RAPID ANALYSIS OF SYNTHETIC PYRETHROIDS IN STORMWATER

Rapid Trace Analysis of Synthetic Pyrethroids in Stormwater Using online pre-concentration followed by Liquid Chromatography-Tandem Mass Spectrometry

David Schiessel, Senior Chemist
dschiessel@babcocklabs.com
Babcock Laboratories, Inc.
6100 Quail Valley Court
Riverside, CA 92507
951-653-3351 ext.268

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

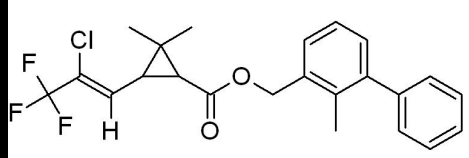
BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

Outline

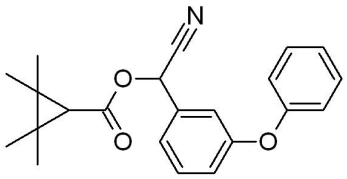
- What are synthetic pyrethroids?
- Why develop a new method?
- Pyrethroid use, toxicity, and occurrences
- Analytical considerations; reference material stability and instrument robustness
- Why choose LC-MS-MS? Current methods.
- Equipment and analytical method
- Method Performance; successes and challenges

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

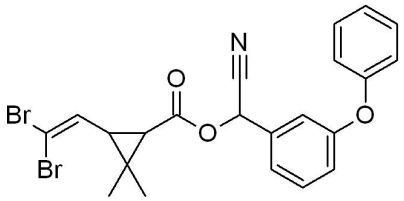
What are synthetic pyrethroids?



Bifenthrin



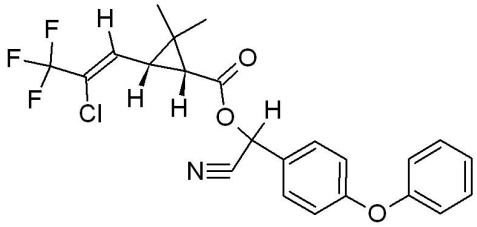
Fenpropathrin



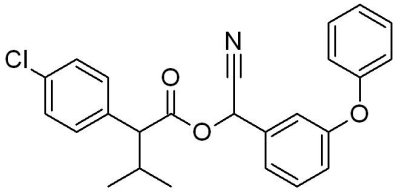
Deltamethrin

ORKIN

TERMINIX®

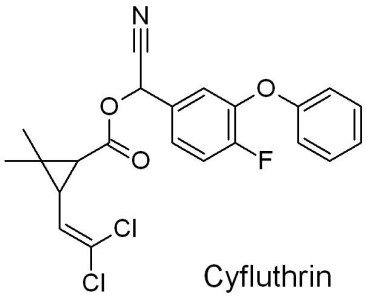


λ-Cyhalothrin

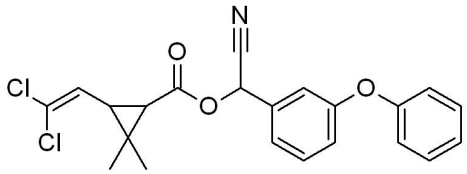


Esfenvalerate

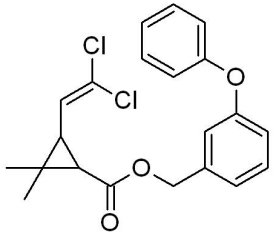
ANTIMITE
Since 1941
Termite & Pest Control



Cyfluthrin



Cypermethrin



Permethrin

Why develop a new method?

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

Client Needs

Regulation & Permits

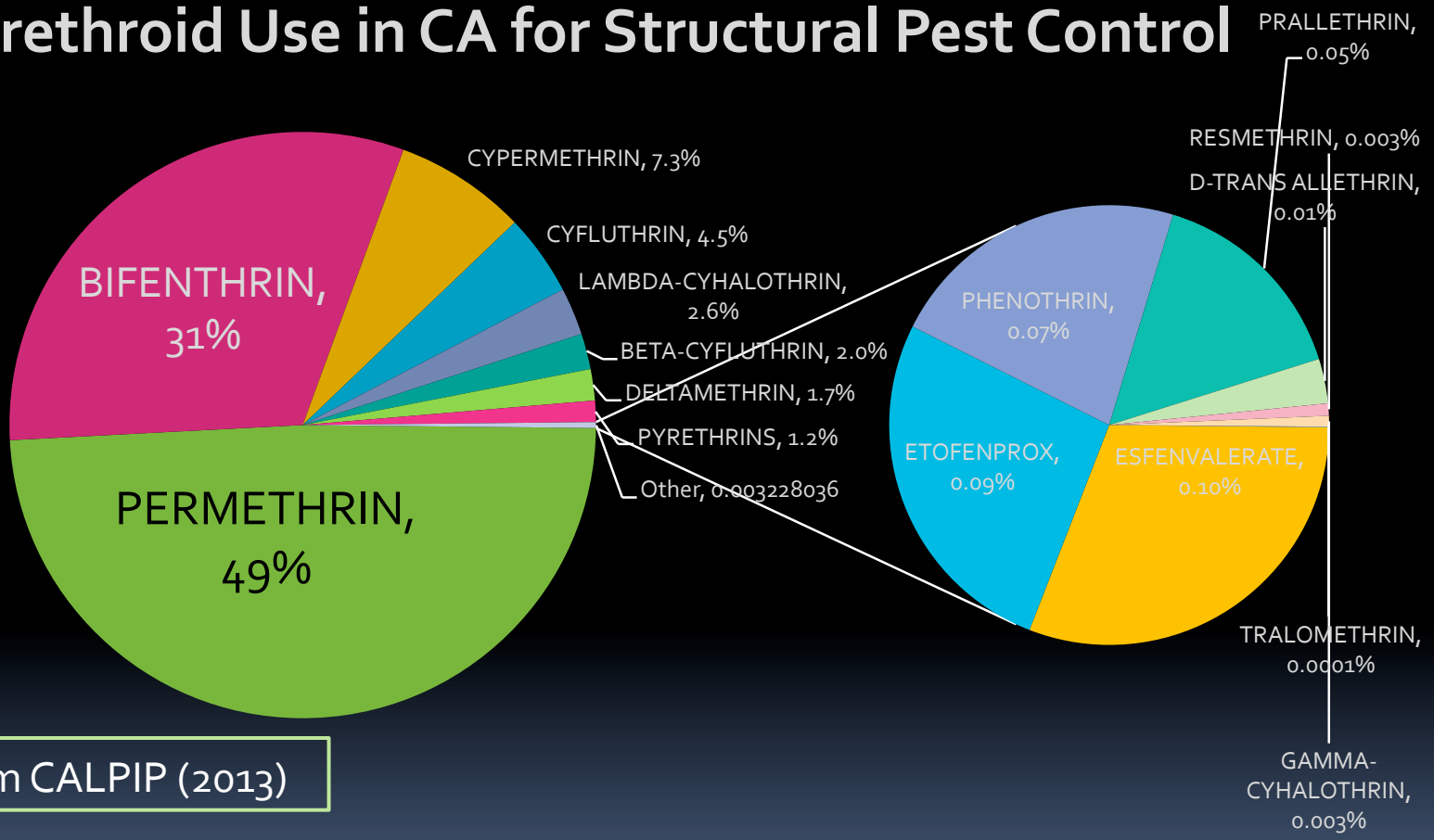
Basin Plan Obj, NPDES, MS4

Usage

Toxicity Research

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

Where are these contaminants coming from?
Pyrethroid Use in CA for Structural Pest Control



Data from CALPIP (2013)

- PERMETHRIN
- BIFENTHRIN
- CYPERMETHRIN
- CYFLUTHRIN
- LAMBDA-CYHALOTHRIN
- BETA-CYFLUTHRIN
- DELTAMETHRIN
- PYRETHRINS
- ESFENVALERATE
- ETOFENPROX
- PHENOTHRIN
- PRALLETHRIN
- D-TRANS ALLETHRIN
- RESMETHRIN
- GAMMA-CYHALOTHRIN
- TRALOMETHRIN

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

Toxicity Data

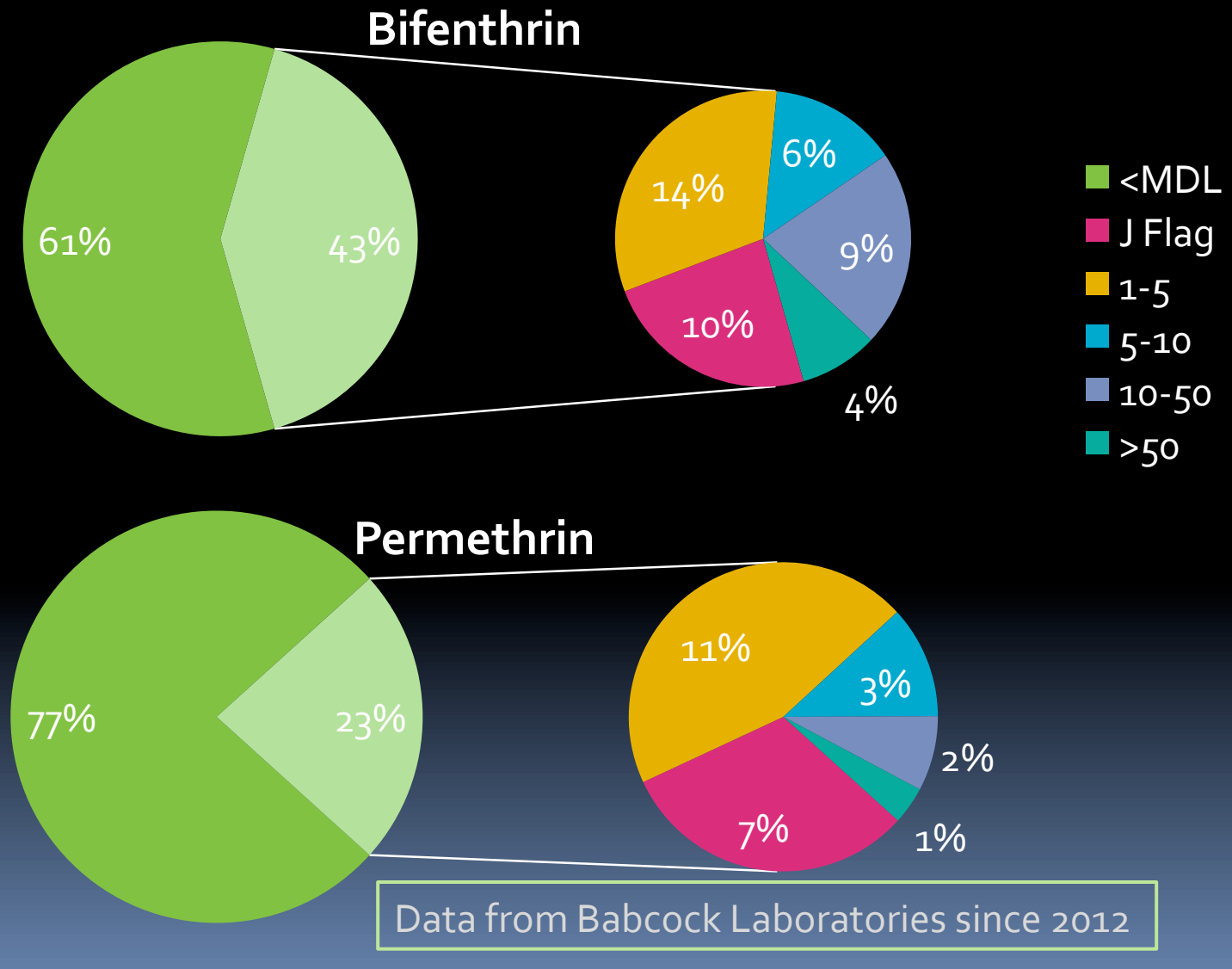
Pyrethroid	LC50 Hyalella Azteca, ng/L	5-10th % LC50	PAL Benchmark (Invert.)
Permethrin	39.1(1,4)	35 - 76(5)	1.4(6)
Bifenthrin	2.2(1,4)	<3.8 - 15(5)	1.3(6)
Cypermethrin	2.0 (3)	3 - 6.4(5)	69(6)
Cyfluthrin	8.7(1,4)	<4 -12 (5)	7.4(6)
Cyhalothrin-λ	1.4(1,4)	<4 - 10(5)	2.0(6)
Deltamethrin	1.1(1,4)	3 - 9(5)	4.1(6)
Esfenvalerate	3.5-8.0(2,4)	3 - 8(5)	17(6)

1) Amweg et al, *Environmental toxicology and chemistry / SETAC* 24.4 (2005): 966–972
2) Weston and Lydy, *Environmental Science & Technology* 44.5 (2010): 1833–1840
3) Weston and Jackson, *Environmental Science & Technology* 43.14 (2009): 5514–5520
4) Laskowski, *Reviews of Environmental Contamination and Toxicology* 174 (2002): 49–170
5) Solomon et al, *Environmental toxicology and chemistry / SETAC* 20.3 (2001): 652–659
6) http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm

Historical Data

Occurrences in water samples

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years



Data from Babcock Laboratories since 2012

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

How low ~~can~~ should we go?

- At or below acute toxicity values
- Be able to differentiate sample from blank (ultra low levels)
- Be able to recover analytes at low levels with accuracy and precision in matrix

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

How low ~~can~~ should we go?

- At or below acute toxicity values
- Be able to differentiate sample from blank (ultra low levels)
- Be able to recover analytes at low levels with accuracy and precision in matrix

1.0 ng/L

Other considerations

- Aquatic toxicity studies vary
- Pyrethroids extremely lipophilic
- Certain SP's degrade through hydrolysis or photolysis(Laskowski, 4)
- Absorption in sediment, suspended solids
- Pyrethroids can be a mixture of 2-8 stereoisomers

Current Methods

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

	USGS (GCMSMS)		CDFG (GCMSMS-ECNI)		CDFG (GC-ECD)		CA Dept. Food & Agri. (GC-ECD)	
Analyte	**RL (ng/L)**	**MDL (ng/L)**	**RL (ng/L)**	**ELOD (ng/L)**	**RL (ng/L)**	**MDL (ng/L)**	**RL (ng/L)**	**MDL (ng/L)**
Permethrins	2.0	0.6		1.0	5.0	3.0	15	3.5
Bifenthrin	2.0	0.7		0.10	1.0	0.5	5.0	1.8
Cypermethrins	5.0	1.1		0.20	4.0	2.0	15	1.8
Cyhalothrins	2.0	0.5		0.20	2.0	1.0	15	1.1
Fenvalerates	2.0	0.5		0.05	2.0	1.0	15	1.8
Fenpropathrin	2.0	0.6		NA	4.0	2.0	15	1.5
Cyfluthrins	5.0	1.1		0.20	4.0	2.0	15	1.7
Deltamethrin	2.0	0.6		0.15	4.0	2.0	15	1.9
	2007 SOP		2011 SWAMP pres.		2011 SWAMP pres.		2007 SOP	

Babcock Methods

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

	LVI (LCMSMS)		Cont Liq-Liq (LCMSMS)		Cont Liq-Liq (GCMSMS)	
Analyte	**RL (ng/L)**	**MDL (ng/L)**	**RL (ng/L)**	**MDL (ng/L)**	**RL (ng/L)**	**MDL (ng/L)**
Permethrins	1.0	0.4	1.0	0.3	5.0	1.9
Bifenthrin	1.0	0.6	1.0	0.4	1.0	0.4
Cypermethrins	1.0	0.4	1.0	0.4	5.0	2.5
Cyhalothrins	1.0	0.3	1.0	0.5	1.0	0.2
Fenvalerates	1.0	0.9	1.0	0.5	5.0	2.4
Fenpropathrin	1.0	0.3	1.0	0.3	1.0	0.3
Cyfluthrins	1.0	0.7	1.0	0.6	5.0	1.6
Deltamethrin	1.0	0.4	1.0	0.5	5.0	1.3

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

Why choose LC-MS-MS?

- Availability; other work with drinking water UCMR3, PPCPs
- Sensitivity/robustness challenges of GC-MS-MS or GC-MS-ECNI
- Few compounds that can't be analyzed; adaptable to new targets
- Adaptable to chiral analysis
- Future in environmental analysis? Detecting known unknowns.

Equipment

- Thermo Scientific TSQ Quantum Ultra
- (2) HPLC Pumps Accela 600 and 1250
- CTC PAL Autosampler equipped with two valves
- Phenomenex Kinetex 2.6um Phenyl-Hexyl
- Thermoscientific HESI-II Probe

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

LC Parameters

- Variable flow rate (0.2-0.5-0.2mL/min)
- High flow loading - 5.0mL of 100% aqueous sample
- Online SPE using Hypersil 12μm aQ Gold columns (Thermo)
- SPE elution with mobile phase; methanol, water, and 0.002% ammonium hydroxide, elution focusing with ACN

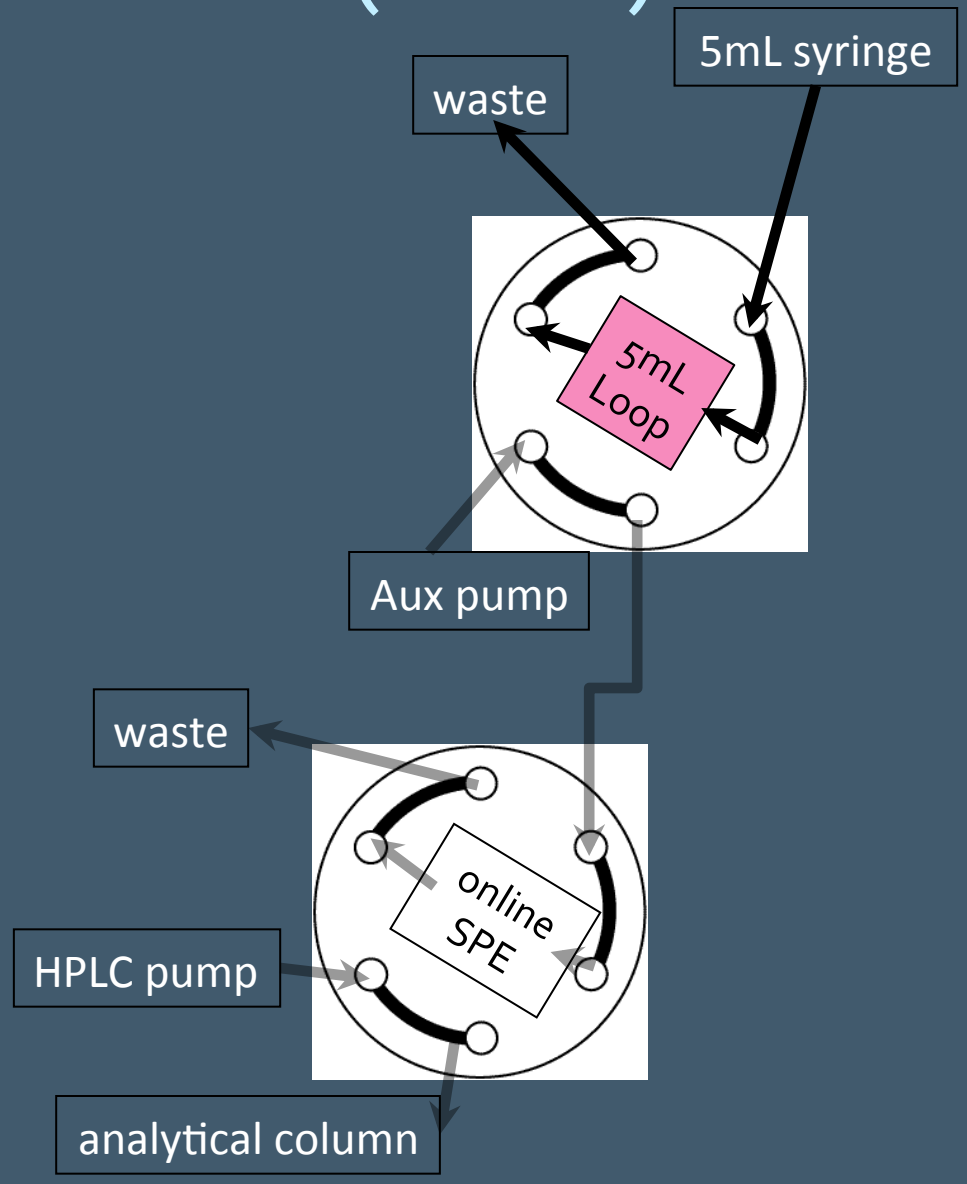
BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

MS Parameters

- Analytes all detected as $[M+NH_4]^+$
- Desolvation Temp: 250C
- Sheath gas: 40arb, Aux Gas: 40arb
- Capillary Temp: 225C
- CID pressure: 1.0mTorr Argon
- All collision energies optimized by direct infusion with eluent

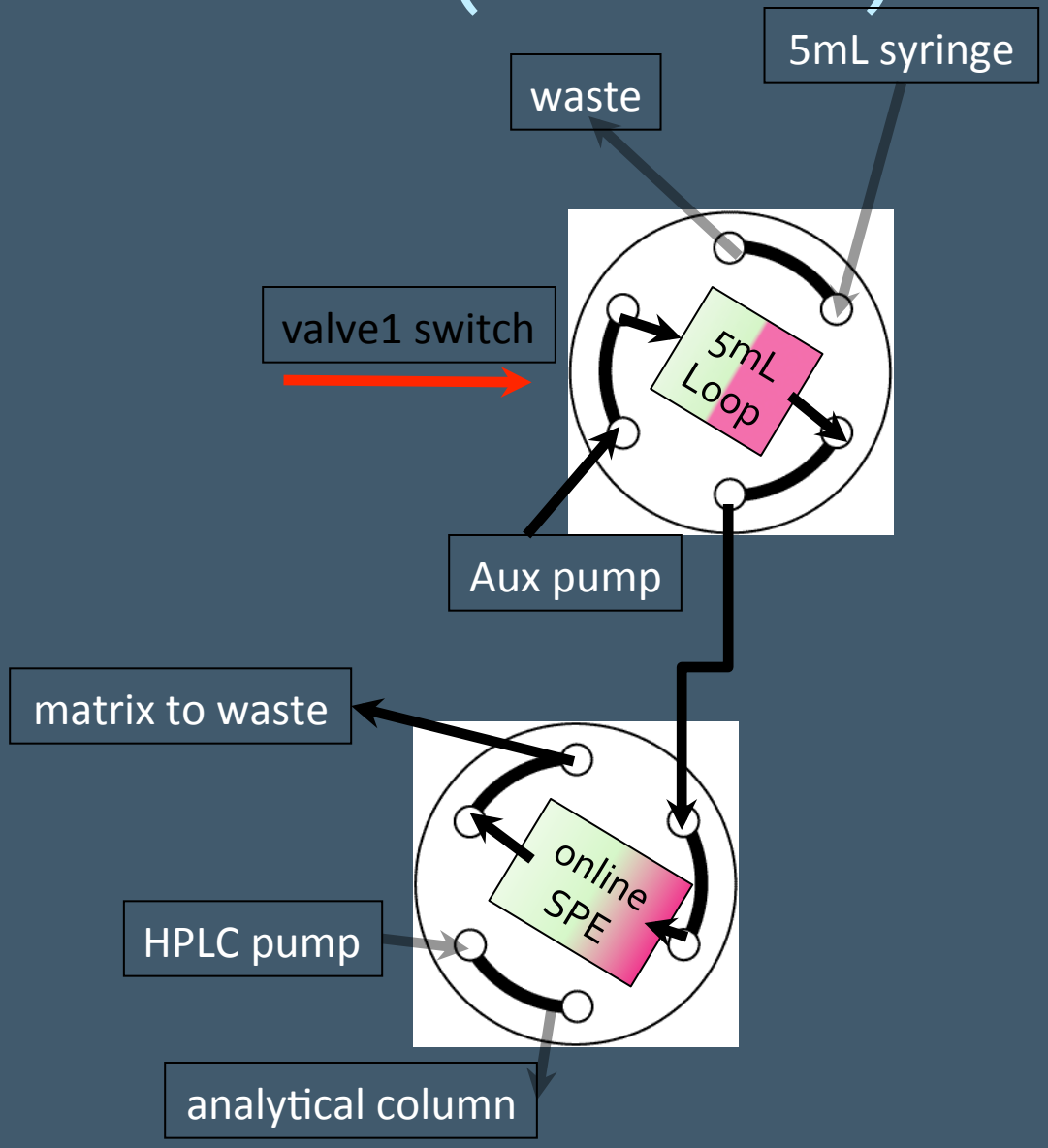
Online SPE (Load)

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years



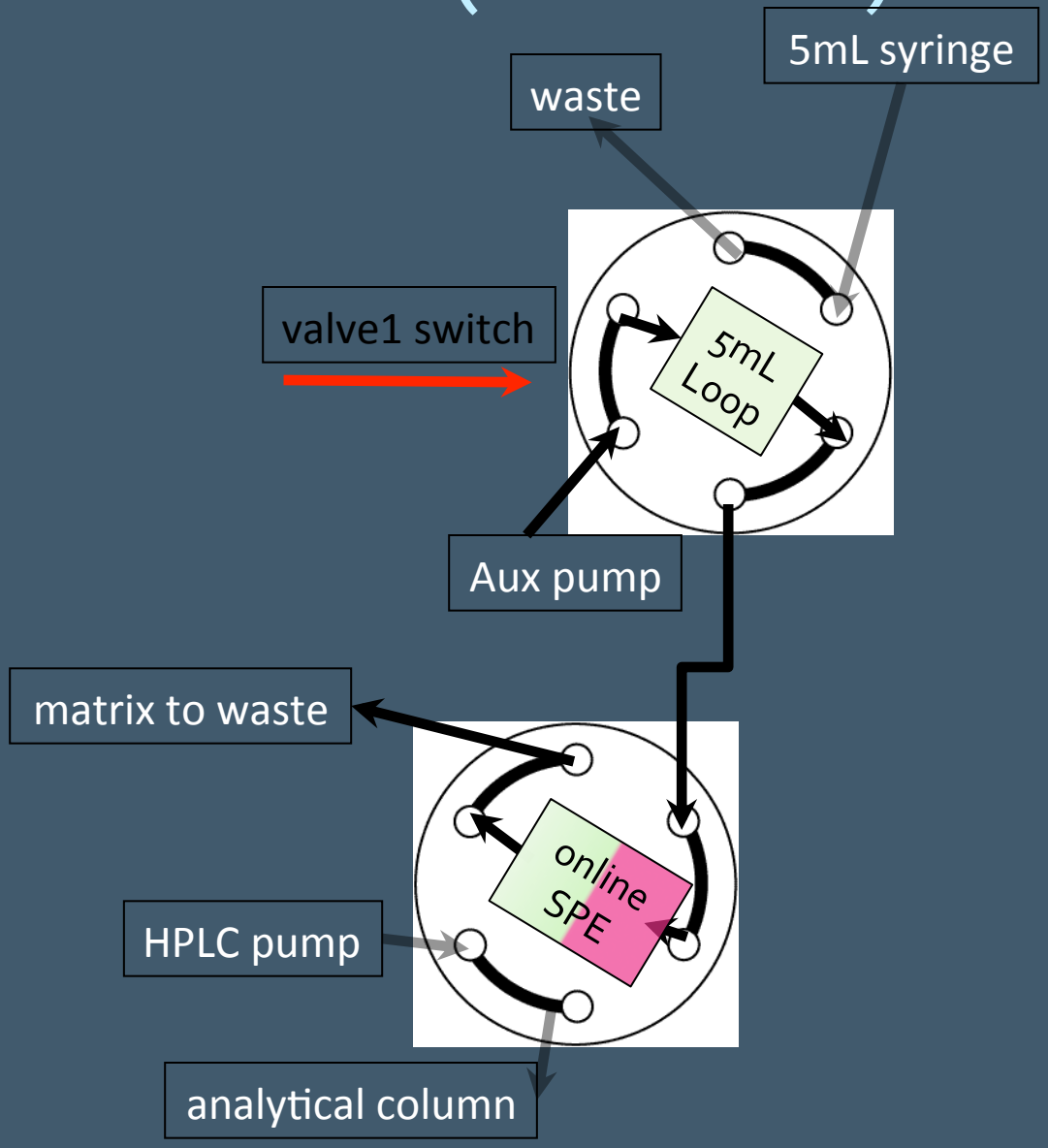
Online SPE (Transfer)

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years



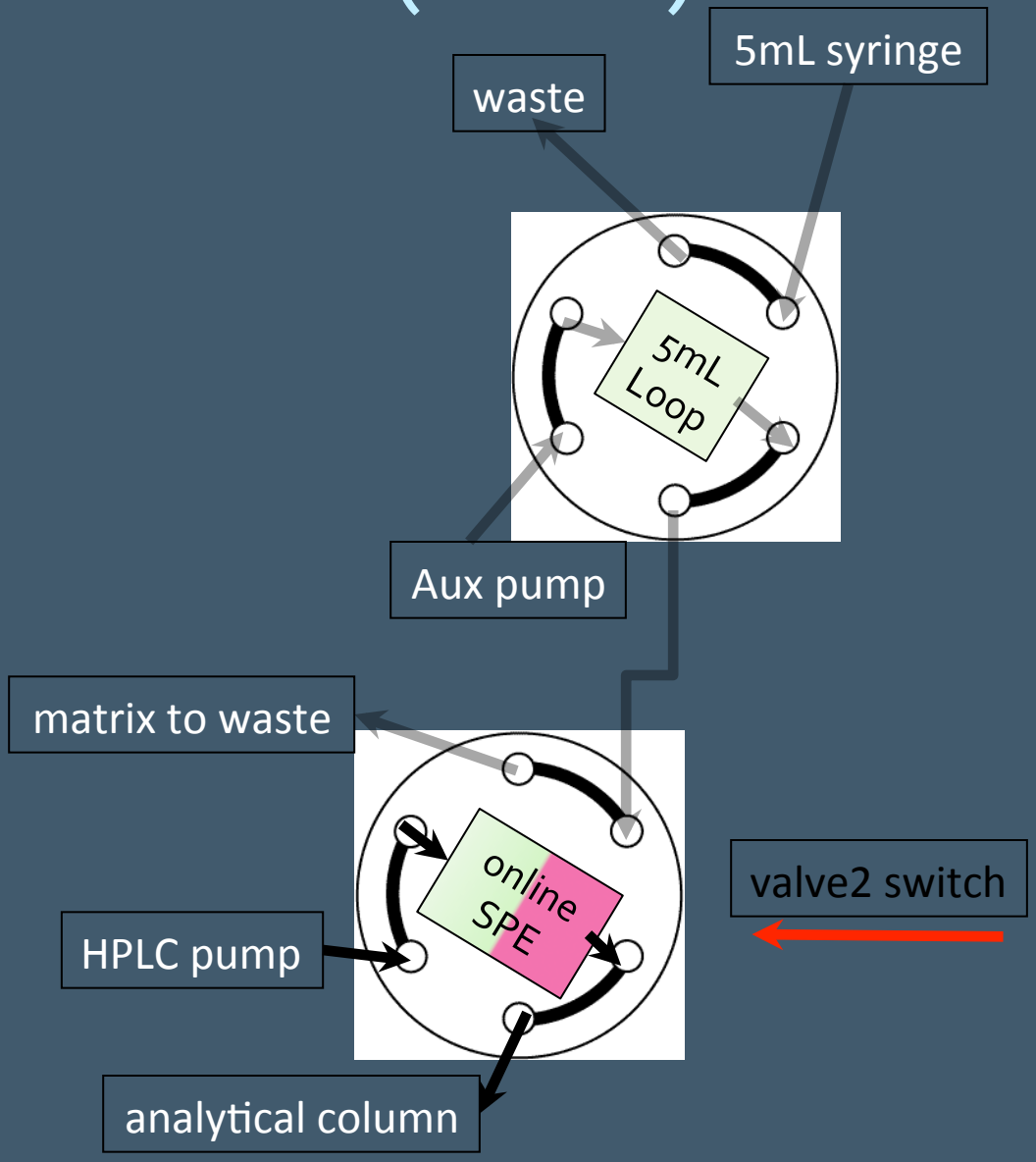
Online SPE (Transfer)

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years



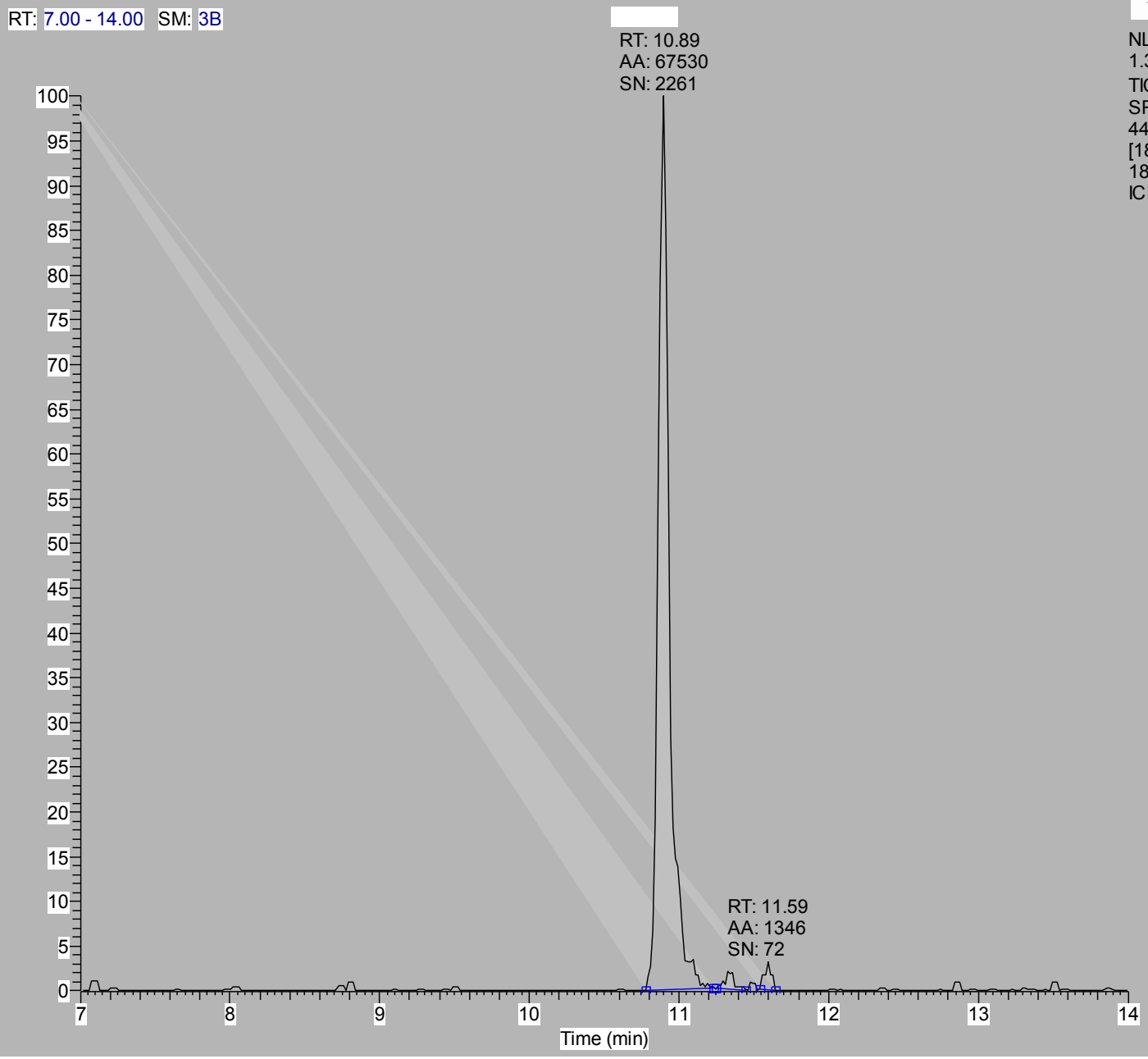
Online SPE (Elute)

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years



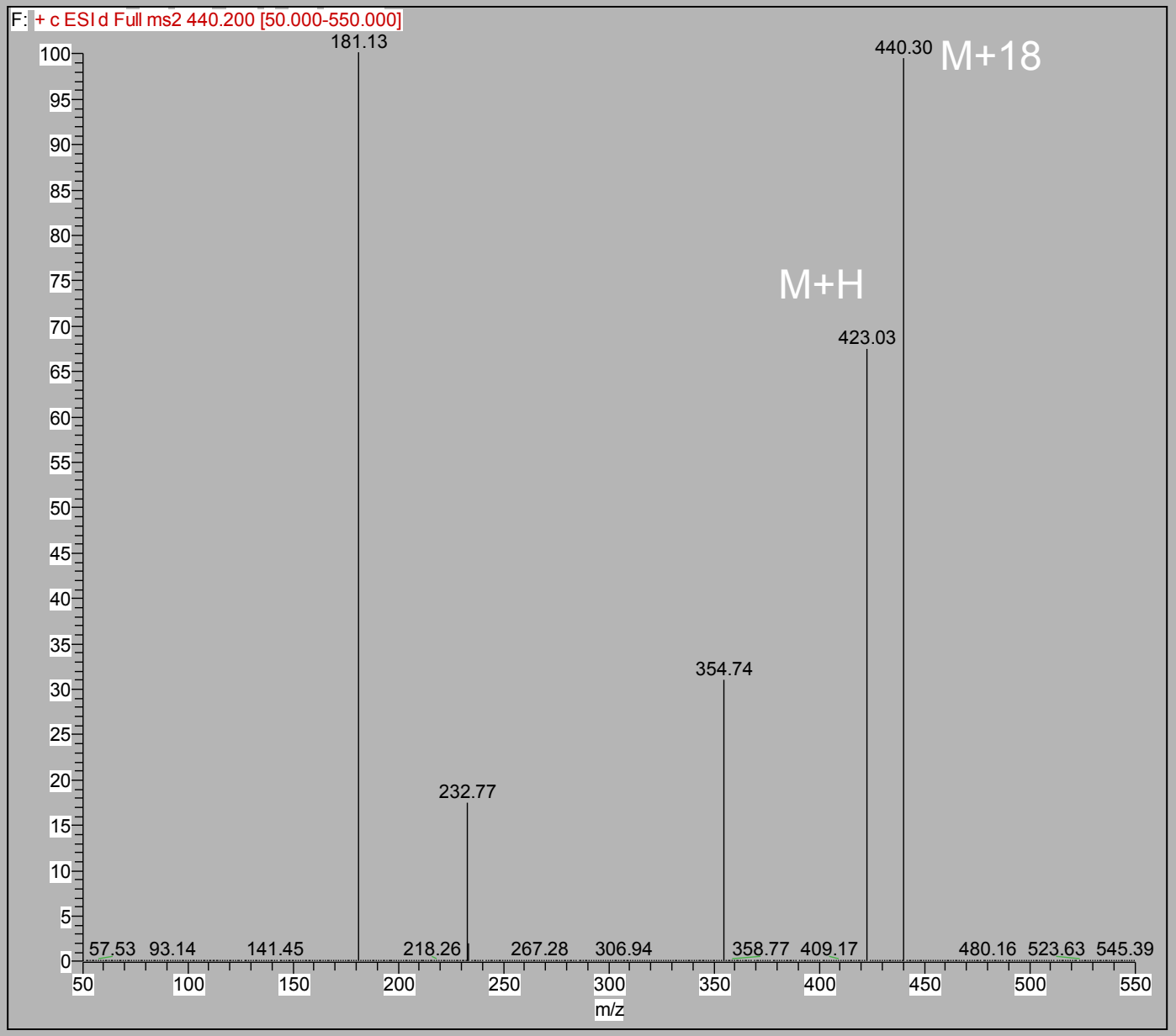
Bifenthrin – 1.0ng/L

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

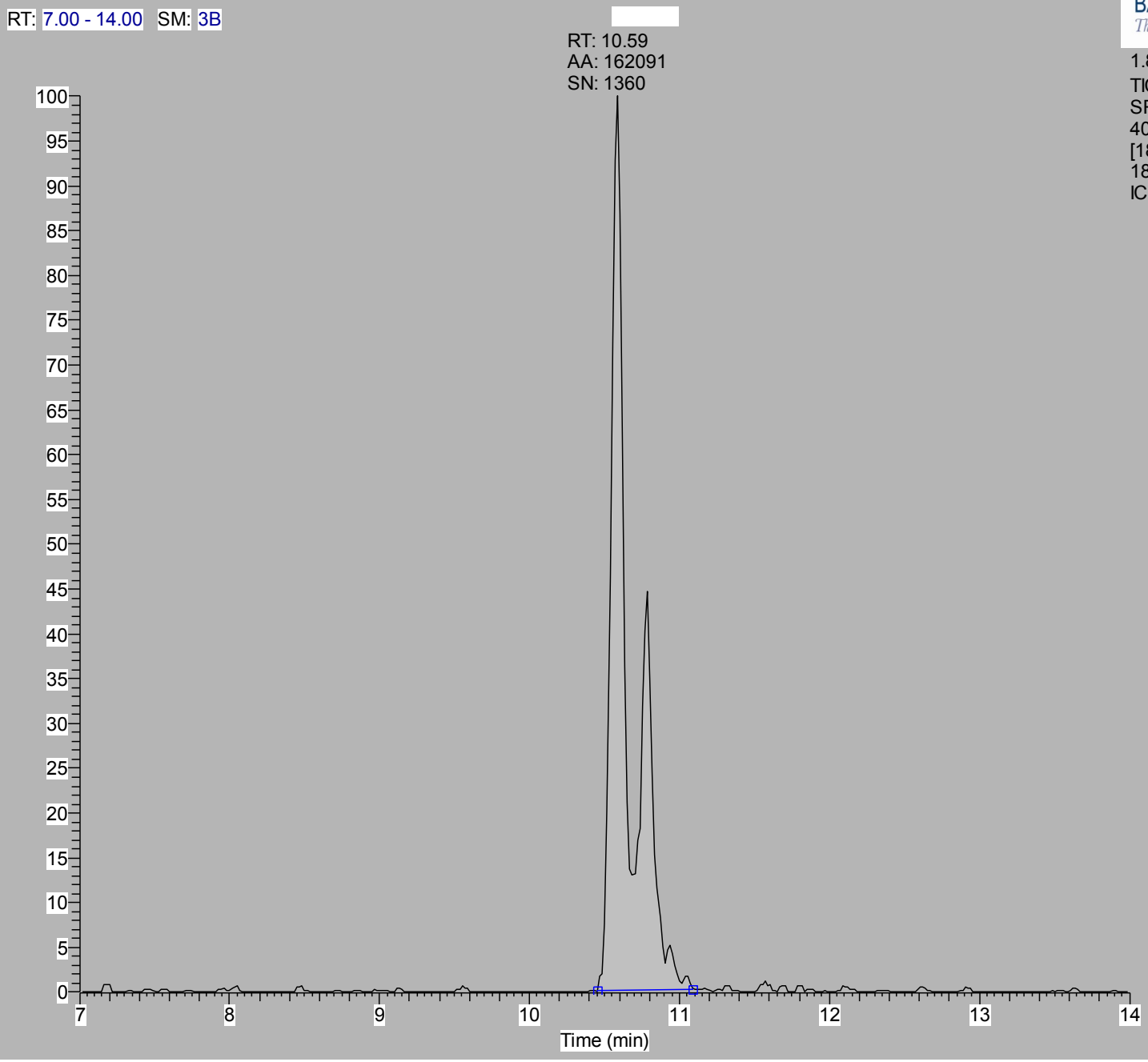


QED Scan - Bifenthrin

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years



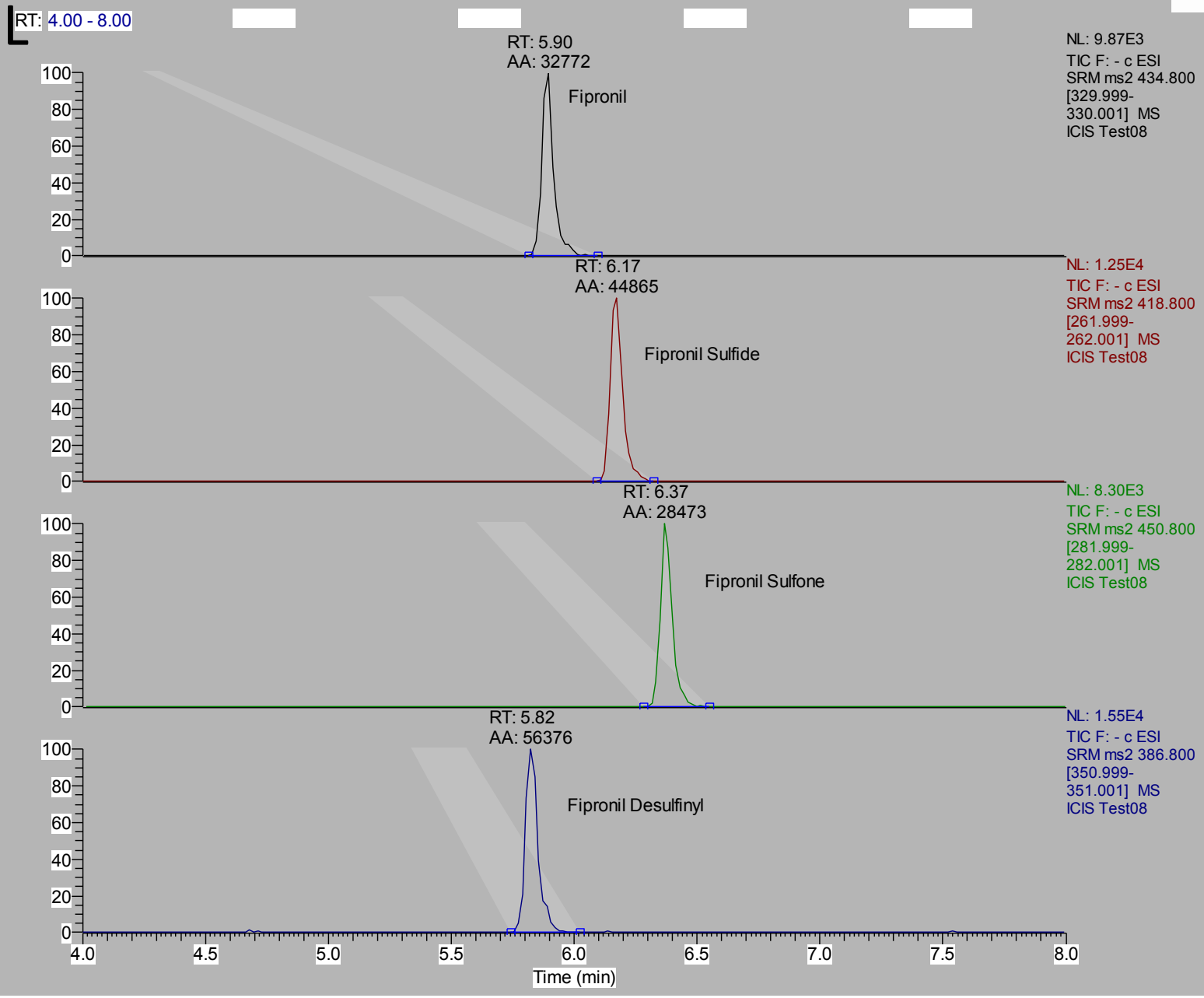
Permethrin – 1.0ng/L



BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

Fipronil+Degs – 1.0ng/

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years



Blank Spike Data

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

CA Rank	Analyte	Spike Conc (ng/L)	Rep1 (ng/L)	Rep2 (ng/L)	Rep3 (ng/L)	Rep4 (ng/L)	Avg % Rec	% RSD
1	Permethrins	10	9.2	8.7	9.4	9.4	92%	3.2%
2	Bifenthrin	10	10.2	9.4	10.6	9.9	100%	5.2%
3	Cypermethrins	10	10.0	8.5	9.8	9.6	95%	7.2%
4	Cyhalothrins	10	9.6	8.9	10.1	10.3	97%	6.5%
5	Fenvalerates	10	10.0	7.6	8.8	8.6	88%	11%
6	Fenpropathrin	10	8.1	7.9	8.4	8.5	82%	3.4%
7	Cyfluthrins	10	10.8	7.9	9.8	9.3	94%	13%
8	Deltamethrin	10	9.3	7.6	8.5	8.3	85%	8.4%
9	Sumithrin	10	11.8	11.0	12.2	12.1	118%	4.5%
10	tau-Fluvalinate	10	9.4	6.6	8.6	10.8	88%	20%
11	Prallethrin	10	9.7	8.9	9.7	10.1	96%	5.1%
12	Resmethrin	10	11.8	11.4	12.6	12.7	121%	5.2%
13	Allethrin	10	9.2	8.8	9.4	9.7	93%	4.1%
14	Tralomethrin	10	11.8	12.9	12.7	11.7	123%	5.1%
15	Tetramethrin	10	12.0	12.1	12.7	13.6	126%	5.8%
NA	Acrinathrin	10	12.4	10.3	11.9	11.8	116%	7.9%
NA	Cyphenothrin	10	12.1	11.2	11.9	11.7	117%	3.1%
NA	Etofenprox	10	9.5	8.8	9.7	9.5	94%	4.4%
NA	Flucythrinate	10	10.6	11.1	12.8	13.8	121%	12%
NA	Kadethrin	10	8.6	8.7	9.5	10.4	93%	8.8%
-	Permethrin-13C6 (Surr)	10	9.8	10.3	10.6	10.7	104%	3.6%

Matrix Spike Data

Simulated Matrix with 25mg/L TSS, 10.0 NTU

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

CA Rank	Analyte	Spike Conc (ng/L)	Rep1 (ng/L)	Rep2 (ng/L)	Rep3 (ng/L)	Rep4 (ng/L)	Avg % Rec	% RSD
1	Permethrins	10	8.6	9.1	9.0	8.6	88%	3.1%
2	Bifenthrin	10	9.9	10.3	10.1	9.7	100%	2.9%
3	Cypermethrins	10	7.4	8.6	8.4	8.2	82%	6.2%
4	Cyhalothrins	10	9.9	12	12	11	111%	8.1%
5	Fenvalerates	10	9.1	10.9	10.5	8.8	98%	11%
6	Fenpropathrin	10	7.9	8.7	9.6	9.5	89%	9.2%
7	Cyfluthrins	10	7.8	10.2	11.5	13.0	106%	21%
8	Deltamethrin	10	7.4	8.2	7.9	7.5	78%	4.7%
9	Sumithrin	10	9.3	9.8	9.9	9.6	96%	2.5%
10	tau-Fluvalinate	10	8.2	9.6	7.4	8.8	85%	11%
11	Prallethrin	10	5.3	5.6	6.1	6.4	59%	8.3%
12	Resmethrin	10	8.3	7.9	9.2	8.5	85%	6.7%
13	Allethrin	10	7.1	6.8	7.8	7.3	73%	5.5%
14	Tralomethrin	10	9.7	10.5	10.6	10.2	103%	3.8%
15	Tetramethrin	10	6.3	6.7	7.6	6.8	68%	7.9%
NA	Acrinathrin	10	10	12	12	11	110%	6.2%
NA	Cyphenothrin	10	8.4	9.0	9.0	8.6	87%	3.2%
NA	Etofenprox	10	7.7	7.8	8.3	8.1	80%	3.5%
NA	Flucythrinate	10	8.4	8.5	9.0	9.4	88%	5.2%
NA	Kadethrin	10	7.5	8.2	10.7	10.1	91%	17%
-	Permethrin-13C6 (Surr)	10	9.6	9.4	9.2	9.0	93%	2.8%

Analyte Stability

Simulated Matrix with 25mg/L TSS, 10.0 NTU

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

CA Rank	Analyte	Spike Conc (ng/L)	Day 0 (%Rec)	Day 1 (%Rec)	Day 4 (%Rec)	Day 6 (%Rec)	
1	Permethrins	20	93%	85%	71%	70%	←
2	Bifenthrin	20	92%	82%	70%	91%	
3	Cypermethrins	20	93%	89%	82%	73%	←
4	Cyhalothrins	20	93%	80%	98%	94%	
5	Fenvalerates	20	88%	80%	53%	58%	←
6	Fenpropathrin	20	101%	92%	103%	78%	
7	Cyfluthrins	20	93%	96%	103%	90%	
8	Deltamethrin	20	103%	105%	89%	96%	
-	Permethrin-13C6 (Surr)	10	109%	103%	96%	107%	

Stored in 40mL unpreserved VOA vials in refrigerator

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

Analytical Challenges

- CRM Availability
- Low response from Cyfluthrin/Esfenvalerate
- CRM Degradation; α-cyano pyrethroids form a carboximidate(?) in methanol
- Stereoisomer confusion/labeling
- Unable to do tefluthrin or transfluthrin by ESI
- Preservation (tetramethrin issues)
- Solubility very low and Log(P) high

BABCOCK Laboratories, Inc.
The Standard of Excellence for Over 100 Years

Developments

- Holding time study and preservation study of simulated matrix with ACN keeper
- Split samples from UC Davis last fall for bioswales.
- Try different online SPE media or analytical column
- Apply method to Fipronil and degradates
- Analyte confirmation
- Chiral separation

Developments

- Holding time study and preservation study of simulated matrix with ACN keeper
- Split samples from UC Davis last fall for bioswales. Mixed results from split lab
- Try different online SPE media or analytical column – Done
- Apply method to Fipronil and degradates - Done
- Analyte confirmation – Done
- Chiral separation – Limited success

References

1) Amweg, Erin L, Donald P Weston, and Nicole M Ureda. 2005. "Use and Toxicity of Pyrethroid Pesticides in the Central Valley, California, USA." *Environmental Toxicology and Chemistry / SETAC* 24 (4): 966–72.
2) Weston, Donald P., Yuping Ding, Minghua Zhang, and Michael J. Lydy. 2013. "Identifying the Cause of Sediment Toxicity in Agricultural Sediments: The Role of Pyrethroids and Nine Seldom-Measured Hydrophobic Pesticides." *Chemosphere* 90 (3): 958–64.
3) Weston, Donald P., and Colin J. Jackson. "Use of Engineered Enzymes to Identify Organophosphate and Pyrethroid-Related Toxicity in Toxicity Identification Evaluations." *Environmental Science & Technology* 43, no. 14 (July 15, 2009): 5514–20.
4) Laskowski, Dennis A. "Physical and Chemical Properties of Pyrethroids." *Reviews of Environmental Contamination and Toxicology* 174 (2002): 49–170.
5) Solomon, K. R., J. M. Giddings, and S. J. Maund. "Probabilistic Risk Assessment of Cotton Pyrethroids: I. Distributional Analyses of Laboratory Aquatic Toxicity Data." *Environmental Toxicology and Chemistry / SETAC* 20, no. 3 (March 2001): 652–59.
6) EPA Aquatic Life Benchmark List http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm