PEST Protectant™ MANAGEMENT
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A study into the leaching properties of the *Protectant*™ polymer barrier components in water.

Purpose of this study

This study was undertaken as part of the stability and environmental data to support the product registration with the Australian Pesticides & Veterinary Medicines Authority.

Methods and Materials

A 28 day study involved the use of four tanks, set up to have a controlled water tempture (24^0 C+/-2) and that the volume of water remained constant (9L) plus this water as moving.
Each tank was filled with 9l of tank water (non-chlorinated), a line was marked across the face at the water line as a volume indicator and the tanks had lids to reduce evaporation.
A 20 L drum of the tank water (non-chlorinated) was retained for “top-up” purposes.
A fish tank water heater was set in each tank as well as a fish tank pump. Each filter pump had the filters removed as they where only to circulate the water.
The water tanks where set up and left running for two days to balance the water temperature with adjustments made to the heating units. Testing was commenced after two days and only when the water temperature remained constant at or around 24^0 C+/-2. (see *table 1.)*

Three samples of Protectant™ fabric where prepared during these two days:
Tank A: water only
Tank B: water and Protectant™ Fabric
Tank C: water and Protectant™ with a standard application of AD-ULETH-TR NTH adhesive. (6mm bead that was spread out flat to 20-25mm)
Tank D: water and Protectant™ painted with a coat of AD-TR-SOL RED paint on glue.

Each day at 6am and 6pm the water temperature was checked and recorded, the water levels where check using the mark on the face and if required water was added from a 20L drum.
Over the 28 days only 2L of water was added to the study.
After the 28 days, 500ml samples where taken from each of the four tanks and the top up drum.
Each sample container was a glass jar with a glass lid closure, with foil was placed between the seal and the glass jar rim.
The sample there placed in a cooler box with ice and taken to AgriSolutions Australia at 75 Thompson Street Deception Bay QLD for testing.
(The AgriSolutions Analytical Report is presented in *Addendum A.)*

Studies into the leaching properties of the Protectant™ polymer barrier components in water found that the product leached < 3 parts per billion after 28 days in moving water. This finding demonstrated the stability of the Bifenthrin in the polymer coating and in the two polymer adhesives. AgriSolutions noted leaching < 10 parts per billion is considered to be non reportable and will not cause any hazard to the environment.

Table 1

Day	Tank A		Tank B		Tank C		Tank D		
	AM	PM	AM	PM	AM	PM	AM	PM	
Start 1	20.1	24.3	20.4	23.8	20.0	23.6	20.3	24.7	
Start 2	24.1	24.5	24.7	23.9	24.9	24.0	23.9	24.1	
1	24.1	24.2	24.2	24.4	24.0	24.1	23.9	24.2	
2	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	
3	24.1	24.2	24.1	24.2	24.1	24.3	24.1	24.2	
4	24.1	24.1	24.2	24.1	24.1	24.2	24.1	24.0	
5	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	
6	24.1	24.0	24.1	24.1	24.1	24.0	24.1	24.0	
7	24.0	24.1	24.1	24.1	24.1	24.1	24.1	24.1	
8	24.1	24.1	24.0	24.1	24.1	24.1	24.1	24.1	
9	24.1	24.2	24.1	24.1	24.2	24.1	24.1	24.1	
10	24.1	24.1	24.1	24.1	24.1	24.1	24.3	24.1	
11	24.0	24.1	24.1	24.1	24.1	24.1	24.1	24.1	
12	24.1	24.2	24.1	24.1	24.1	24.1	24.1	24.1	
13	24.1	24.1	24.1	24.1	24.1	24.1	24.0	24.1	
14	24.1	24.1	24.2	24.1	24.1	24.1	24.1	24.1	
15	24.1	24.1	24.1	24.3	24.0	24.1	24.1	24.1	
16	24.1	24.1	24.1	24.1	24.3	24.1	24.3	24.1	
17	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	
18	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	
19	24.1	24.1	24.0	24.1	24.1	24.0	24.1	24.1	
20	24.0	24.1	24.1	24.1	24.1	24.1	24.1	24.1	
21	24.1	24.1	24.3	24.1	24.1	24.1	24.1	24.1	
22	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	
23	24.1	24.1	24.1	24.2	24.1	24.1	24.1	24.1	
24	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	
25	24.0	24.1	24.1	24.1	24.1	24.1	24.1	24.1	
26	24.1	24.3	24.1	24.1	24.0	24.1	24.1	24.1	
27	24.1	24.2	24.1	24.1	24.1	24.0	24.1	24.1	
28	24.1	24.1	24.1	24.1	24.1	24.1	24.2	24.1	

ADDENDUM A

AgriSolutions Australia

BUSINESS CONFIDENTIAL

SPONSOR: THE WHITEANT CO PTY LTD	**Laboratory Project No:** ASA-09-204a	**Date:** 11/01/10	**Total Pages:** 18 **Revision:** 1

Author: **Scott Winner**

Title: **Analytical Report for: ASA-09-204a "Determination of bifenthrin residues in water due to leeching after 28 days exposure to the Protectant Treated Fabric manufactured product."**

Send to: **Tony Di Betta**

1. Introduction

The aim of study ASA-09-204a was to generate data on the level of bifenthrin residues resultant from leeching of the active ingredient bifenthrin from the Protectant Treated Fabric manufactured product into water. Samples of the exposed water were forwarded by THE WHITEANT CO PTY LTD.

The scope of the analytical phase of this study includes the analysis and reporting of bifenthrin residues in water specimens taken from the Trial No. *ASA-09-204a*, as forwarded to the analytical facility under arrangement by the sponsor THE WHITEANT CO PTY LTD.

Specimens were received in November 2009, by AgriSolutions Australia Pty Ltd (see Section 11 - Specimen Receipt, Processing and Storage Prior to Analysis).

The analytical study specimens were frozen at time of sample receipt; and extraction, purification and instrumental analysis were conducted in November 2009 at the analytical facility of AgriSolutions Australia Pty Ltd.

Specimens were analysed using GC/MS/MS after extraction from the water samples by liquid/liquid partitioning into hexane. An aliquot was cleaned-up on a Florisil SPE cartridge. The residues were eluted and then evaporated to dryness using a rotary-evaporator. Residues were reconstituted in acetone ready for instrument analysis.

A Limit of Quantitation (LOQ) of 0.002 mg/L for bifenthrin residues in the water specimens. The LOQ was based on the lowest level of recovery analysis successfully applied as per the analytical method.

N.B. *The field phase of this study was performed independently of AgriSolutions Australia Pty Ltd's activities; therefore field phase information has not been included as a formal part of this analytical report. This report details the residue results obtained from the analyses of coded field specimens and for assessment purposes it is not intended that this report be reviewed in isolation from the study plan and/or final study report. For full information relating to the treatment and sampling of the coded specimens, see the associated study plan and/or final study report.*

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CONTENTS

2. Key Study Assignment Details

Study Title

Determination of bifenthrin residues in water due to leeching after 28 days exposure to the Protectant Treated Fabric manufactured product.

Data Requirement

Permit Application/Product Registration

Sponsor

Tony Di Betta
Technical & Field Operations Manager
THEWHITEANTCO
PO Box 230
BANORA POINT NSW 2486

Study Dates

Study Initiation: 20/11/09
Completion (Analytical Phase): 11/01/10

Performing Analytical Test Site

AgriSolutions Australia Pty Ltd
75 Thompson St
Deception Bay, QLD, 4508

Trial Number

ASA-09-204a

3. Statement of Confidentiality

The information herein is CONFIDENTIAL and is the property of THE WHITEANT CO PTY LTD.

This analytical report has been provided to THE WHITEANT CO PTY LTD to facilitate the authoring of a final study report, which in turn is to be used to support a submission for CodeMark certification. The analytical report and information contained herein may not be disclosed to other parties nor be used for any other purpose, without permission from THE WHITEANT CO PTY LTD.

4. Archive Statement

Samples of the reference substances used in this study will be retained by AgriSolutions Australia for a period of up to 3 months from the reporting date.

Sub-sampled homogenate specimens associated with this study will continue to be stored at ≤ -18°C for a period of no less than 3 months from the date of this report. Unless otherwise instructed by the study director, these specimens will be disposed of in accordance with local authority requirements, at a time after 3 months from the date of this report.

All analytical phase raw data, documentation, records, related correspondence, copy of the final analytical report as well as copies of the study plan with amendments and deviations, will be retained in the AgriSolutions Australia archives for a maximum of 3 years.

Digitally signed by Scott Winner
Reason: I am the author of this document
Location: Deception Bay, Queensland 4508 Australia

11/01/10

Scott Winner
Chemist
AgriSolutions Australia Pty Ltd

Date

Digitally signed by Andrew Keats

11/01/10

Andrew Keats
Facility Management
AgriSolutions Australia Pty Ltd

Date

8. Principal Personnel Involved in the Study

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9. Abbreviations and Formulas

ALM	=	analytical laboratory method
Conc	=	concentration
C.V.	=	coefficient of variation
DALA	=	days after last application
Diff	=	difference
g	=	gram
GC	=	gas chromatography
kg	=	kilogram
L	=	litre
LOD	=	limit of detection
LOQ	=	limit of quantitation
m	=	metre
mg	=	milligram
mL	=	millilitre
mm	=	millimetre
min	=	minute
MS	=	mass spectrometry
N/A	=	not applicable
N/F	=	not found
nm	=	nanometres
ppb	=	parts per billion
PPE	=	personal protective equipment
QC	=	quality control
RSD	=	relative standard deviation
RT	=	retention time
SPE	=	solid phase extraction
STD	=	standard
Std Dev	=	standard deviation
µg	=	microgram
µL	=	microlitre
µm	=	micrometre
UTC	=	untreated control
@	=	at
°C	=	degrees Celsius
≤	=	less than or equal to
/	=	per
%	=	percent
±	=	plus or minus

10. Reference Item Details

Common Name:	Bifenthrin
Chemical Name:	(2-methyl[1,1'-biphenyl]-3-yl)methyl (1*R*,3*R*)-*rel*-3-[(1*Z*)-2-chloro-3,3,3-trifluoro-1-propenyl]-2,2-dimethylcyclopropanecarboxylate
CAS No:	82657-04-3
Lot No:	120806RD-AC
Purity:	99.7 ± 0.5%
Manufacturer:	AccuStandard Inc.

11. Specimen Receipt, Processing and Storage Prior to Analysis

Site Received	Arrival to AgriSolutions Australia Laboratory	Preparation Before Analysis	Lab Storage Condition	Instrumental Analysis	Storage Duration
Site 1	20/11/09 Received chilled.	23/11/09 Specimens homogenised and sub-sampled.	Frozen @ ≤ -18°C	23/11/09	20/11/09 to 23/11/09

12. Summary of Analytical Method Employed During Analytical Phase

The method utilised for the analyses of the specimens obtained during Study No. *ASA-09-204A* was as follows:

> FMC Corporation Method Number P-2550M: "*RESIDUE ANALYTICAL METHOD FOR THE DETERMINATION OF BIFENTHRIN AND 4'-HYDROXY BIFENTHRIN IN/ON CORN MATRICES*". Date: May 26, 1992.

Analytical method involves water samples being extracted by liquid-liquid partitioning into hexane. Extracts are filtered and cleaned up on a Florisil SPE cartridge, then evaporated to dryness. The residues were then reconstituted in acetone. The final extract was analysed by GC/MS on a Phenomenex 'Zebron' ZB-5MS column using a Mass Spectrometer Detector (GC/MS). The quantitative determination is carried out by external standardisation.

AgriSolutions Australia Pty Ltd used the following alterations to analytical method P-2550M during analysis of samples for study *ASA-09-204A*:

1) *FMC Method P-2550M, Section V. A) Extraction:* For initial extraction of water samples 30 mL of the water specimen was used, and total extraction volume reduced to 10 mL of hexane.
2) *FMC Method P-2550M, Section V. A) Florisil Column Procedure:* The Florisil packed column cleanup step was not required. Analysis proceeded straight to the Florisil SPE cartridge clean-up step.
3) *FMC Method P-2550M, Section V. A) Florisil Prep Sep Cartridge:* Extract (10 mL aliquot) was loaded onto a Florisil SPE cartridge (1000mg/6mL), pre-conditioned with 6 mL acetone followed by 10 mL of hexane. After loading the extract onto the cartridge was washed with 10 mL of hexane. Residues are eluted with 10 mL of 10% ethyl acetate/hexane. The eluant was then evaporated to dryness on a rotary vacuum evaporator. Evaporated residues were reconstituted into 1 mL of acetone for all samples.
4) *FMC Method P-2550M, Section V. B) Instrumentation:* ThermoFinnigan TraceGC gas chromatograph with a PolarisQ ion-trap mass spectrometer replacing HP 5880A gas chromatograph fitted with an electron capture detector (GC-ECD). For details on this change, see Section 12.1 below.

12.1 Instrument

Thermo-Finnigan Trace GC Gas-chromatograph, Split/Splitless Injector, AS2000 Autosampler and PolarisQ MS mass-spectrometer.

Injector

Split/Splitless Injector:	Splitless Constant septum purge
Insert:	5 mm ID
Injection Volume:	2.0 µL
Injection Rate:	10.0 µL/sec
Injection Temperature:	270°C isothermal

Carrier Gas

Carrier Gas:	Ultra High Purity Helium Splitless 1 minute, then split 10:1 1.5 mL constant flow (vacuum compensation on) Surge pressure 110 kPa for 0.10 mins

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Capillary Column

Liquid Phase:	ZB-5MS	
Dimensions:	Length:	20 m
	Internal Diameter:	0.25 mm
	Film Thickness:	0.25 µm

Column Temperature Program

Temperature (°C)		Rate	Hold Time
Start	End	(°C/min)	(min)
100	100	0	0.50
100	280	50	1.50

Mass Spectrometer Conditions

Ionisation Mode:	Electron Ionisation (+EI)
Trap Storage Mode:	MS/MS
Filament Current:	250 mA
Ionisation Temperature:	260°C
Transfer Line Temperature:	270°C
Electron Multiplier Voltage:	1425 V
Ionisation Time:	24999 µs

MS Segment Parameters

Segment No.	Target Component	Parent Ion (m/z)	Product Quant. Ions (m/z)	Segment Time (min)
1	Bifenthrin	181	165 + 166	2.00 min – 3.00 min

A filament delay of 2.00 minutes was included.

Retention Time

Target Component	Retention Time* (mins)
Bifenthrin	2.4 mins

**Actual retention times may vary slightly.*

14. Recovery & Storage Stability Determinations

14.1 Recovery Determination

The recovery of bifenthrin residue analytes in water specimens was measured as follows:

ii) Fortification of homogenised untreated specimens with known levels of bifenthrin analyte.

iii) Residue analysis of the fortified specimens and their respective untreated control specimens as per the analytical method.

iiii) Recovery calculation as follows:

$$\text{Recovery \%} = 100 \times \left(\frac{\text{Residues recovered in fortified specimen - Levels in UTC}}{\text{Fortification Level}} \right)$$

The recovery rates of bifenthrin residues in the fortified UTC specimens corresponded to:

Portion Fortified	Range of Fortification Rate	Average Recovery	Coefficient of Variation
Water	0.002 - 0.03 mg/L as Bifenthrin	99.6% n = 9	7.2%

15. Quality Control

During the investigation the following QC measures were determined.

15.1 Limit of Quantitation (LOQ)

The limit of quantitation was determined as the lowest level of target analyte fortification and subsequent successful recovery analysis in each of the associated specimens and/or portions of specimens.

LOQ = 0.002 mg/L for each of bifenthrin residues in the water specimens.

15.2 Precision

Acceptance criteria for instrument calibrant analyses were set as ± 20% absolute concentration. Results from calibrant analyses for each of the calibrant levels were found to be acceptable in all cases.

Acceptance criteria for % C.V. @ 0.002 mg/L to 0.03 mg/L bifenthrin recoveries in water samples were set as ± 20 % (being the allowable maximum % C.V. as prescribed in the APVMA document "Residue Guideline No. 19 – Residue analytical method").

Results from bifenthrin recovery analyses @ 0.002 mg/L to 0.03 mg/L for water samples indicate acceptable precision in all cases. See the Coefficient of Variation results in Section 13.1 "Recovery Determinations".

15.3 Specificity

Specificity of the analytical method was determined through the analysis of untreated control (UTC) specimens from the matrix under study.

All UTC specimen analyses indicated no detectable residues (i.e. less than the maximum incipient signal contribution of 30% of LOQ, as prescribed in the APVMA document "Residue Guideline No. 19 - Residue Analytical Method").

15.4 Accuracy

Accuracy of the analytical method was determined via recovery of fortified UTC specimens over the acceptable range of 70% - 110%, as prescribed in the APVMA document "Residue Guideline No. 19 - Residue analytical method". Recovery levels at LOQ to 15x LOQ for water were performed in each of the matrices and yielded acceptable results in all cases. See the average recovery results in Section 13.1 "Recovery Determinations".

15.5 Decontamination

To reduce the potential for cross-contamination between specimens and equipment, all glassware and equipment was thoroughly washed and rinsed before use and after each application where equipment had the potential for coming into contact with active ingredients being analysed. The equipment was washed down with phosphate free detergent ("Decon 90"), rinsed with hot potable quality water, rinsed with distilled water and finally rinsed with acetone. Freshly cleaned dedicated glassware was used for each specimen. A new pair of nitrile gloves was also allocated for each specimen and analytical phase to minimise the risk of cross-contamination.

16. Occupational Health and Safety

Standard Personal Protective Equipment (PPE), applicable to the nature of the sampling procedures and analyses involved was used. Personnel wore lab coats, covered shoes, nitrile gloves and safety glasses. The analytical method was carried out in a well-ventilated laboratory, and all steps using organic solvents were performed in appropriate fume-cupboards.

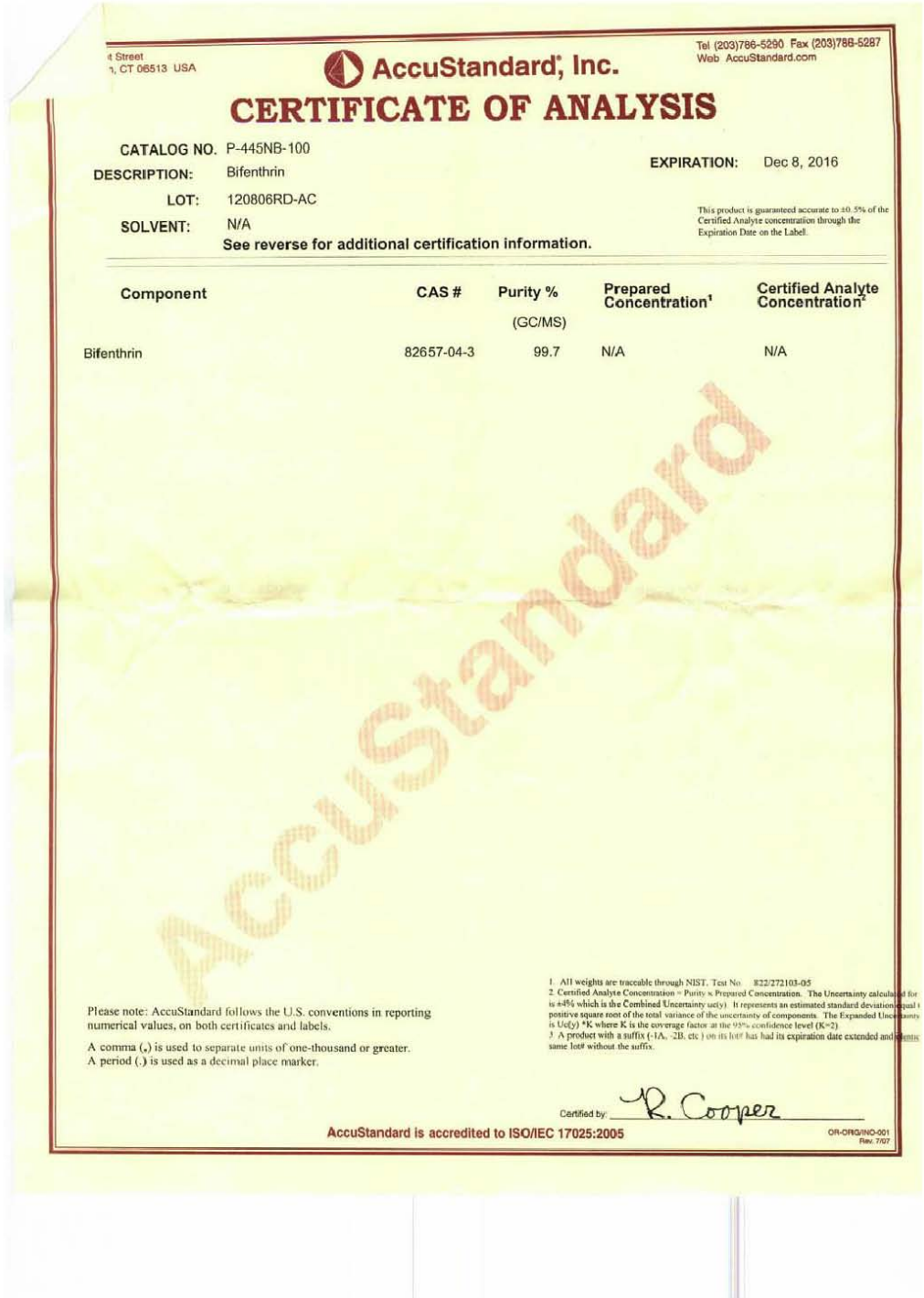
17. Residue Results From Specimen Analyses

Table 1 – Residue Results for Analyses of Bifenthrin Residues in Water

Specimen Number	Test Item	Test Item Exposure Duraction (Days)	Sample Volume	Total Bifenthrin Residues[2] (mg/kg)
Site 1 – Water Specimens				
BASE SAMPLE	Pre-Treatment Water	28	9 L	<LOQ
A	Untreated Control	28	9 L	<LOQ
B	Protectant Treated Fabric	28	9 L	<LOQ
C	Protectant Treated Fabric	28	9 L	<LOQ
D	Protectant Treated Fabric	28	9 L	<LOQ

LOQ = 0.002 mg/kg for bifenthrin residues in water specimens.
Please see section 14.2 Precision, for %C.V. as applicable to the final results.

18. Reference Item Certificates of Analysis



4 Street
1, CT 06513 USA

Tel (203)786-5290 Fax (203)786-5287
Web AccuStandard.com

AccuStandard, Inc.

CERTIFICATE OF ANALYSIS

CATALOG NO. P-445NB-100
DESCRIPTION: Bifenthrin
LOT: 120806RD-AC
SOLVENT: N/A
See reverse for additional certification information.

EXPIRATION: Dec 8, 2016

This product is guaranteed accurate to ±0.5% of the Certified Analyte concentration through the Expiration Date on the Label.

Component	CAS #	Purity % (GC/MS)	Prepared Concentration[1]	Certified Analyte Concentration[2]
Bifenthrin	82657-04-3	99.7	N/A	N/A

Please note: AccuStandard follows the U.S. conventions in reporting numerical values, on both certificates and labels.

A comma (,) is used to separate units of one-thousand or greater.
A period (.) is used as a decimal place marker.

1. All weights are traceable through NIST, Test No. 822/272103-05
2. Certified Analyte Concentration = Purity x Prepared Concentration. The Uncertainty calculated for is ±4% which is the Combined Uncertainty u(c)y. It represents an estimated standard deviation equal positive square root of the total variance of the uncertainty of components. The Expanded Uncertainty is U(c)y) *K where K is the coverage factor at the 95% confidence level (K=2).
3. A product with a suffix (-1A, -2B, etc.) on its lot# has had its expiration date extended and retains same lot# without the suffix.

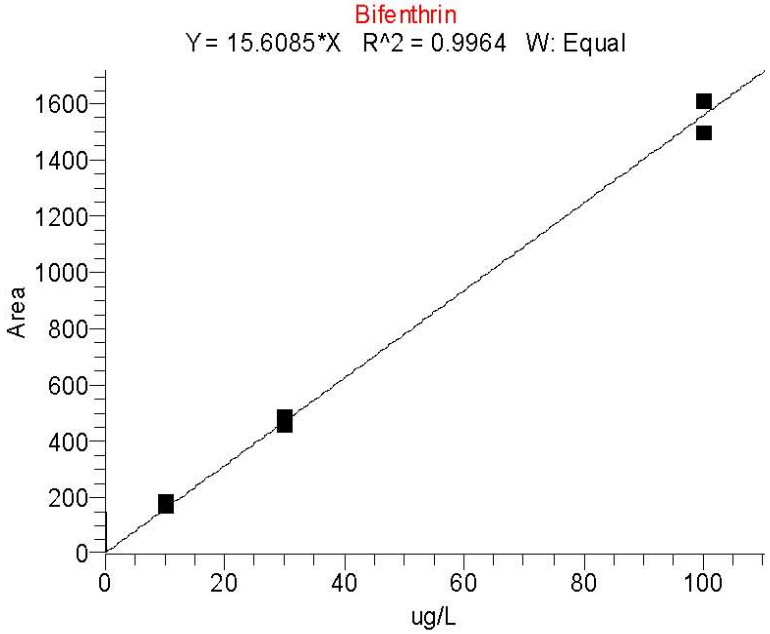
Certified by: R. Cooper

AccuStandard is accredited to ISO/IEC 17025:2005

OR-ORG/INO-001 Rev. 7/07

19. Calibration Curve

Component Calibration Curve

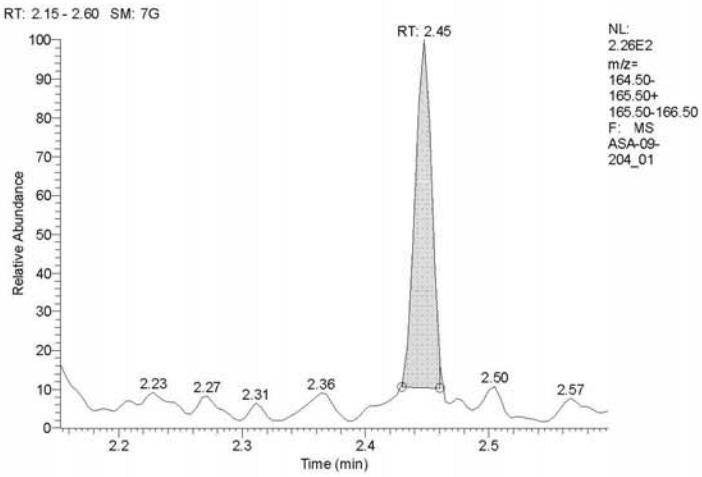


Filename	Sample Name	Area	Level (ug/L)	Amount	%Diff	%RSD
ASA-09-204_01	10 ppb Bifenthrin	187	10.000	11.982	20%	6.5%
ASA-09-204_02	10 ppb Bifenthrin	171	10.000	10.929	9%	6.5%
ASA-09-204_06	30 ppb Bifenthrin	457	30.000	29.287	-2%	4.2%
ASA-09-204_07	30 ppb Bifenthrin	485	30.000	31.081	4%	4.2%
ASA-09-204_11	100 ppb Bifenthrin	1612	100.000	103.296	3%	5.0%
ASA-09-204_12	100 ppb Bifenthrin	1503	100.000	96.302	-4%	5.0%

20. Typical Chromatograms

Page No.	Sample Chromatograms
16	10 µg/L Bifenthrin Reference Standard
17	Untreated Water Specimen
18	Treated Water Specimen

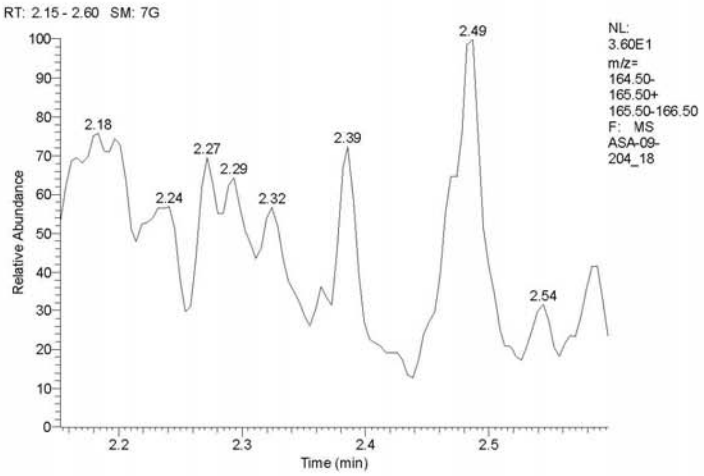
Bifenthrin



Actual RT:	**2.45**
Specified Amount:	**10.000**
Calculated Amount:	**11.982**
% Diff:	**19.82**
Response:	**187**
Response Ratio:	**N/A**
Ion Ratio Status:	**Not Used**
Peak Purity:	**N/A**
Base Line:	**MM**
Signal To Noise:	**12.09**
Saturated:	**No**
Expected RT:	**2.44**
Sample Type:	**Standard**
Component Type:	**Target Compound**
Peak Status:	
System Suitability:	
Data Flags:	
Calibration Flags:	

ASA-09-204_01.RAWASA-09-204_01 Page 1 of 1

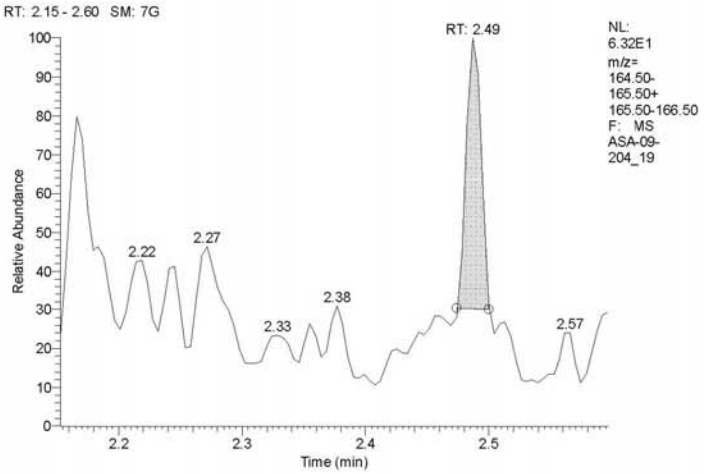
Bifenthrin



Actual RT:	**N/A**
Specified Amount:	**N/A**
Calculated Amount:	**N/A**
% Diff:	**N/A**
Response:	**N/A**
Response Ratio:	**N/A**
Ion Ratio Status:	**N/A**
Peak Purity:	**N/A**
Base Line:	**N/A**
Signal To Noise:	**N/A**
Saturated:	**N/A**
Expected RT:	**N/A**
Sample Type:	**Unknown**
Component Type:	**Target Compound**
Peak Status:	**Not Found**
System Suitability:	**N/A**
Data Flags:	**N/A**
Calibration Flags:	**N/A**

ASA-09-204_18.RAWASA-09-204_18 Page 1 of 1

Bifenthrin



Actual RT:	**2.49**
Specified Amount:	**N/A**
Calculated Amount:	**0.078**
% Diff:	**N/A**
Response:	**37**
Response Ratio:	**N/A**
Ion Ratio Status:	**Not Used**
Peak Purity:	**N/A**
Base Line:	**MM**
Signal To Noise:	**2.53**
Saturated:	**No**
Expected RT:	**2.44**
Sample Type:	**Unknown**
Component Type:	**Target Compound**
Peak Status:	
System Suitability:	
Data Flags:	
Calibration Flags:	

ASA-09-204_19.RAWASA-09-204_19 Page 1 of 1