Analysis Service Co., Kanagawa, Japan.

The analytical method involves the extraction by octadecyl (C_{18}) solid phase extraction (SPE) column chromatography followed by octadecyl (C_{18}) solid phase extraction (SPE) column chromatographic clean-up. The eluate is reduced to dryness and re-dissolved. The residues of Acetamiprid are determined by high performance liquid chromatography (HPLC) using ultraviolet (UV) detection.

The limit of detection (LOD) for Acetamiprid in surface water was 0.033 ppb as established by the registrant. ECL confirmed the LOD for Acetamiprid in deionized water to be 0.033 ppb and the limit of quantitation (LOQ) to be 0.100 ppb. The accuracy and precision results between ECL and the registrant at spiking concentrations of 1.00 ppb, 0.100 ppb, and 0.033 ppb were comparable. The Nisso Chemical Analysis Service Co laboratory demonstrated average percent recoveries @ 1.00 ppb (10 x LOQ) and @ 0.100 ppb (LOQ) of 96% and 106%, respectively. ECL analyses revealed average percent recoveries @ 1.00 ppb (10 x LOQ) in surface water and @ 0.100 ppb (LOQ) of 86.4% and 52.4%, respectively. The Nisso Chemical Analysis Service Co laboratory demonstrated relative standard deviations (RSDs) @ 1.00 ppb and @ 0.100 ppb of 2.5% and 3.2%, respectively. The relative standard deviations (RSDs) for the ECL analyses at the 1.00 ppb and 0.100 ppb levels were 2.09% and 4.40%.

Although the recovery of Acetamiprid at @ 1.00 ppb (10 x LOQ) in surface water met the ECB QA/QC targets, there was a background interference in the surface water that reduced the recovery of Acetamiprid below the lower recovery limit of 70%. Deionized water was substituted for the surface water at the LOQ (0.1 ppb) and the LOD (0.033 ppb). ECL analyses revealed an average percent recovery @ 0.10 ppb (LOQ) in deionized water of 73.1 and a relative standard deviation of 5.95. Thus, both laboratories were within the average percent recovery target range of 70% to 120% and the relative standard deviation of ≤ 20%.

ECL estimates that it takes approximately ten (10) working hours to extract and analyze one set of four (4) samples with appropriate blanks and standards.

PART II

Analytical Results

Method: Nisso Chemical Analysis Service Co, Technical Report Number NCAS 97-007, **"Analytical Method for the Determination of Acetamiprid in Water."**

TABLE 1. Recovery of Acetamiprid from Deionized Water
Acetamiprid - **LOD (0.033 ppb)**

Sample #	Added, µg/L (ppb)	Detected (ppb)
D-1	0.000	0.000
D-2	0.000	0.000
D-3	0.033	0.008
D-4	0.033	0.008
D-5	0.033	0.009
D-6	0.033	0.010

Acetamiprid - **LOQ (0.100 ppb)**

Sample #	Added, µg/L (ppb)	Detected (ppb)	(% Recovery)
Q-1	0.000	0.000	--
Q-2	0.000	0.000	---
Q-3	0.100	0.0722	72.2
Q-4	0.100	0.0722	72.2
Q-5	0.100	0.0705	70.5
Q-6	0.100	0.0705	70.5

Mean	71.3
[1]SD	1.10
[1]RSD	1.54%

TABLE 1. (continued)

Recovery of Acetamiprid from Surface Water

Acetamiprid - **LOQ (0.100 ppb)**

Sample #	Added, µg/ L (ppb)	Detected (ppb)	(% Recovery)
Q-1	0.000	0.0	---
Q-2	0.000	0.0	---
Q-3	0.100	0.0522	52.2
Q-4	0.100	0.0527	52.7
Q-5	0.100	0.0496	49.6
Q-6	0.100	0.0552	55.2
		Mean	52.4
		[1]SD	2.31
		[1]RSD	4.40%

Acetamiprid - **10 x LOQ (1.00 ppb)**

Sample #	Added, µg/ L (ppb)	Detected (ppb)	(% Recovery)
10x-1	0.00	0.0	---
10x-2	0.00	0.0	---
10x-3	1.00	0.862	86.2
10x-4	1.00	0.849	84.9
10x-5	1.00	0.856	85.6
10x-6	1.00	0.890	89.0
		Mean	86.4
		[1]SD	1.81
		[1]RSD	2.09%

NOTES:

(1) SD - Standard Deviation; RSD - Relative Standard Deviation

(2) D - Limit of Detection, Q - Limit of Quantitation, 10x - 10 x Limit of Quantitation; 1 - Method Blank, 2 - Matrix Blank, 3 - Replicate #1, 4 - Replicate #2, 5 - Replicate #3, 6 - Replicate #4.

PART III
Experimental Details

General Description of Method:

Extraction and Filtration

A 200 ml volume of surface water was measured into a 400 ml Griffin beaker and fortified with the appropriate quantity of spiking solution of Acetamiprid. The solution was transferred onto a pre-washed Mega Bond Elut Octadecyl (C_{18}) solid phase extraction (SPE) column (6 cc: 1 g) and eluted with 30 ml of acetonitrile:water (3:17) eluting solution. The eluate was reduced to dryness on a rotary evaporator at 65°C and a vacuum of 50 mbars. The residue was dissolved with 10 ml of distilled water. This extract was transferred onto a pre-washed Sep-Pak Octadecyl (C_{18}) solid phase extraction (SPE) column, and eluted with 30 ml of acetonitrile:water (3:17) eluting solution. The eluate was reduced again to dryness and re-dissolved with 2 ml of the acetonitrile: water (3:7) mobile phase solution. The residues of Acetamiprid were determined by high performance liquid chromatography (HPLC) with ultraviolet (UV) detector.

Special Precautions to be Taken:

None

Major Problem

The major problem associated with the evaluation of this method was the unresolved organic envelope that interfered with the resolution of the Acetamiprid peak at the LOQ and LOD on the chromatograms. Deionized water was used in place of surface water at these levels.

Source of Analytical Reference Standards:

The standards were received from one source:
Nisso Chemical Analysis Service Co, Kanagawa, Japan.

Acetamiprid, NI-25, Lot NNI-01
≥99.9% Purity, Re-Certification Date -12/22/00,
100 mg, Chemical Structure (Appendix 1).

Sample Matrix:

The surface water was collected by the staff of the USEPA Environmental Chemistry Laboratory at a wetland area in the John C. Stennis Space Center, Mississippi. Deionized water was of HPLC grade. Water quality characteristics are listed in Appendix 2.

Instrumentation for Quantitation:

HPLC Chromatograph:	Waters Model 2690, Model 2487 Dual Wavelength UV Detector
Column:	Inertsil ODS-3, 4.6 mm x 150 mm

Instrument for Confirmation: None applicable

Instrument Parameters:

Mobile Phase: Acetonitrile:Water (3:7, v/v)
Column Temperature: 40°C
Flow Rate: 1 ml/min
Detector Wavelength: 248 mm (UV)
Injector Volume: 50 µl

Sample Calculation:

Calibration standards were prepared at 0.01, 0.02, 0.05, 0.10, 0.50 and 1.0 µg/ml:
A standard curve was prepared by plotting the concentration of Acetamiprid (µg/ml) (x-axis) versus peak area of the standards (y-axis). The initial sample volume was 200 ml. The final sample volume was 2 ml. A linear regression equation was determined:
y (area of the sample) = m [slope] * **x** (concentration of the sample) + b [x-intercept]

Concentration of the sample (µg/ml) = (Area of the sample - b)/ (m)

$$\text{Acetamiprid Concentration (ppb)} = \frac{\text{Concentration (µg/ml) x Final Volume (ml)}}{\text{Initial Sample Volume (ml)}}$$

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

Sample Calculation for Q-3:
Extract Concentration (µg/ml) = (2260 -344)/ (265225)
= 0.00722 µg/ml

$$\text{Concentration of Acetamiprid (ppb)} = \frac{0.00722 \text{ µg/ml} \times 2 \text{ ml}}{200 \text{ ml}}$$

= 0.0000722 µg/ml
= 0.0000722 µg/ml/ 1000 ml/L
= 0.0722 µg/L
= 0.0722 µg/L x 1000 ng/µg
= 72.2 ng/g

Recovery = $\frac{79.5 \text{ ng/L}}{100 \text{ ng/L}}$ x 100% = 79.5%

Chromatograms and Calibration Curves:

A. Calibration Standards Acetamiprid for Determination of the Recovery of Acetamiprid from Water @ 0.100 ppb (LOQ)

Calibration Standard-1	0.005 µg/ml
Calibration Standard-2	0.010 µg/ml
Calibration Standard-3	0.020 µg/ml
Calibration Standard-4	0.050 µg/ml
Calibration Standard-5	0.100 µg/ml
Calibration Standard-6	0.500 µg/ml
Calibration Standard-7	1.000 µg/ml

Linear Regression Graph - Acetamiprid (LOQ)

B. Acetamiprid Fortification, Water @ 0.033 ppb , 0.100 ppb, & 1.00 ppb

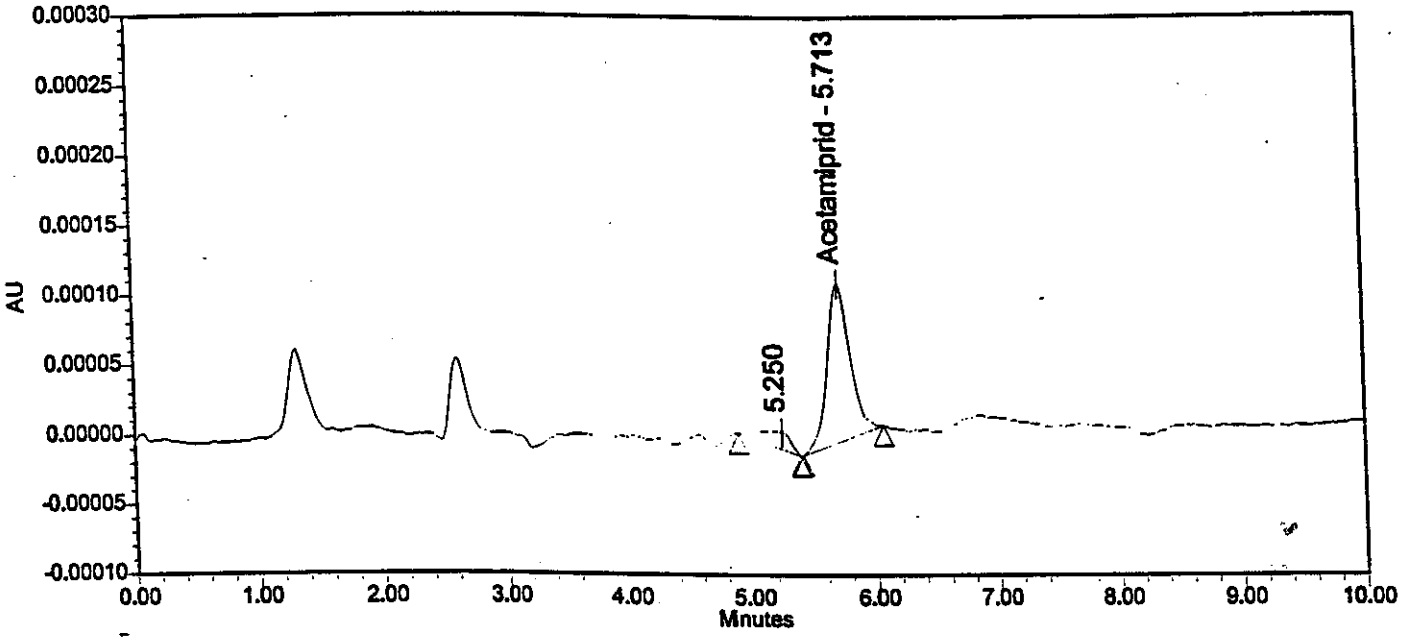
D-1	Method Blank (LOD)
Q-2	Deionized Water Matrix Blank (LOQ)
D-3	Deionized Water Fortified @ 0.033 ppb (Replicate #1)
Q-3	Deionized Water Fortified @ 0.100 ppb (Replicate #1)
10x-2	Surface Water Matrix Blank
Q-6A	Surface Water Fortified @ 0.100 ppb (Replicate #4)
10x-3	Surface Water Fortified @ 1.000 ppb (Replicate #1)

Notes:

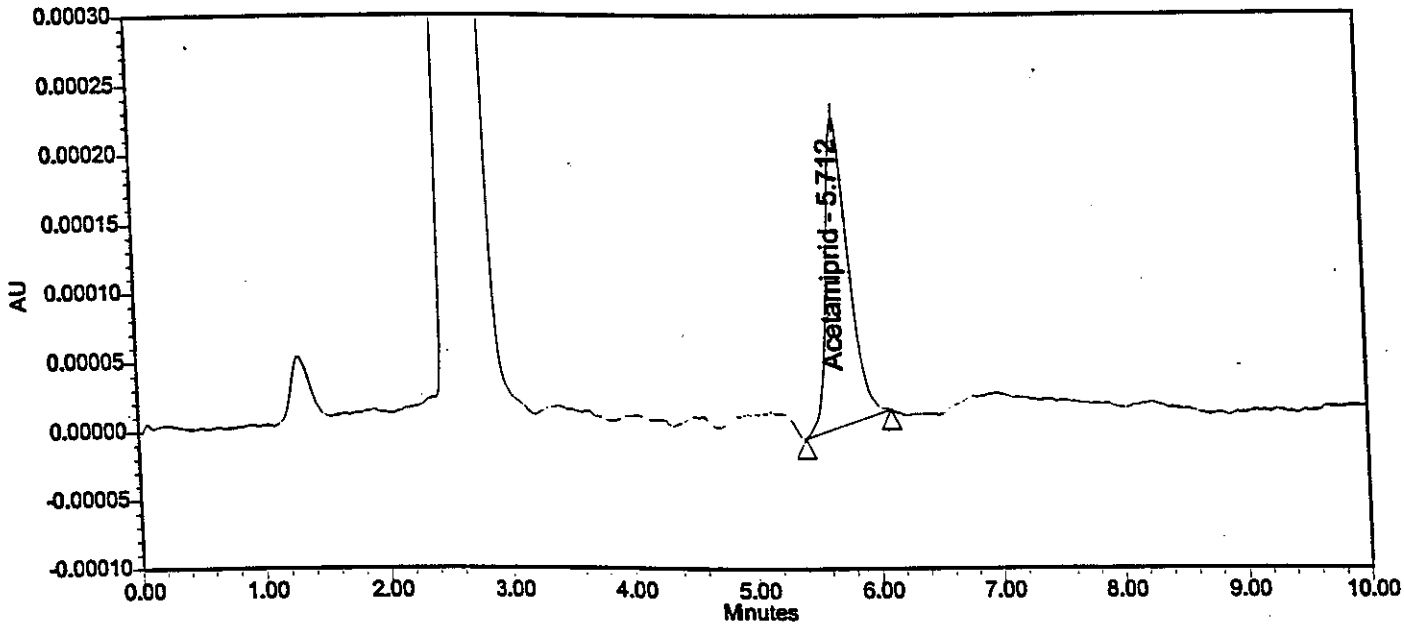
(1) Abbreviations -

D-1: Limit of Detection Extraction Series -	Solvent Blank
Q-2: Limit of Quantitation Extraction Series -	Matrix Blank
D-3: Limit of Detection Extraction Series -	Replicate #3 - @ 0.033 ppb

Chromatograms:

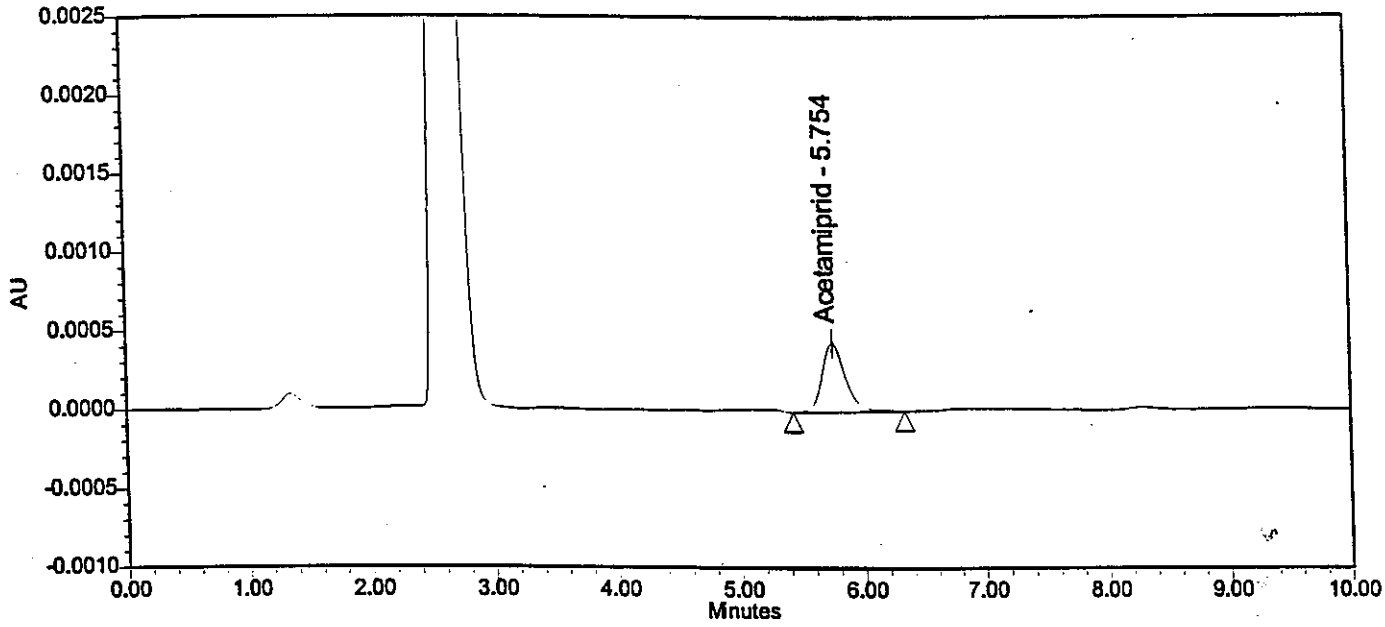


Calibration Standard-1 @ 0.005 µg/ml
Peak Area = 1431

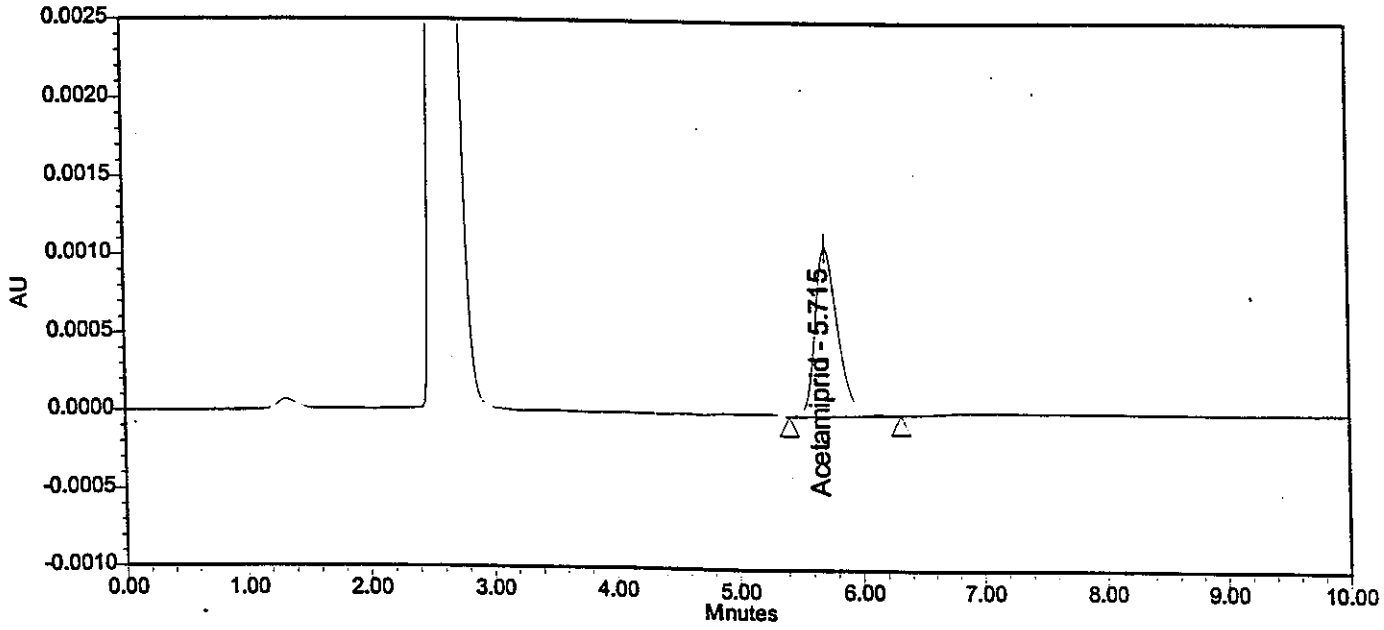


Calibration Standard-2 @ 0.010 µg/ml
Peak Area = 2823

Chromatograms:

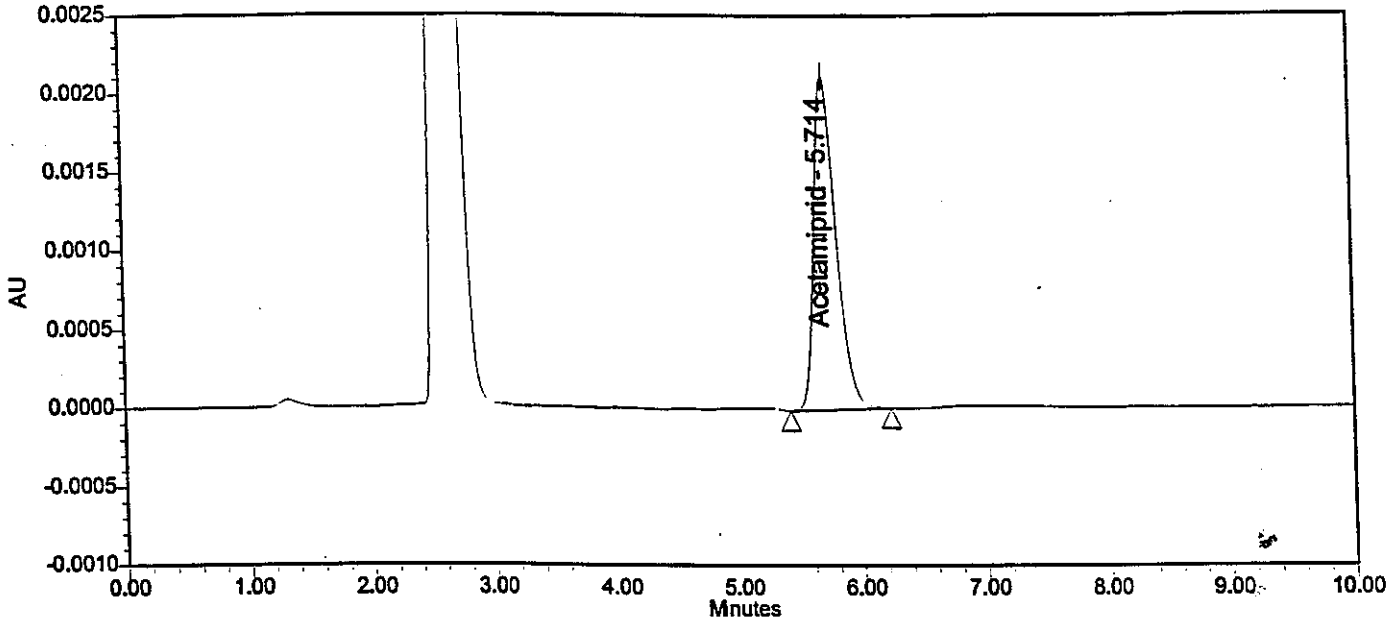


Calibration Standard-3 @ 0.020 µg/ml
Peak Area = 5663

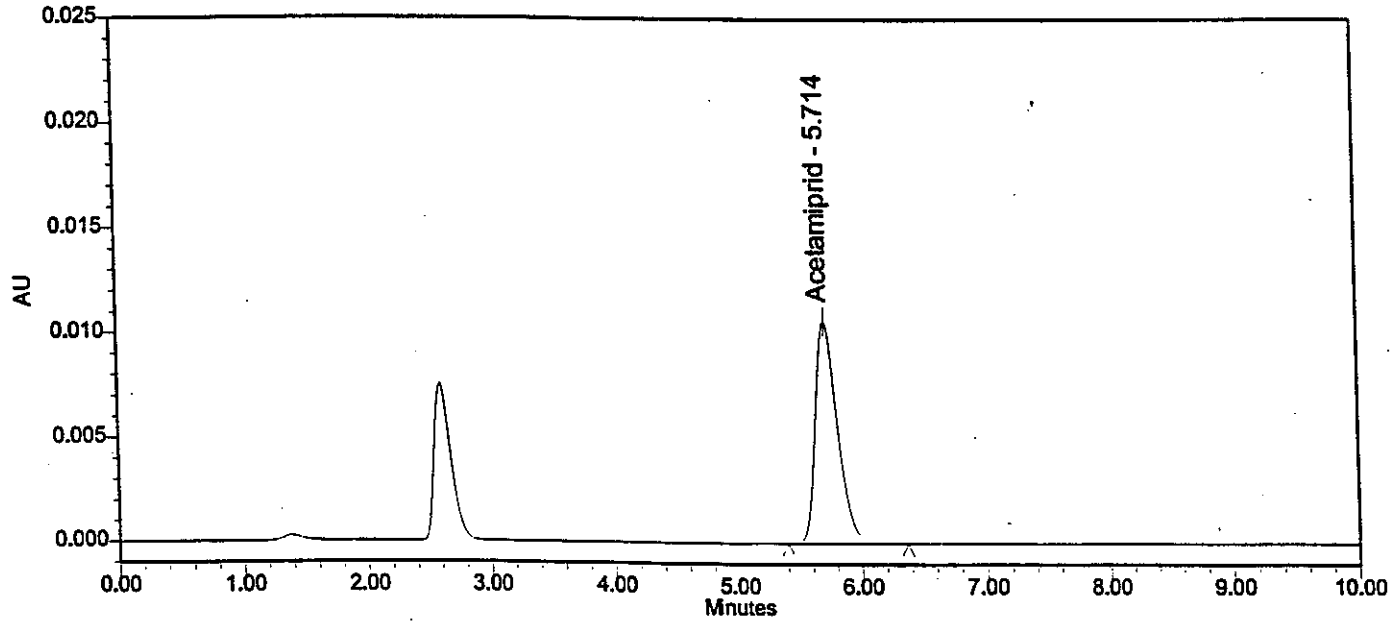


Calibration Standard-4 @ 0.050 µg/ml
Peak Area = 13657

Chromatograms:

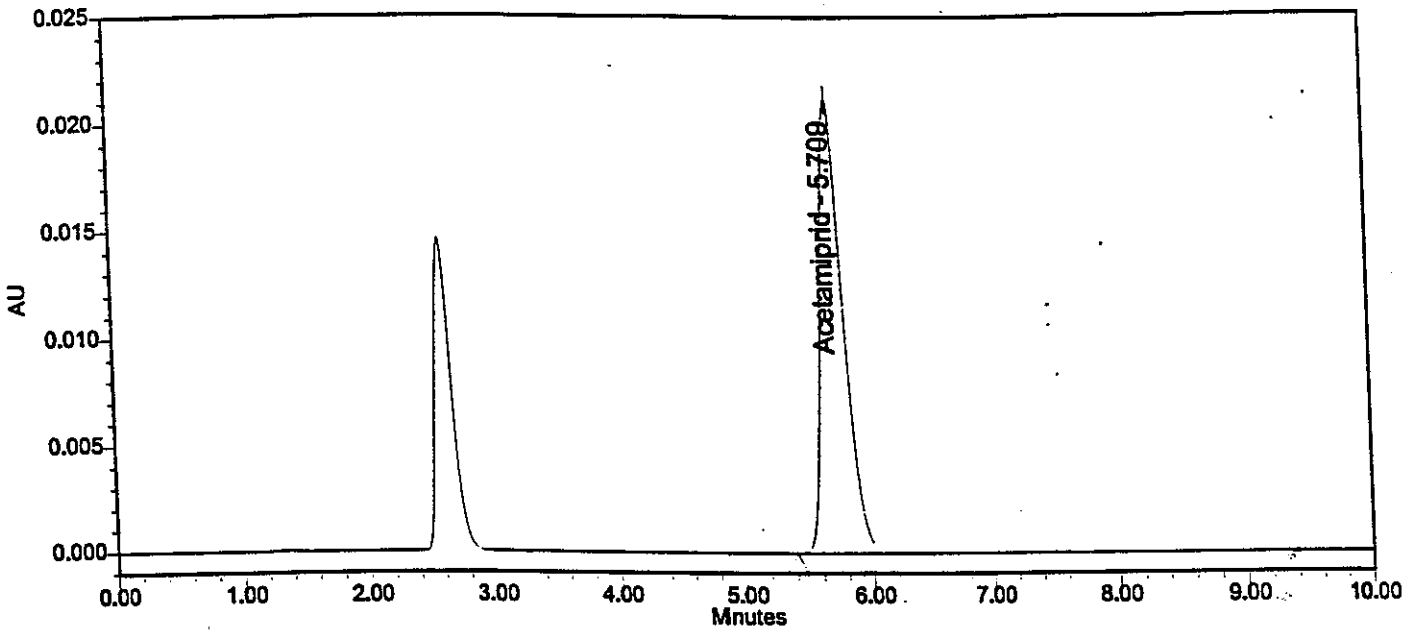


Calibration Standard-5 @ 0.100 µg/ml
Peak Area = 26593
Chromatograms:

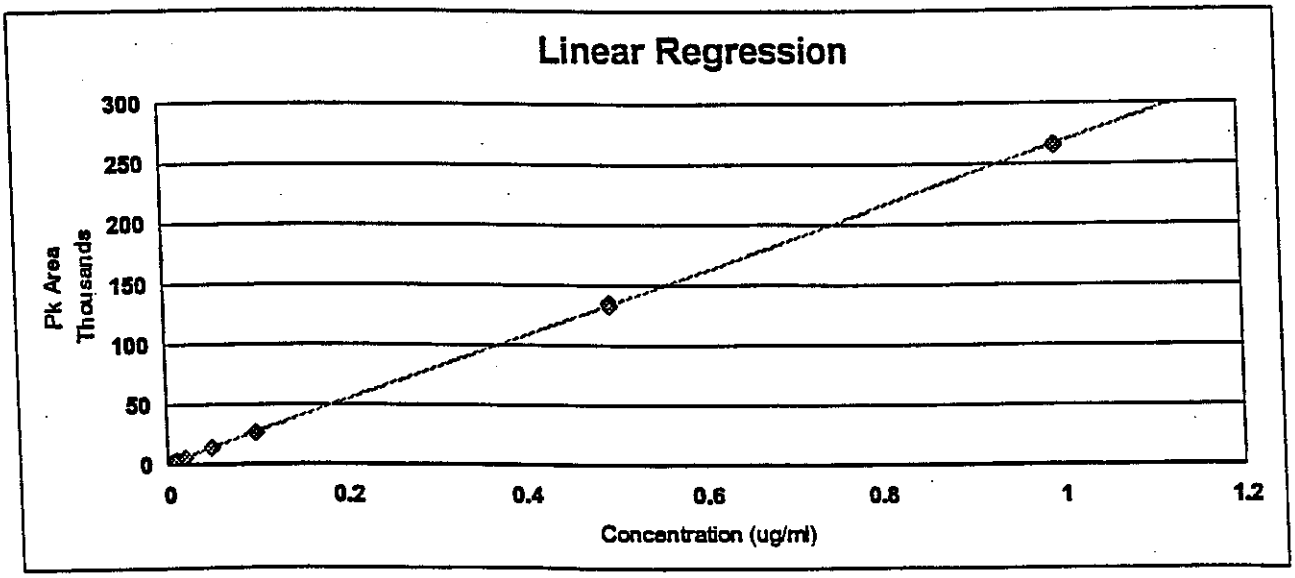


Calibration Standard-6 @ 0.500 µg/ml
Peak Area = 135522

Chromatograms:

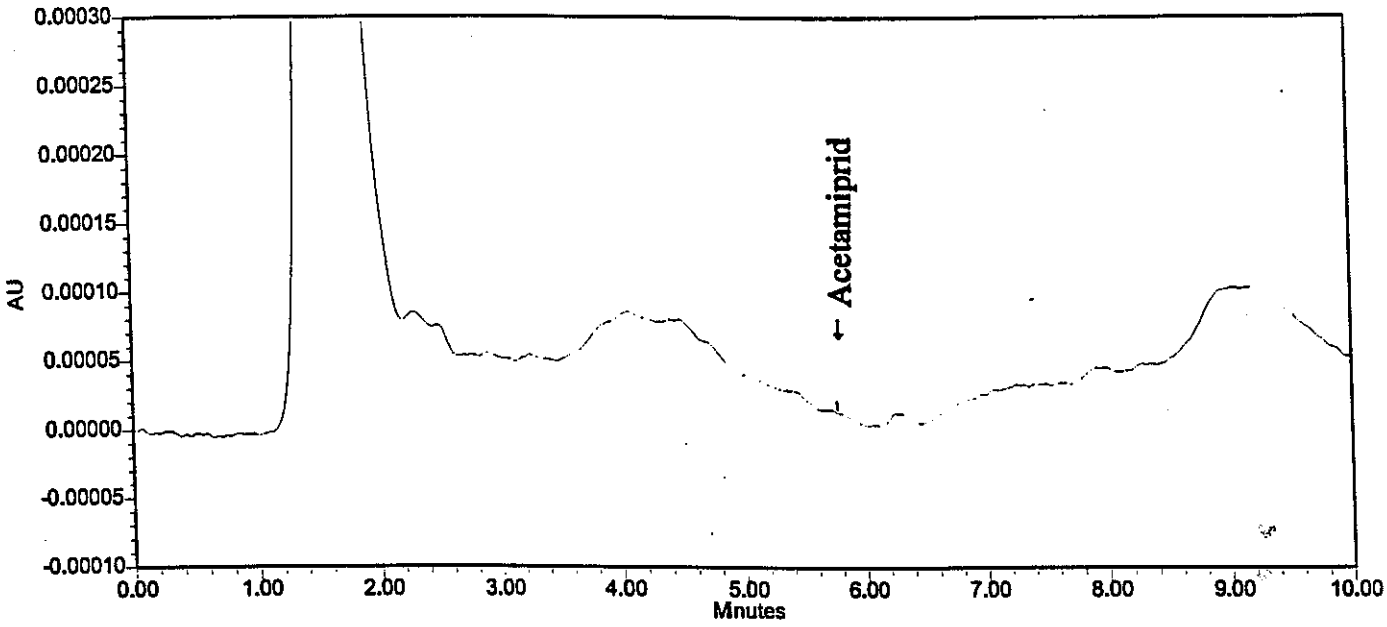


Calibration Standard-7 @ 1.000 µg/ml
Peak Area = 265456

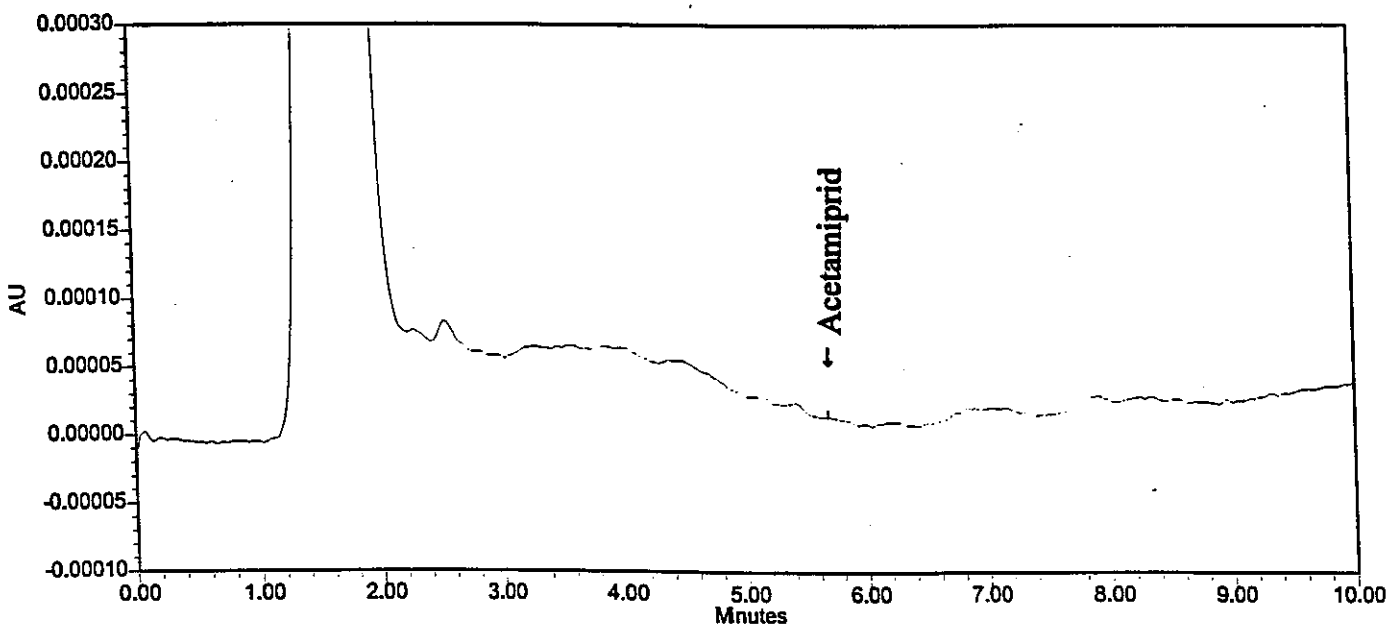


Linear Regression Graph for Acetamiprid
C (µg/ml) = [Peak Area - 344]/265225 (µg/ml)
Observations = 5 R^2 = 0.9994

Chromatograms:

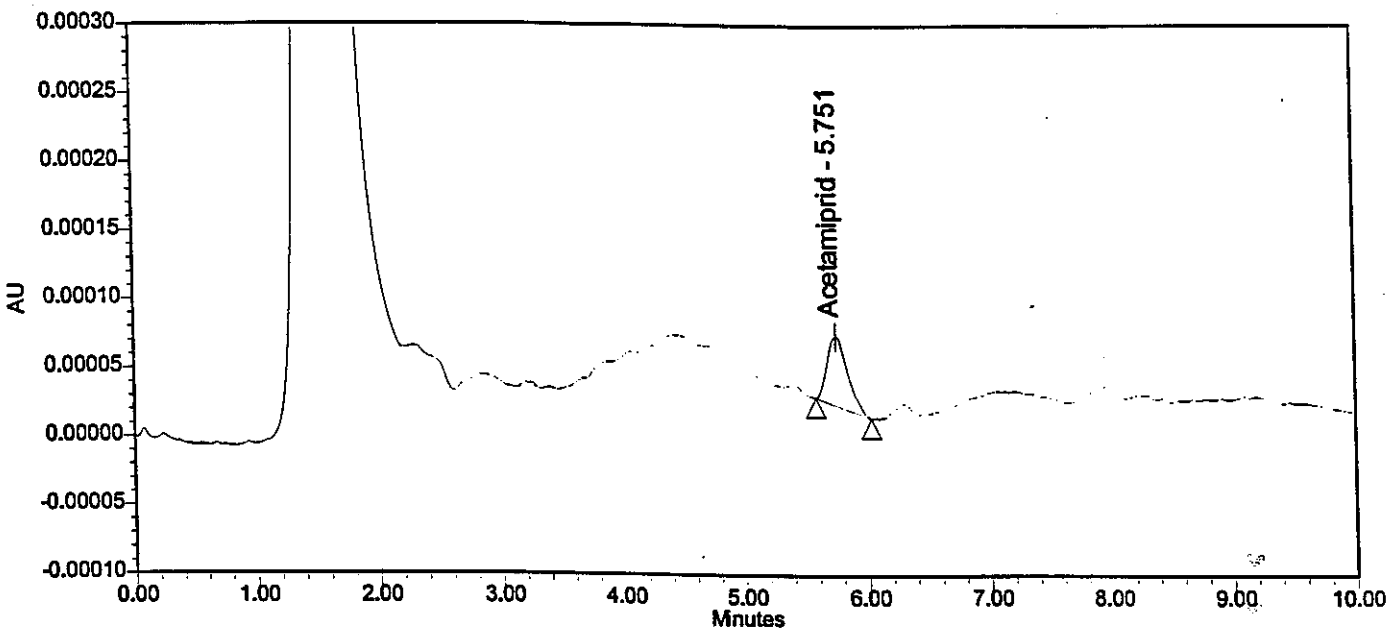


D-1 (Method Blank) @ LOD
Peak Area = 0

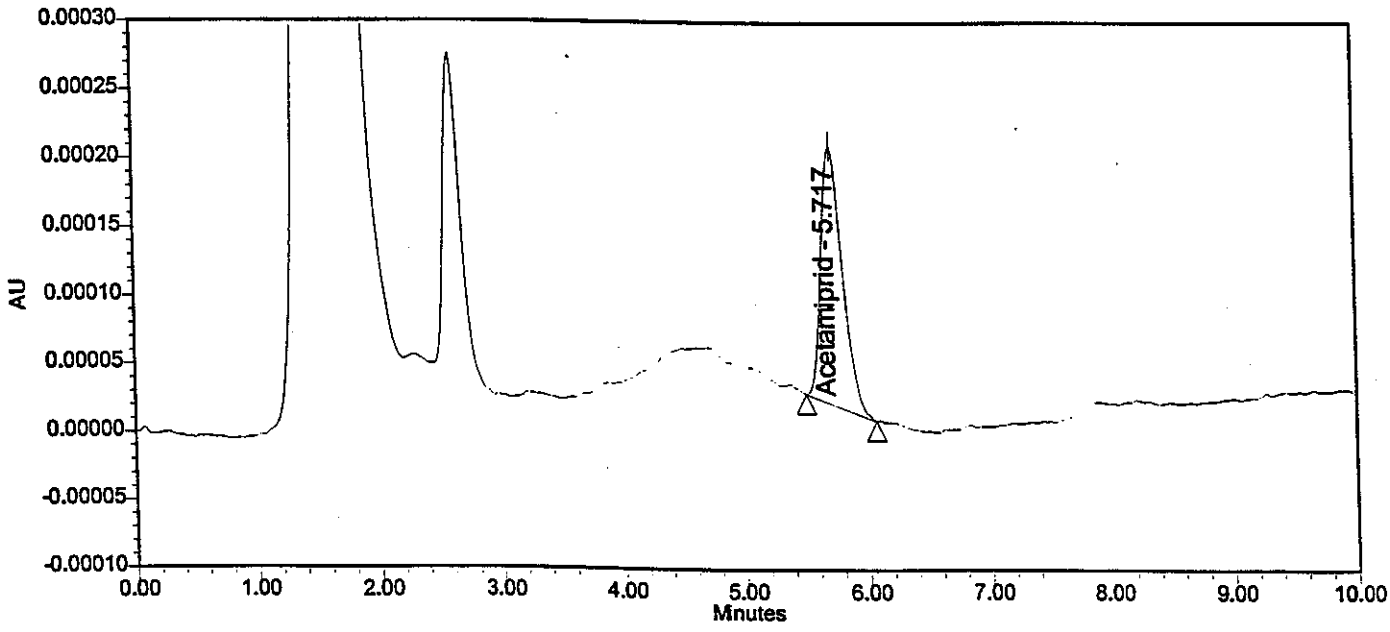


Q-2 Deionized Water Matrix Blank (LOQ)
Peak Area = 0

Chromatograms:

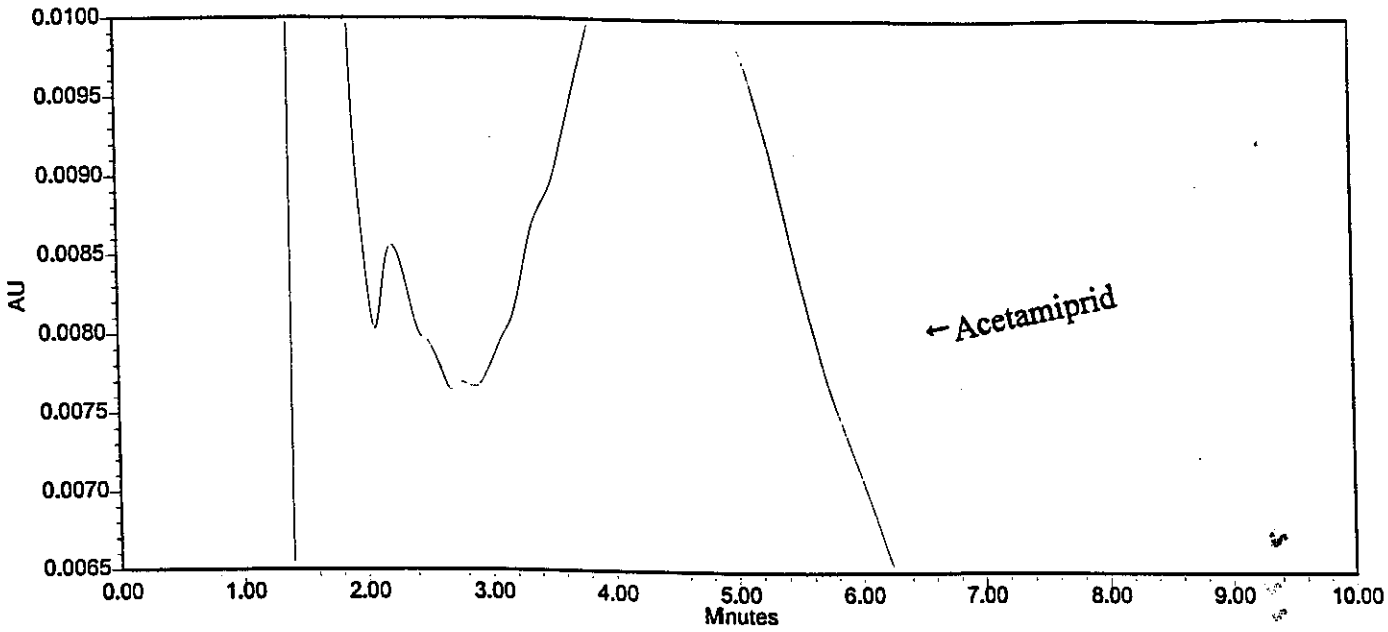


D-3 Deionized Water Fortified @ 0.033 ppb (Replicate #1)
Peak Area = 587

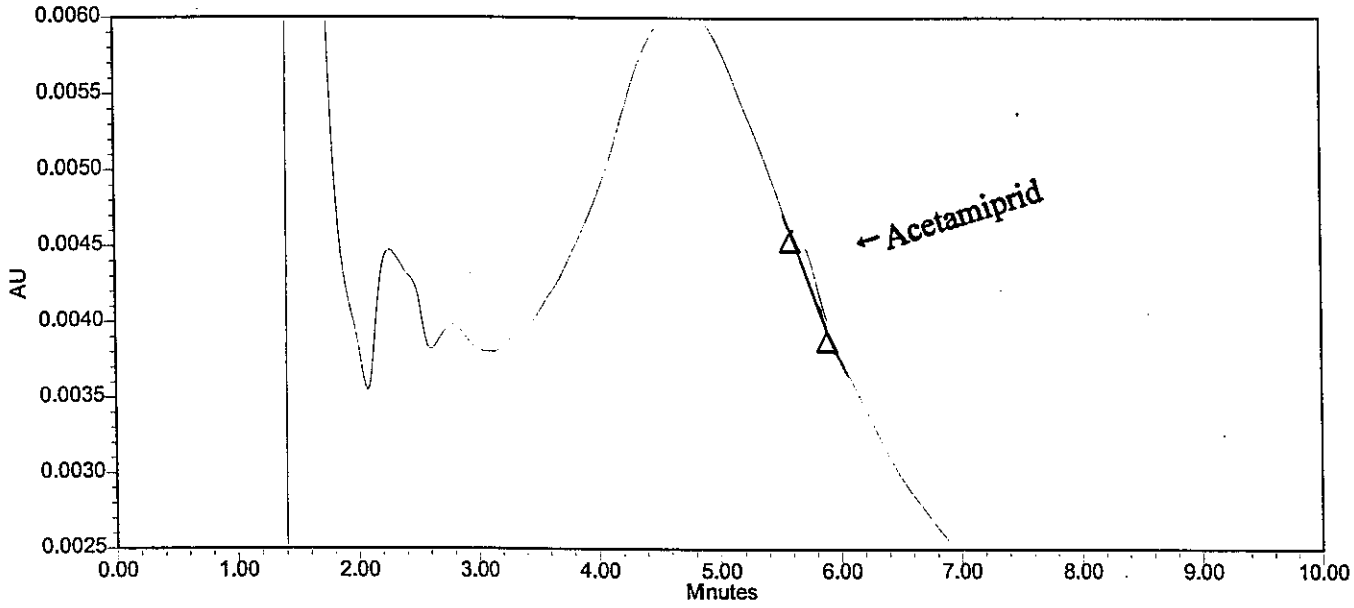


Q-3 Deionized Water Fortified @ 0.100 ppb (Replicate #1)
Peak Area = 2260

Chromatograms:

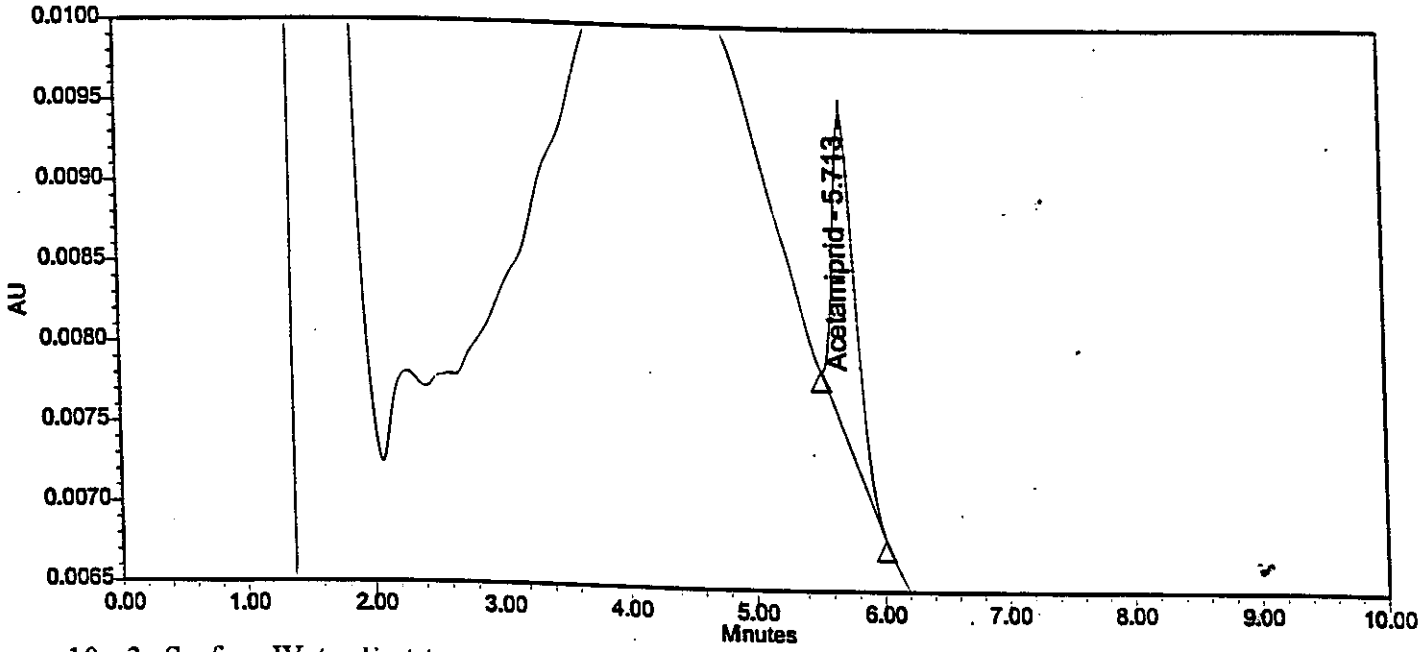


10x-2 Surface Water Matrix Blank
Peak Area = 0



Q-6A Surface Water Fortified @ 0.100 ppb (Replicate #4)
Peak Area = 1587

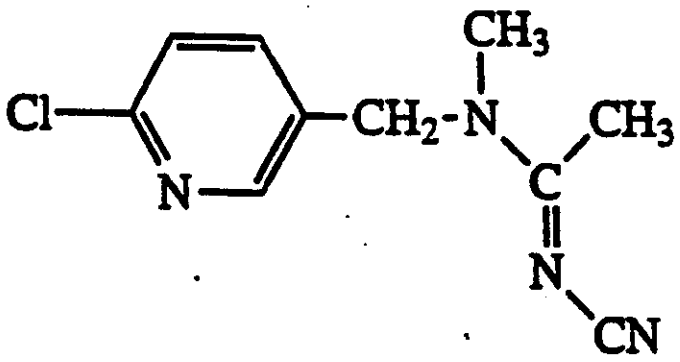
Chromatograms:



10x-3 Surface Water Fortified @ 1.00 ppb (Replicate # 1)
Peak Area = 23406

Appendix 1

Chemical Structure of Acetamiprid



Appendix 2

Water Quality Parameters of Surface Water Collected
at a Selected Wetlands in the John C. Stennis Space Center, Mississippi

Conducted by the NASA Environmental Services Laboratory

Parameter:	Technique	
pH	Electrode	6.65
Dissolved Oxygen	Electrode	0.60 mg/L
Turbidity	TU Meter	1.61 NTU
Conductivity	Cond. Meter	1.051 mmhos/cm

Water Quality Parameters of Deionized Water (HPLC Grade)

Parameter:	Technique	
Color	Spectrometer	5 APHA
Residue after Evaporation	Balance	0.4 ppm