Analytical Advancements: Acid Herbicides Case Study

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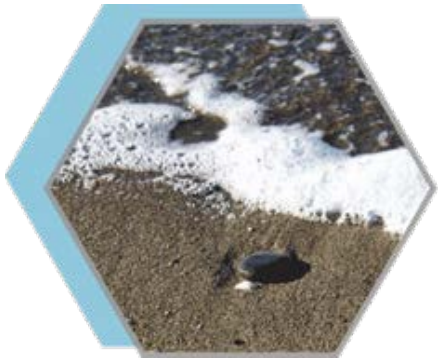


Outline

- Who is CARO?
- About Pesticides
- Case Study: Acid Herbicides
  - The Challenge
  - Equipment Developments
  - Technique Developments
  - Results & Benefits
- Conclusion

Who is CARO?

- **Western Canadian full service environmental lab:**
  - Vancouver, British Columbia (Head Office)
  - Kelowna, British Columbia
  - Edmonton, Alberta
  - Whitehorse, Yukon

- **Vision:** ***CARING ABOUT RESULTS***
  - Technical Leadership
  - Client Collaboration
  - Developed & Motivated Staff

- **Capabilities:**
  - Contaminated Sites: Hydrocarbons, SVOCs, VOCs, Metals
  - Water Quality: Physical Parameters, Nutrients, Anions, Metals
  - Microbiology and Toxicology

Analytical Advancements

- Thermal Desorption Tube (SVI™)
  - Supporting new BCMOE Soil Vapour regulations
  - Sampling improvements
  - Analytical improvements

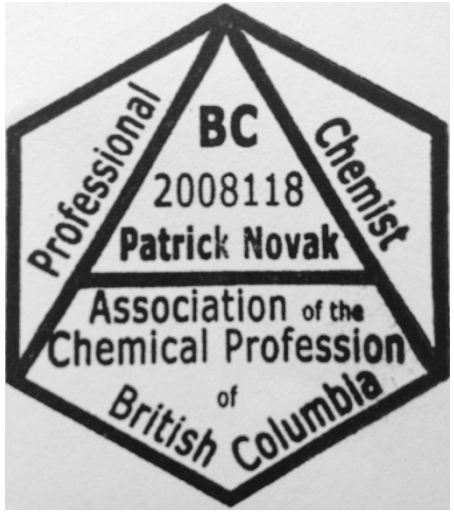
- Siloxanes in Water, Air & Soil
  - Supporting new federal regulations

- ITEX VOCs
  - Supporting AB Teir1 with lower DLs

Why Advance?

Why Advance

- It's Cool & Fun
  - New Expensive Toys
- Solve Problems
  - Client Issues
  - Regulatory Needs
- Professional Responsibility
  - Industry, Environment, Safety
  - Chemist Practice



Pesticides

"Pesticides are *compounds used to prevent, control, destroy, or mitigate any pest*"

- 9 of 12 most dangerous and persistent organic chemicals are organochlorine pesticides (Gilden, Huffling, Sattler, 2010)
- Over 95% of sprayed pesticides (and herbicides) reach a destination other than their target; including non-target species, air, water and soil (Miller, 2004)
- Human health and environmental cost from pesticides in the United States is estimated at $9.6 billion (Pimentel, 2011)

Lots of Use, Regulations, & Concern

Why Not So Much Testing?

Sept 2014 Headlines

Canadian beekeepers sue Bayer and Syngenta over neonicotinoid pesticides

Class action lawsuit seeks $400 million in damages

CBC News Posted: Sep 03, 2014 1:48 PM ET | Last Updated: Sep 05, 2014 4:49 PM ET

EcoWatch® TRANSFORMING GREEN

16-Year Study Blames Pesticides for Significant Sperm Decline

Study: Pesticides Could Cause Unexpected Allergic Reactions

TIME

GlobalResearch
Centre for Research on Globalization
globalresearch.ca / globalresearch.org

Pesticide Exposure Can Cause Disease Across Four Generations

NATURE WORLD NEWS

The Pesticide Problem: Aquatic Life Imperiled

SCIENTIFIC AMERICAN™

Pesticides a Concern for Aquatic Life in Most U.S. Urban Streams

Pesticide Challenges

1. Not Well Understood
   - Many Compounds – 1000s
   - Many Classes – ON, OP, OC, Carbamates, Acid Herbicides, etc…
   - Many Names - Picloram = 4-Amino-3,5,6-trichloro-2-pyridinecarboxylic acid; Tordon = Grazon, etc.

2. Historical usage
   - Broad; not always consistent;
   - Since before 2000BC

3. Analytical Techniques
   - Many - GC, LC, MS, MS/MS, ECD, Derivatization, etc…
   - Complex
   - Reliability
   - Expensive

Pesticide Regulations

- Canadian Drinking Water Quality Guidelines
- CCME
- British Columbia: Contaminated Sites Regulations, Schedule 4, 5, 6, 9, 10
- BC Water Quality Guidelines
- Local Governments
- Many Others

CCME Water Quality Guidelines

		Water Quality Guidelines for the Protection of Aquatic Life					
		Freshwater			Marine		
		Concentration (µg/L)	Concentration (µg/L)	Date	Concentration (µg/L)	Concentration (µg/L)	Date
Chemical name	Chemical groups	Short Term	Long Term		Short Term	Long Term	
3-Iodo-2-propynyl butyl carbamate IPBC CASRN 55406-53-6	Organic Pesticides Carbamate pesticides	*No data*	1.9	1999	*No data*	*No data*	*No data*
Aldicarb CASRN 116063	Organic Pesticides Carbamate pesticides	*No data*	1	1993	*No data*	0.15	1993
Aldrin	Organic Pesticides Organochlorine compounds	*No data*	~~0.004~~	1987	*No data*	*No data*	*No data*
Atrazine CASRN 1912249	Organic Pesticides Triazine compounds	*No data*	1.8	1989	*No data*	*No data*	*No data*
Bromacil CASRN 314409	Organic Pesticides	*No data*	5	1997	*No data*	Insufficient data	1997
Bromoxynil	Organic Pesticides Benzonitrile compounds	*No data*	5	1993	*No data*	Insufficient data	1993
Captan CASRN 133062	Organic Pesticides	*No data*	1.3	1991	*No data*	*No data*	*No data*
Carbaryl CASRN 63252	Organic Pesticides Carbamate pesticides	3.3	0.2	2009	5.7	0.29	2009
Carbofuran CASRN 1564662	Organic Pesticides Carbamate pesticides	*No data*	1.8	1989	*No data*	*No data*	*No data*
Chlordane	Organic Pesticides Organochlorine compounds	*No data*	~~0.006~~	1987	*No data*	*No data*	*No data*

CCME Water Quality Guidelines

Chlorothalor Yahoo! http://my.yahoo.com/ CASRN 1897456	Organic Pesticides	*No data*	0.18	1994	*No data*	0.36	1994
Chlorpyrifos CASRN 2921882	Organic Pesticides Organophosphorus compounds	0.02	0.002	2008	NRG	0.002	2008
Cyanazine CASRN 2175462	Organic Pesticides Triazine compounds	*No data*	2	1990	*No data*	*No data*	*No data*
Deltamethrin CASRN 52918635	Organic Pesticides	*No data*	0.0004	1997	*No data*	Insufficient data	1997
Dicamba CASRN 1918009	Organic Pesticides Aromatic Carboxylic Acid	*No data*	10	1993	*No data*	*No data*	*No data*
Dichloro diphenyl trichloroethane; 2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane DDT (total)	Organic Pesticides Organochlorine compounds	*No data*	~~0.001~~	1987	*No data*	*No data*	*No data*
Diclofop-methyl CASRN 51338273	Organic Pesticides	*No data*	6.1	1993	*No data*	*No data*	*No data*
Didecyl dimethyl ammonium chloride DDAC CASRN 7173515	Organic Pesticides	*No data*	1.5	1999	*No data*	Insufficient data	1999
Dimethoate CASRN 60515	Organic Pesticides Organophosphorus compounds	*No data*	6.2	1993	*No data*	Insufficient data	1993
Dinoseb CASRN 88857	Organic Pesticides	*No data*	0.05	1992	*No data*	*No data*	*No data*
Endosulfan	Organic Pesticides Organochlorine compounds	0.06	0.003	2010	0.09	0.002	2010
Endrin	Organic Pesticides Organochlorine compounds	*No data*	~~0.0023~~	1987	*No data*	No data	*No data*
Glyphosate CASRN 1071836	Organic Pesticides Organophosphorus compounds	27,000	800	2012	NRG	NRG	2012

CCME Water Quality Guidelines

Heptachlor Heptachlor epoxide	Organic Pesticides Organochlorine compounds	*No data*	~~0.01~~	1987	*No data*	*No data*	*No data*
Hexachlorocyclohexane Lindane	Organic Pesticides Organochlorine compounds	*No data*	0.01	1987	*No data*	*No data*	*No data*
Linuron CASRN 41205214	Organic Pesticides	*No data*	7	1995	*No data*	*No data*	1995
Methylchlorophenoxyacetic acid (4-Chloro-2-methyl phenoxy acetic acid; 2-Methyl-4-chloro phenoxy acetic acid) MCPA CASRN 94746	Organic Pesticides	*No data*	2.6	1995	*No data*	4.2	1995
Metolachlor CASRN 51218452	Organic Pesticides Organochlorine compounds	*No data*	7.8	1991	*No data*	*No data*	*No data*
Metribuzin CASRN 21087649	Organic Pesticides Triazine compounds	*No data*	1	1990	*No data*	*No data*	*No data*
Permethrin CASRN 52645531	Organic Pesticides Organochlorine compounds	*No data*	0.004	2006	*No data*	0.001	2006
Phenoxy herbicides 2,4 D; 2,4-Dichlorophenoxyacetic acid	Organic Pesticides	*No data*	4	1987	*No data*	*No data*	*No data*
Picloram CASRN 1918021	Organic Pesticides	*No data*	29	1990	*No data*	*No data*	*No data*
Simazine CASRN 122349	Organic Pesticides Triazine compounds	*No data*	10	1991	*No data*	No data	*No data*
Tebuthiuron CASRN 34014181	Organic Pesticides	*No data*	1.6	1995	*No data*	Insufficient data	1995
Toxaphene	Organic Pesticides Organochlorine compounds	*No data*	~~0.008~~	1987	*No data*	*No data*	*No data*
Triallate CASRN 2303175	Organic Pesticides Carbamate pesticides	*No data*	0.24	1992	*No data*	*No data*	*No data*

Acid Herbicides

- Broad Leaf Weed Killer for Lawn and Grain
  - Examples: Picloram, clopyralid, dicamba, 2,4-D, MCPA, Trichlopyr, 2,4-DP, MCPP, 2,4-DB

- Past Analytical Techniques
  - Instrumentation
    - LC – sensitivity
    - GC/ECD/MS – reliability, sensitivity
  - Sample Preparation
    - Difficult & dangerous

Old Method

- Sample Size = 1 litre
- Extraction Process
  - Extract 3x with DCM
  - pH adjustment
  - Extract 3x with DCM
- Extract Preparation
  - Reduce volume to 1mL
  - Derivatize with Diazomathane


C&EN
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Issue Date: May 5, 2011
Firm Fined For Chemist's Death
Safety: Sepracor Canada admits lack of lab ventilation in worker fatality case
By Jyllian N. Kemsley

- Extraction Time = 1.5 days
- Instrument Set Up & Analysis – 24 hours

Equipment Developments

- LC/MS/MS – Agilent 6490 Triple Quad
  - The First Environmental Lab in Western Canada
- Increased Precision & Accuracy
- High Sensitivity
- New Analytes Possible
  - Pharmaceuticals and Personal Care Products (PPCPs)
  - Pesticides
  - THC?
  - Others?

Technique Developments

- Facilities
  - Purpose built laboratory space
- Reagents & Supplies
  - Improved internal standards
  - More reliable reagents and standards
  - LC Columns developed to suit purpose
- People
  - Professional Chemists

New Method

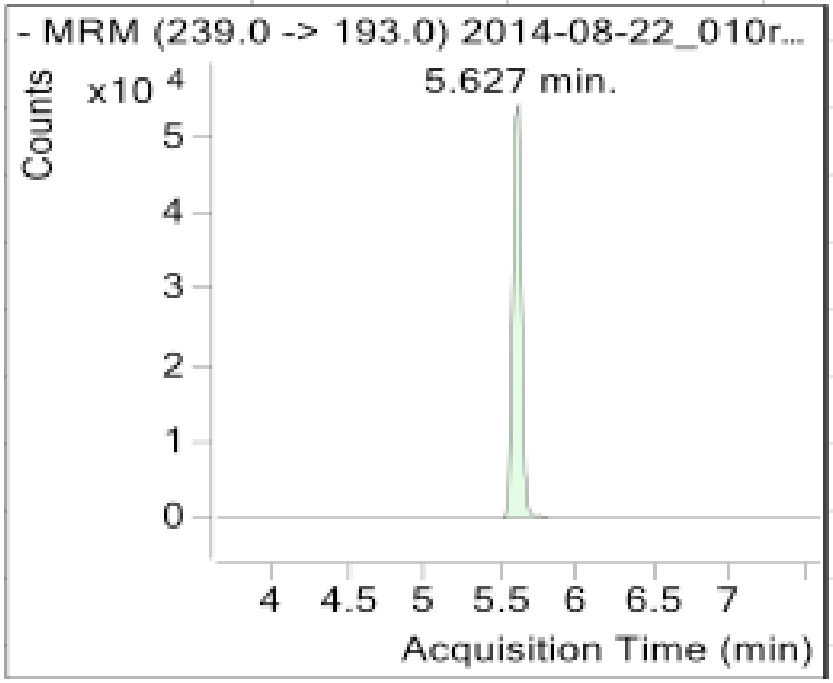
- Sample Volume
  - As little as **1mL**
- Sample Preparation
  - Limited Steps
  - Internal Standard Addition
  - Direct Injection (no extraction for water samples)
- Prep time <30mins
- LC/MS/MS set up and run 2 hours for batch of 7 samples

New Method Results

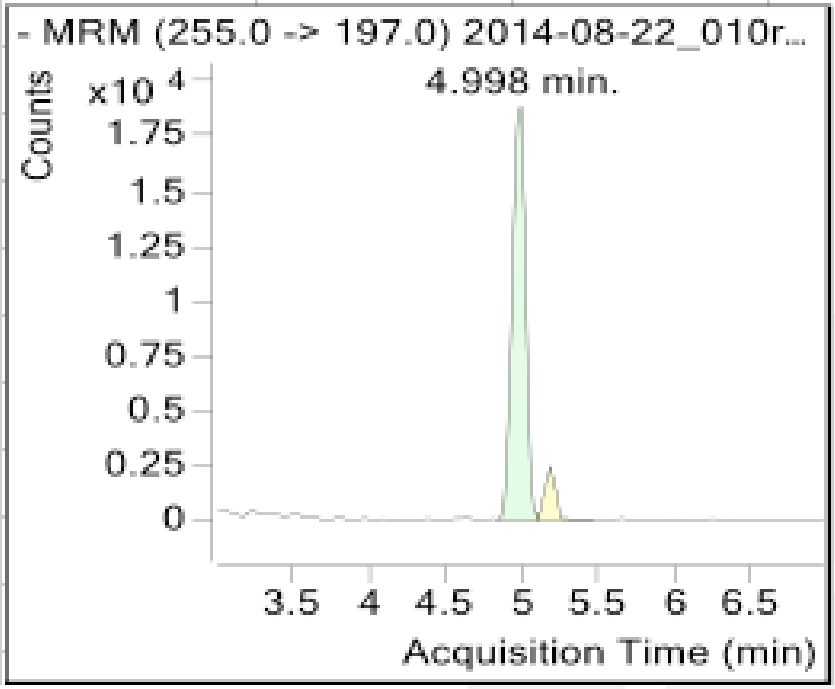
Target	New LC/MS/MS Method LOD (ug/l) ppb	Reported Detection Limit (ug/l)	Canadian Drinking Water Guideline Drinking Water (ug/l)	BCMOE lowest CSR (ug/l)	Linear Range	r2
2,4 D	0.01	0.1	100	40	0.001 - 0.500	0.995
2,4,5-T	0.01	0.1	none	20	0.01-1.0	0.995
MCPA	0.01	0.1	100	0.5	0.001-0.500	0.997
Dicamba	0.02	0.1	120	0.1	0.02-1	0.995
Dinoseb	0.01	0.1	10	0.5	0.005-0.5	0.995
Picloram	0.05	0.1	190	0.5	0.05-0.5	0.998

New Method Results

Dinoseb at 0.1 ug/l

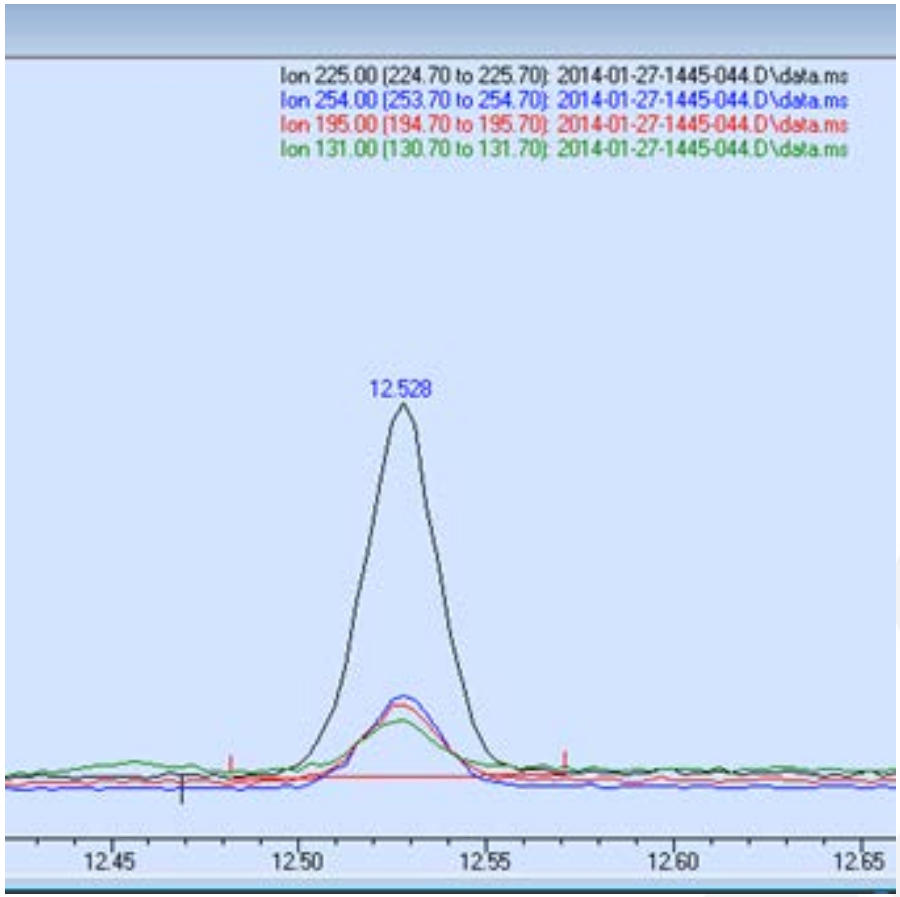


2,4,5 - T at 0.1 ug/l



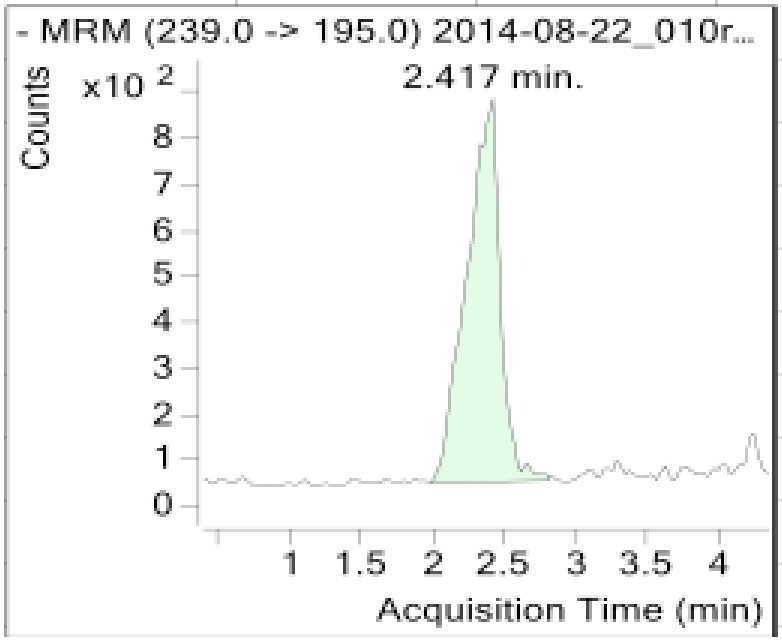
Old Method Chromatography

Dinoseb 0.2 ug/L

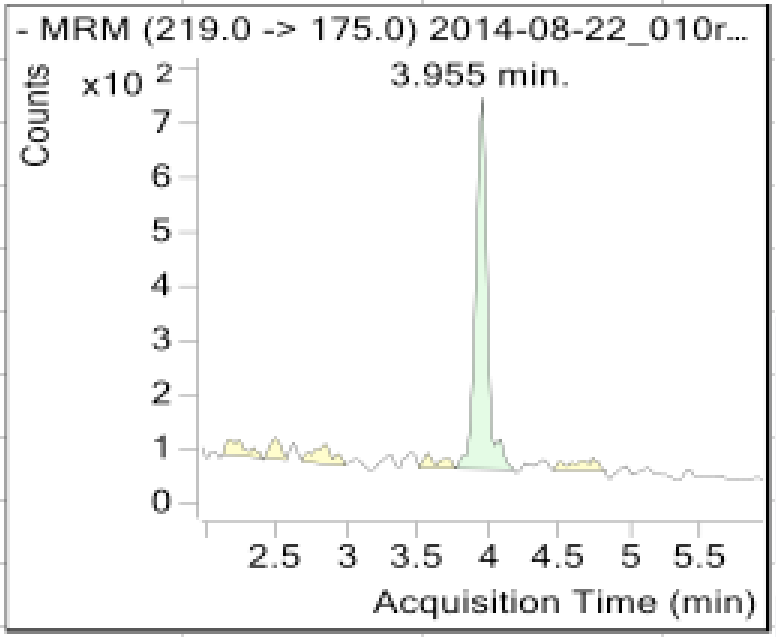


New Method Results

Picloram at 0.1 ug/l

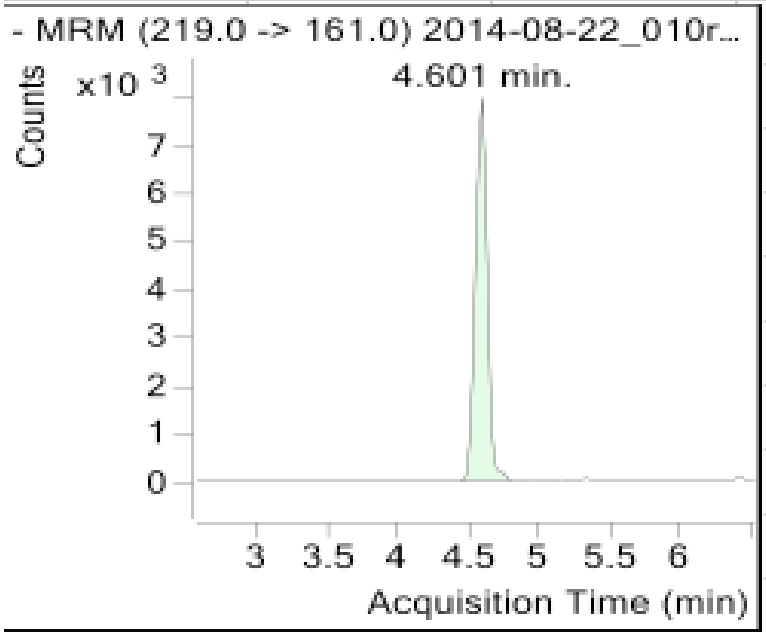


Dicamba at 0.1 ug/l

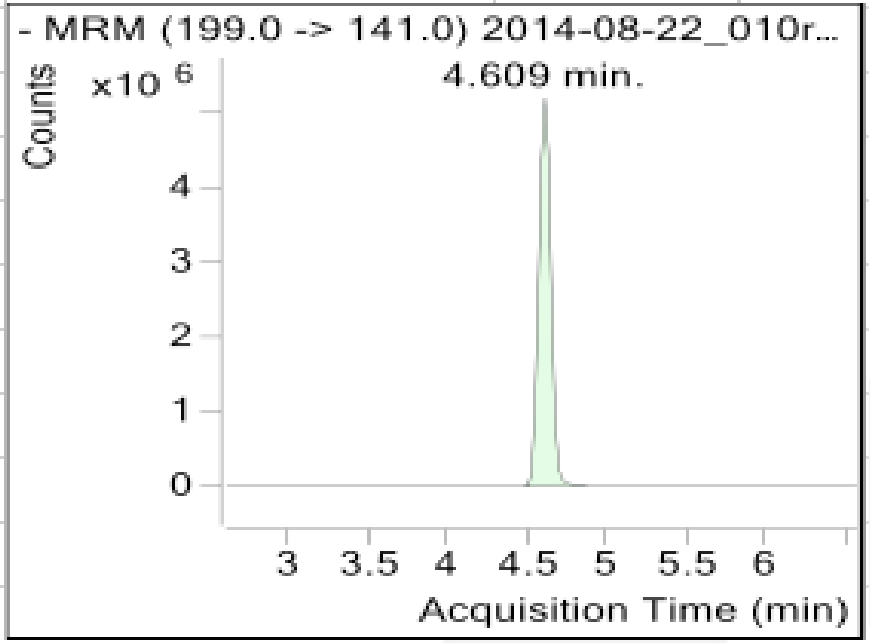


New Method Results

2,4 D at 0.1 ug/l



MCPA at 0.1 ug/l



New Method Highlights

- Small Sample Requirements 1mL of Sample Not 1L
- Short Prep Time –
- Prep time 30mins from 1.5 days
- Less steps = less potential variability, contamination, etc.
- Analysis Time
- LC/MS/MS set up and run 2 hours for batch of 7 samples down from ~24 hours
- One instrument, one run
- Safety - No Diazomethane
- Environment No Dichloromethane

New Method Results

- Safety & Environmental Game Changers
  - No Dichloromethane (DCM) Use
  - No Diazomethane
  - Less Sample Disposal
  - Lower Courier Costs – Lower GHG Emmisions

New Method Results

- Operational Enhancements
  - Significant labour savings
  - Less instrument time
  - More time for other things

Client Benefits

- Data Reliability
  - Improved Precision & Accuracy
  - Fewer step = lower potential for variability
- Detection Ability
  - Broad list of compounds
  - Improved detection limit ablity
  - Risk Assessment, Environmental Fate & Persistence
- Improved Processes
  - Easier to Collect & Ship Samples
  - Faster TATs
- Lower Costs

Conclusion

- Innovation Is Important
  - Industry Leadership
  - Scientific Improvement
  - Safety Improvements
  - Environmental Improvements

- Cost Savings
  - More Data = Better Understanding of Issues
- Successful & Engaged Clients & Employees
- Future Opportunities
  - Drugs & Hormones
  - CCME

Acknowledgements

CARO Analytical Services

CARING **A**BOUT **R**ESULTS…**O**BVIOUSLY

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