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A New Method for the Analysis of Polar Pesticides and Herbicides in Water Samples

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Polar Pesticide and Herbicide Analysis Overview

- Currently, most of these compounds are run by various methods using GC-ECD, GC-NPD or PFPD, and LC with post column reactors.

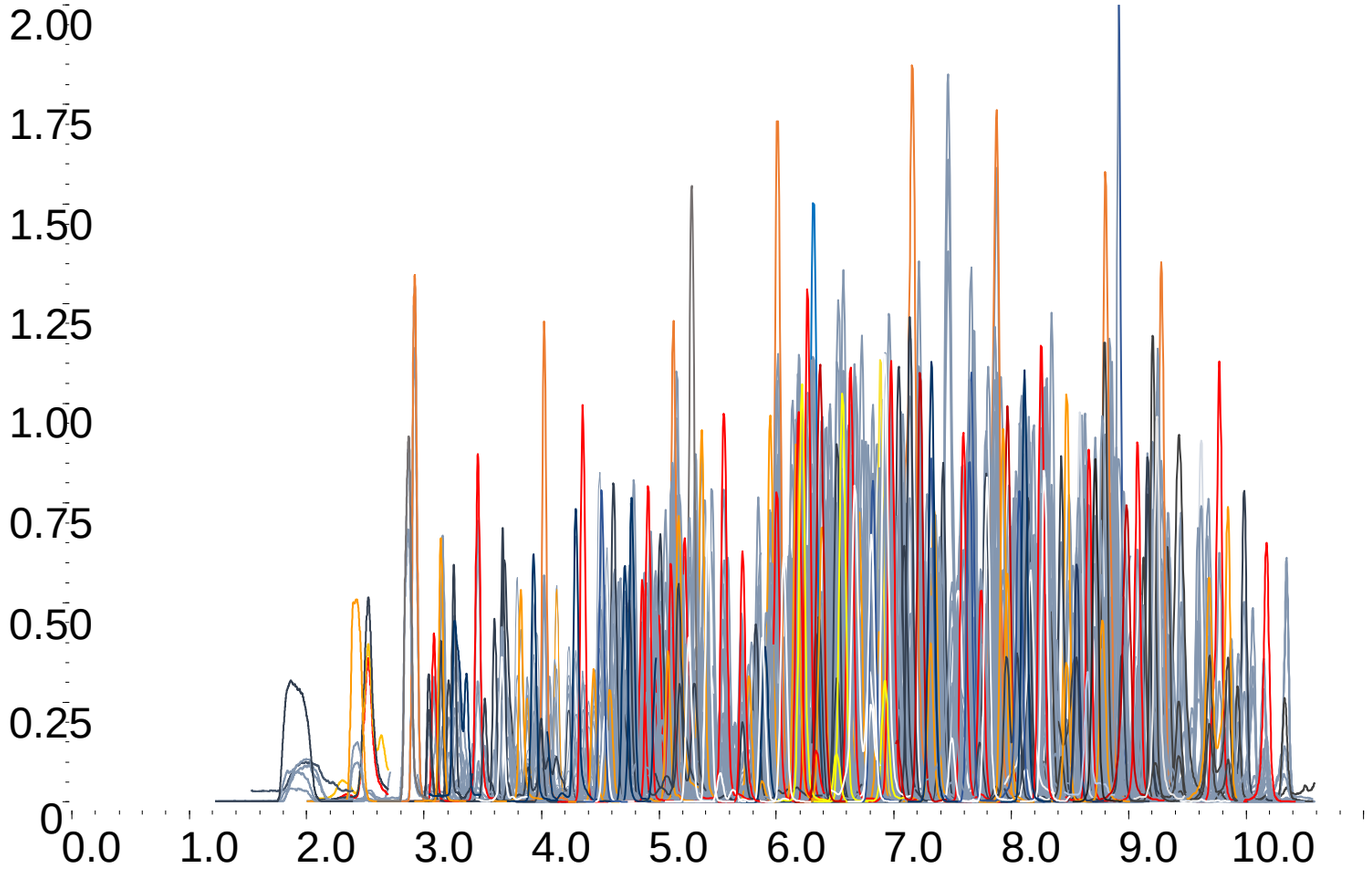
- Acid herbicides require a methylene chloride extraction, solvent exchange and diazomethane (mostly) derivatization. Analysis by GC-ECD

- Organophosphorus and organonitrogen pesticides require a methylene chloride extraction, solvent exchange, and GC with a “finicky” detector.

- Carbamates require LC with a post column reaction – dedicated instrument.

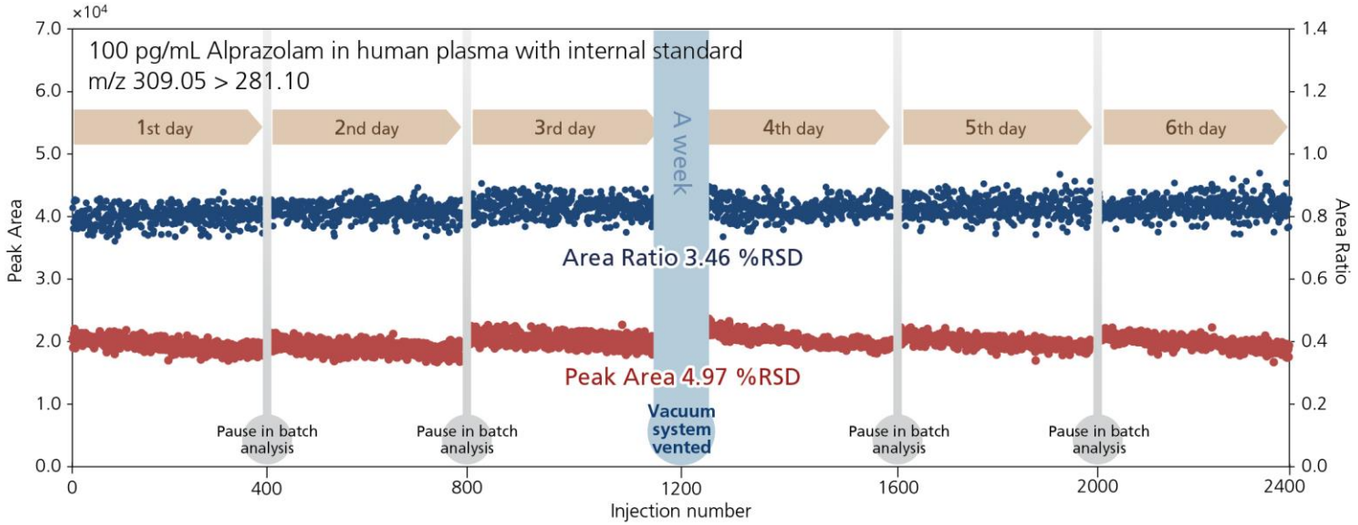
LC-MS/MS is an ideal instrument for polar pesticides and herbicides

- No Derivatization
- Qualitative
- Quantitative
- Incomplete Separation is OK

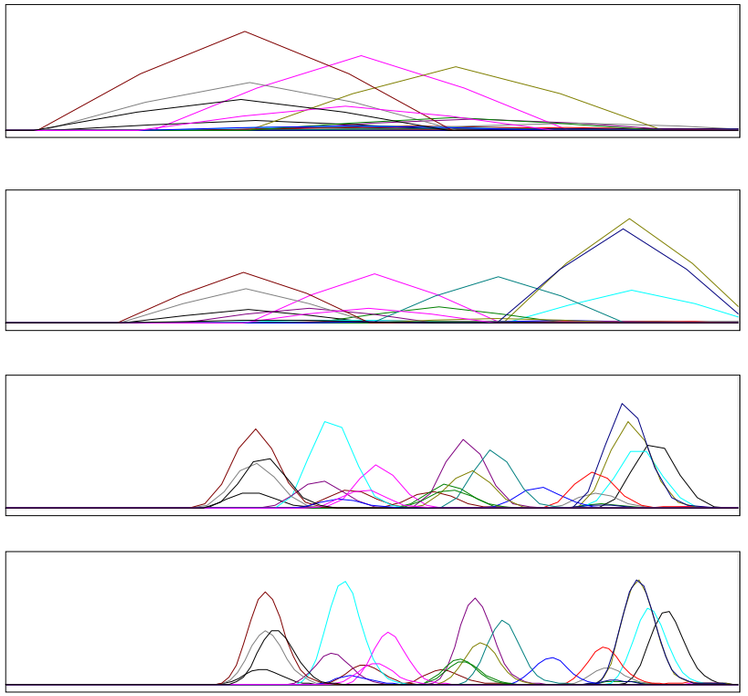


Important benefits of LC-MS/MS instruments

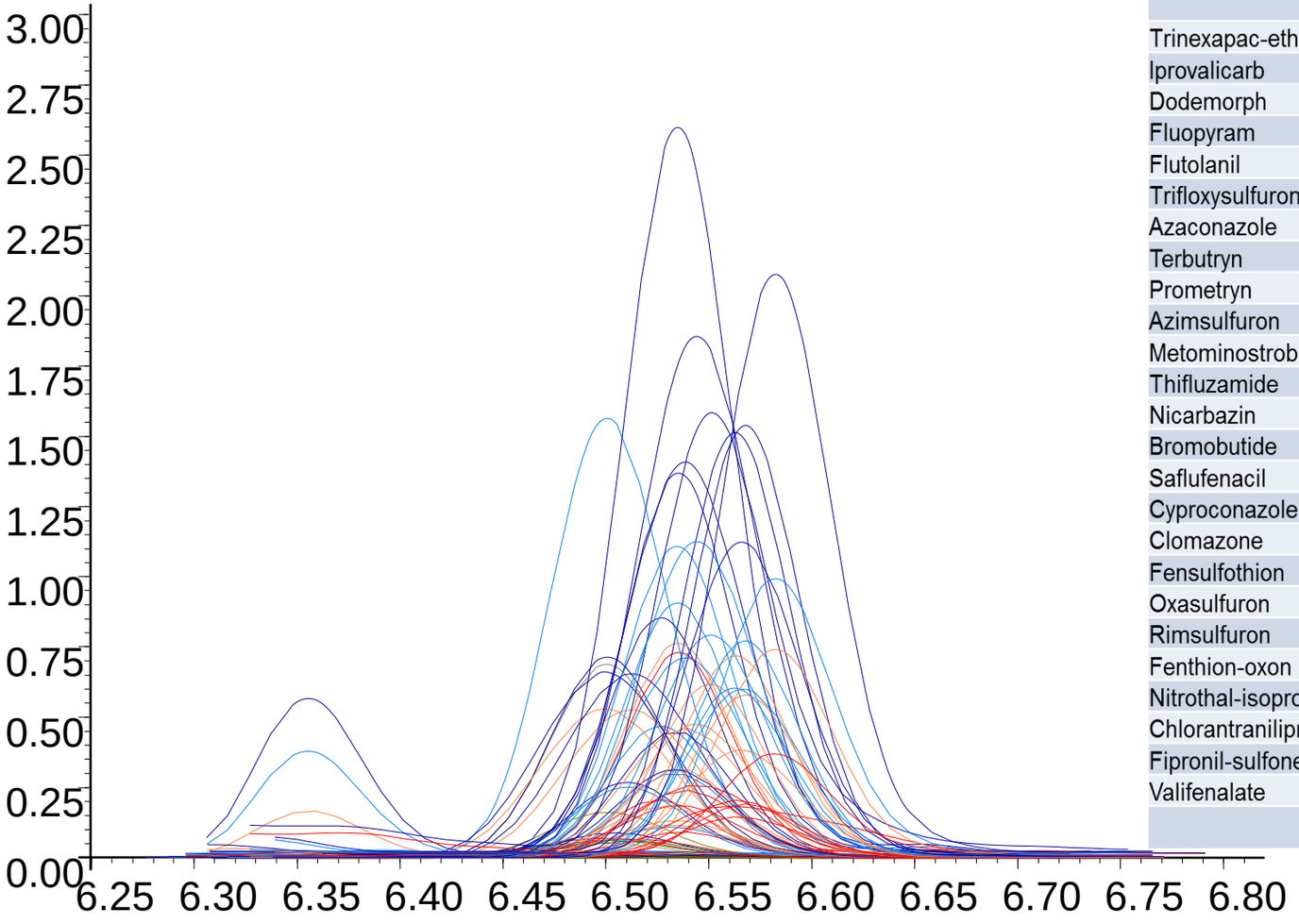
- Rapid Scanning helps resolve numerous peaks within small windows
- Rapid Polarity Switching enables positive and negative mode in a single injection
- Long-term stability minimizes recalibration and QC failure



Long term stability study on LCMS-8060



For example, here is the Quantitative Analysis of a bunch of pesticides between 6.4 and 6.7 minutes



Compound Name	CAS number	Formula	M	Polarity	MRM	RT	%RSD
Identifiers					Quantitation Ion	(mins)	(n=6)
Trinexapac-ethyl	95266-40-3	C13H16O5	252.0998	+	252.90>69.05	6.45	**3.1**
Iprovalicarb	140923-17-7	C18H28N2O3	320.2100	+	321.20>119.15	6.46	**2.8**
Dodemorph	1593-77-7	C18H35NO	281.2719	+	282.30>116.15	6.47	**4.2**
Fluopyram	658066-35-4	C16H11ClF6N2O	396.0464	+	397.00>145.00	6.47	**1.9**
Flutolanil	66332-96-5	C17H16F3NO2	323.1133	+	324.10>242.00	6.48	**2.7**
Trifloxysulfuron	145099-21-4	C14H14F3N5O6S	437.0617	+	438.00>182.15	6.48	**2.5**
Azaconazole	60207-31-0	C12H11Cl2N3O2	299.0228	+	300.00>159.00	6.50	**2.0**
Terbutryn	886-50-0	C10H19N5S	241.1361	+	242.10>157.95	6.50	**3.4**
Prometryn	7287-19-6	C10H19N5S	241.1361	+	242.10>158.00	6.50	**2.6**
Azimsulfuron	120162-55-2	C13H16N10O5S	424.1026	+	425.10>182.10	6.50	**1.8**
Metominostrobin	133408-50-1	C16H16N2O3	284.1161	+	285.10>193.95	6.51	**1.7**
Thifluzamide	130000-40-7	C13H6Br2F6N2O2S	525.8421	+	528.60>148.05	6.51	**5.9**
Nicarbazin	330-95-0	C13H10N4O5	302.0651	-	301.10>137.15	6.52	**2.6**
Bromobutide	74712-19-9	C15H22BrNO	311.0885	+	312.10>194.10	6.53	**2.1**
Saflufenacil	372137-35-4	C17H17ClF4N4O5S	500.0544	+	501.00>198.00	6.53	**2.3**
Cyproconazole	94361-06-5	C15H18ClN3O	291.1138	+	292.10>70.05	6.54	**1.7**
Clomazone	81777-89-1	C12H14ClNO2	239.0713	+	239.90>125.00	6.54	**1.7**
Fensulfothion	115-90-2	C11H17O4PS2	308.0306	+	309.00>281.00	6.54	**1.4**
Oxasulfuron	144651-06-9	C17H18N4O6S	406.0947	+	407.10>150.15	6.54	**1.1**
Rimsulfuron	122931-48-0	C14H17N5O7S2	431.0569	+	432.00>182.00	6.55	**1.8**
Fenthion-oxon	6552-12-1	C10H15O4PS	262.0429	+	263.10>231.00	6.55	**1.4**
Nitrothal-isopropyl	10552-74-6	C14H16NO6Na	317.0875	+	295.10>230.95	6.56	**3.0**
Chlorantraniliprole	500008-45-7	C18H14BrCl2N5O2	480.9708	+	483.90>452.90	6.57	**2.7**
Fipronil-sulfone	120068-36-2	C12H4Cl2F6N4O2S	451.9336	-	451.00>414.90	6.57	**2.0**
Valifenalate	283159-90-0	C19H27ClN2O5	398.1608	+	399.20>155.00	6.59	**1.9**

ASTM WK85842, a new method for the analysis of pesticides and herbicides in water samples using LC-MS/MS.

- We compiled a list of all regulated pesticides and herbicides and narrowed to those that work best by LC
- Goal → as many as possible with one injection. (two for instruments that need separate runs for positive and negative mode)
- LOQ needs to be lower than regulatory limit

Proposed Sample Preparation for ASTM WK85842, same as ASTM D8025

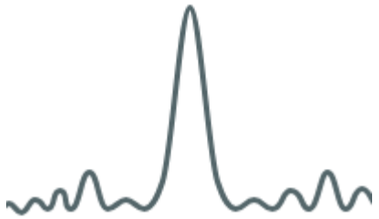
Collect Sample

Add Surrogate

Add Methanol

Mix

Filter



Analyze

Advantages and disadvantages for LC-MS/MS analysis of polar pesticides and herbicides

Advantages	Disadvantages
Sensitive enough for the analysis	<u>Not currently approved</u>
No extraction, solvent exchange, or derivatization	
Can use same instrument for PFAS, PPCP, Cyanotoxins, ….	

A triple quadrupole LC method for the analysis of pesticides and herbicides can potentially replace:

- EPA method 531.x
- EPA Method 515.x

EPA Method 632
EPA Method 615
EPA Method 614
EPA Method 622

EPA Method 8318
EPA Method 8151
EPA Method 8141

Determination of Select Pesticides and Herbicides in Water by Liquid Chromatography Tandem Mass Spectrometry (LC-MS/MS)

- Why not just use SW-846 method 8321 modified?
  - Not approved for drinking water
  - Not approved for wastewater
  - Method 8321 states = This method covers the use of high-performance liquid chromatography (HPLC), coupled with both thermospray-mass spectrometry (TS-MS) and an ultraviolet (UV) detector
    - Modification of SW-846 method may or may not be OK

We intend to validate the method in multiple matrices to attempt approval for all

1. Minimum 9 wastewater matrices, 3 drinking water matrices, and one leachate
2. MS/MSD pairs and unspiked samples
3. MDL study required
4. IDAC study required
5. 6 labs minimum needed

A minimum of 57 injections excluding calibration and QC per lab ~ 342 injections X 52 analytes = 17,784

All QC written as required in the method must be analyzed and met

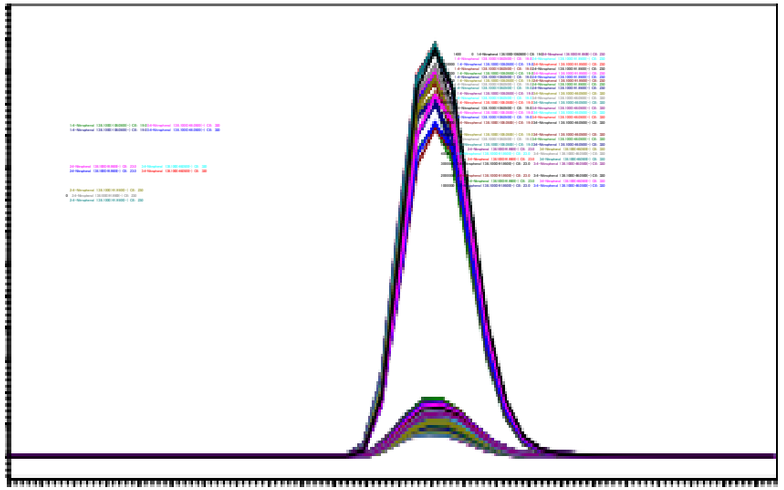
- Instrument tuning
- MRM optimization
- Calibration
- Demonstrate capability
- MRL or LLOQ checks
- ICV, CCV, method blanks

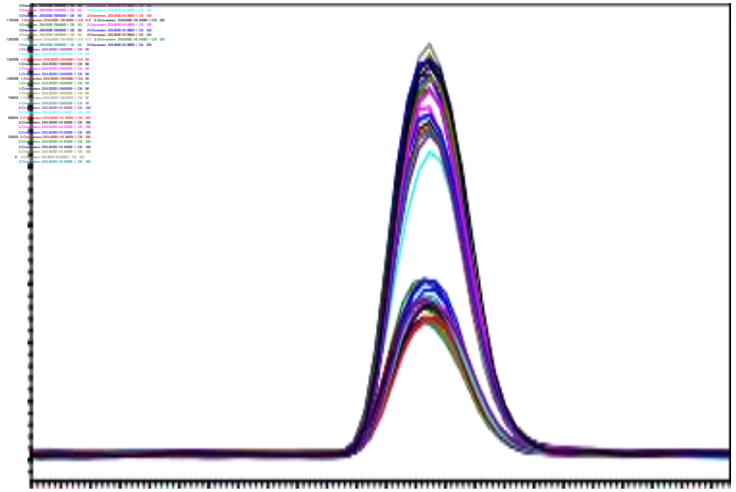
Development and optimization of the instrument method.

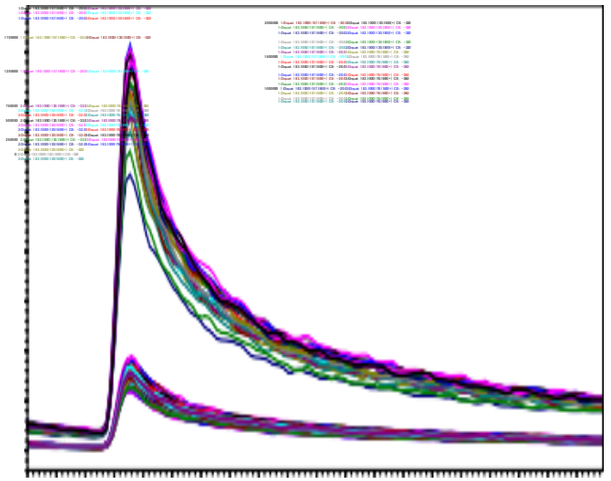
Compiled potential compound list by listing all regulated pesticides and herbicides amenable to LC

Compound	CAS	Monoisotopic Mass	Lowest EPA MDL	Target sensitivity	GCMS DB/MP	LCMS DB/MP
4-Nitrophenol	100-02-7	139.026947	0.13µg/L	0.409µg/L	○	×
2,4,5-TP (Silvex)	93-72-1	267.946075	0.018µg/L	0.057µg/L	×	×
Merphos	150-50-5	298.101257	0.018µg/L	0.057µg/L	×	×
Desethylatrazine	6190-65-4	187.062469	-µg/L	-µg/L	?	×
Desisopropylatrazine	1007-28-9	173.046829	-µg/L	-µg/L	?	×
Chloramben	133-90-4	204.969727	0.057µg/L	0.179µg/L	?	×
3,5-Dichlorobenzoic acid	51-36-5	189.958832	0.049µg/L	0.154µg/L	?	×
Baygon	114-26-1	209.105194	1µg/L	3.143µg/L	?	×
1-Naphthol	90-15-3	144.05751	0.034µg/L	0.107µg/L	?	×
Diquat	85-00-7	184.098953	0.72µg/L	2.263µg/L	×	○
Paraquat	1910-42-5	256.053406	0.68µg/L	2.137µg/L	?	○
Glyphosate	1071-83-6	169.014008	5.99µg/L	18.827µg/L	×	○

Optimized MRM transitions and CE for all listed compounds



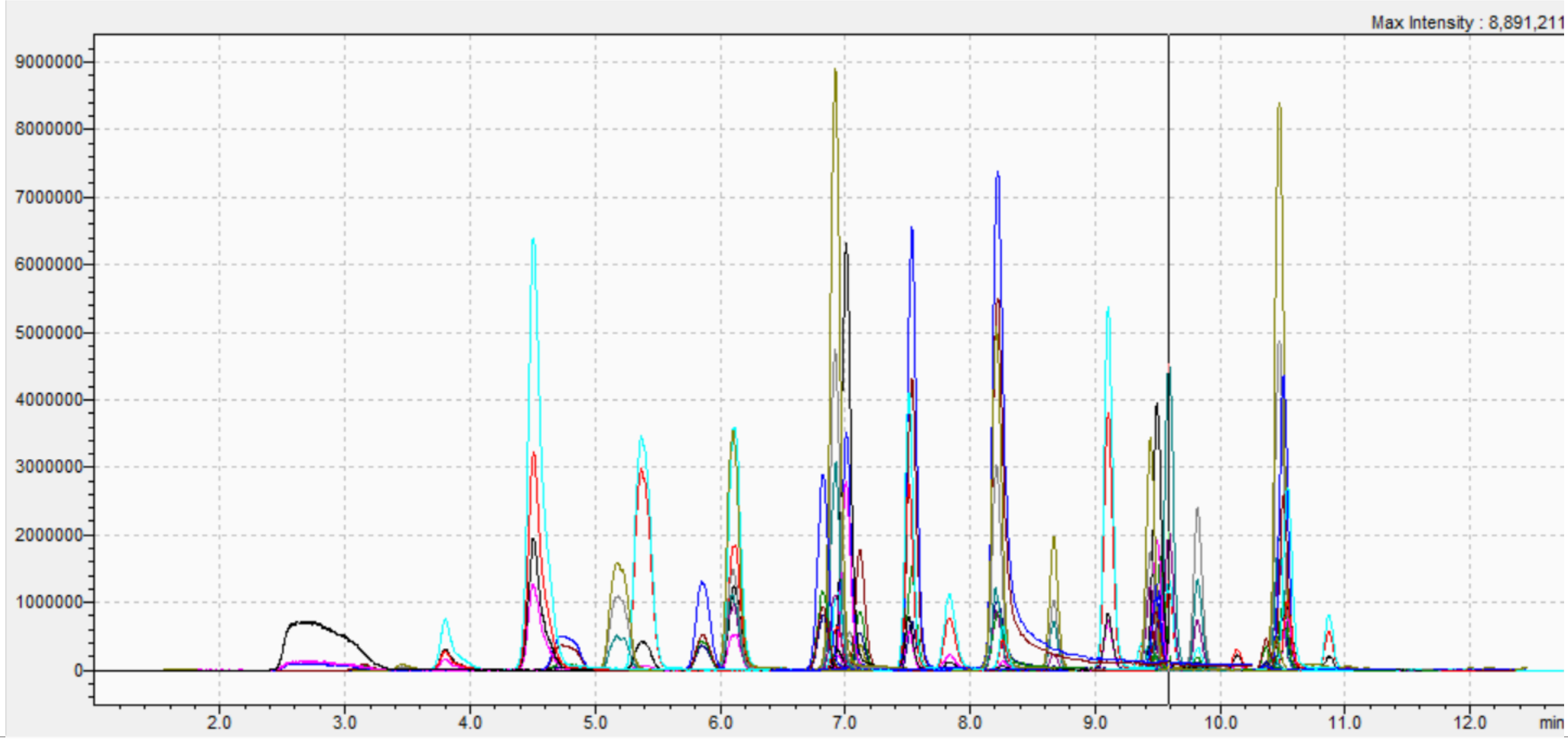




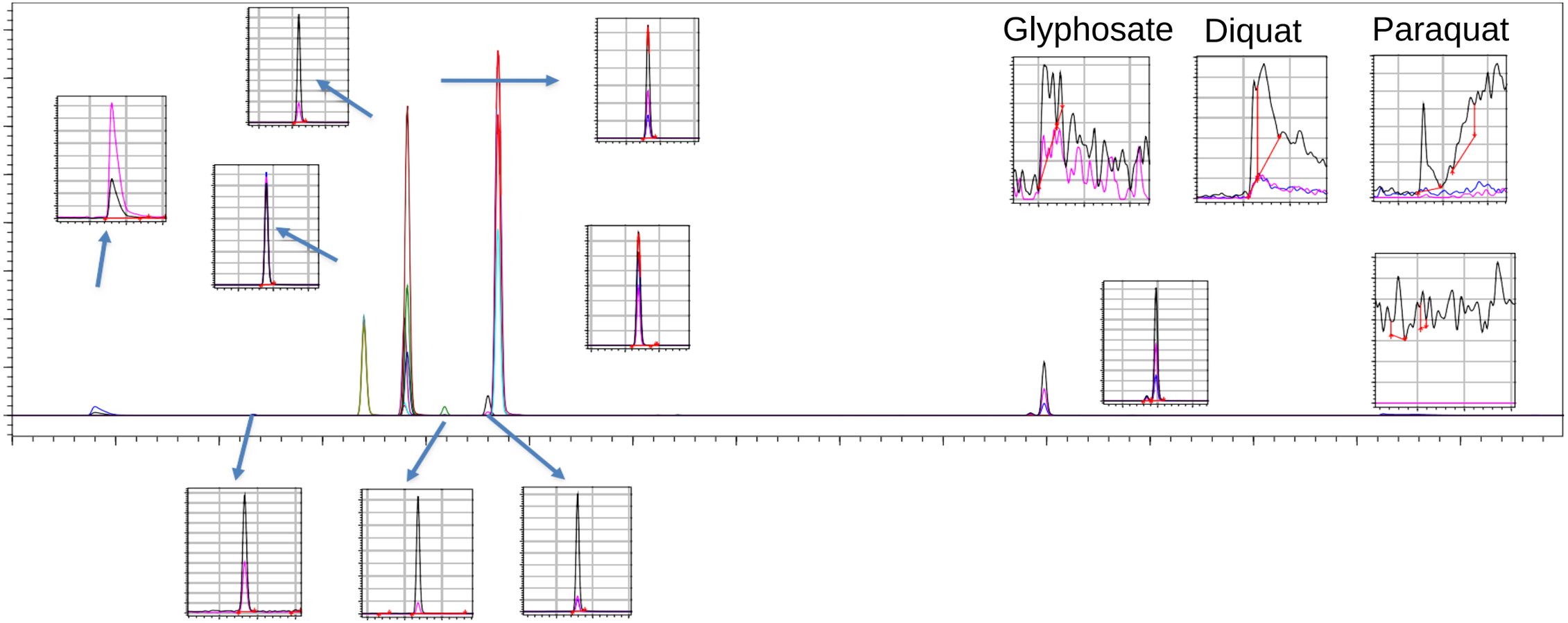
Optimized column, gradient, and ionization conditions (shown)

			MP condition		
Nebulizer gas (L/min)		1.5	3		
Heating gas (L/min)		5	10	15	
Interface temperature (deg. C)	200	300	350	400	
DL Temperature (deg. C)			150	200	250
Heat block temperature (deg. C)			300	350	400
Drying gas (L/min)		3	10	20	
CID gas pressure (kPa)		150	210	250	300
Interface voltage (kV)		±0.5	±1	±2	

Optimized chromatography for separation in minimal analysis time



Some compounds were excluded because there was no response, or they did not elute at the same time in (+) and (-) mode



The probe position was optimized for maximum overall response

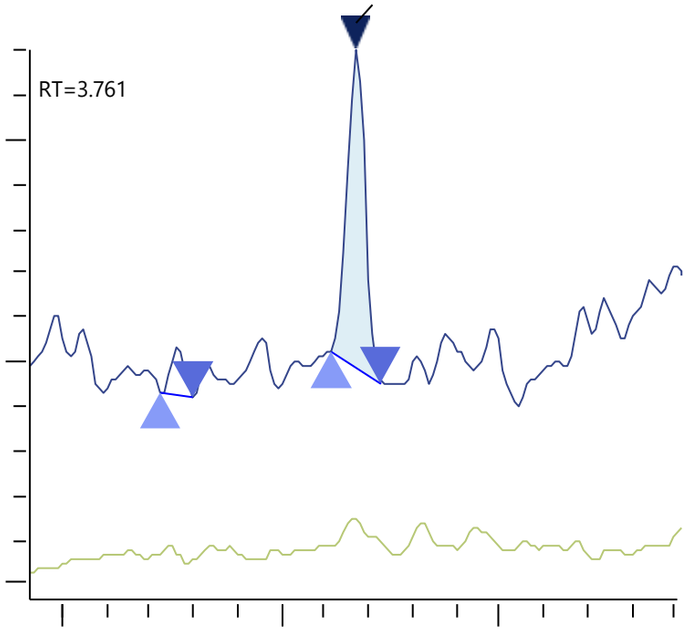
Compound	Probe position			
	1mm	2mm	3mm	4mm
Merphos	304,923	586,717	708,136	820,712
Desethylatrazine	5,252,283	7,952,947	9,834,334	10,778,161
Desisopropylatrazine	1,582,991	2,184,422	2,552,983	2,814,245
Baygon	8,352,992	12,966,224	16,781,359	17,906,933
1-Naphthol	104,235	117,079	101,426	62,505
4-Nitrophenol	1,103,810	1,736,718	2,402,995	2,554,066
2,4,5-TP	164,777	295,716	382,630	410,931
Chloramben	9,220	13,071	18,090	19,165
3,5-Dichlorobenzoicacid	60,472	125,004	180,878	196,239

Example not listing all peaks

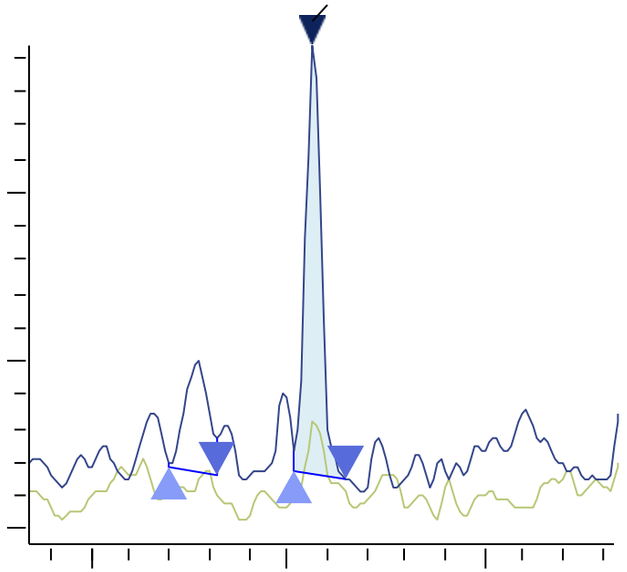
The dwell time was optimized for maximum overall response

		Default		DT40msec		LP0.6sec		DT30msec	
ID	Compound	Minimum calibration point (µg/L)	Remarks	Minimum calibration point (µg/L)	Remarks	Minimum calibration point (µg/L)	Remarks	Minimum calibration point (µg/L)	Remarks
1	1-Naphthol	0.1	Twice as much as Blank	0.05		0.05		0.05	
2	Chloramben	1		1		1	barely	1	
3	Desisopropylatrazine	0.01		0.01		0.01		0.01	Twice as much as Blank
4	4-Nitrophenol	0.05	Twice as much as Blank	0.05	Twice as much as Blank	0.5	Twice as much as Blank	0.02	Twice as much as Blank
5	Desethylatrazine	0.01	Twice as much as Blank	0.01	Twice as much as Blank	0.01	Twice as much as Blank	0.01	Five times Blank
6	3,5-Dichlorobenzoic acid	0.5		0.5		0.5		0.2	
7	2,4,5-TP (Silvex)	0.02		0.02		0.02		0.02	
8	Baygon	0.01		0.01		0.01	50 µg/L is saturated	0.01	50 µg/L is saturated
9	Merphos	0.5	Twice as much as Blank	0.5	Twice as much as Blank	0.5	Twice as much as Blank	1	

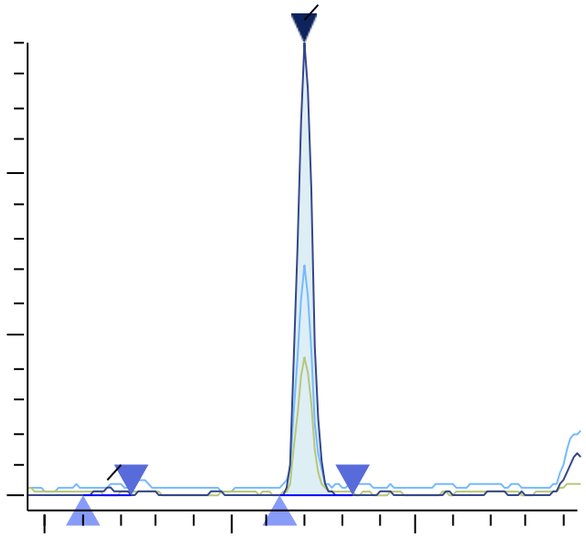
Example peaks under optimized conditions at the LOQ



3,5-Dichlorobenzoicacid (0.05µg/L)



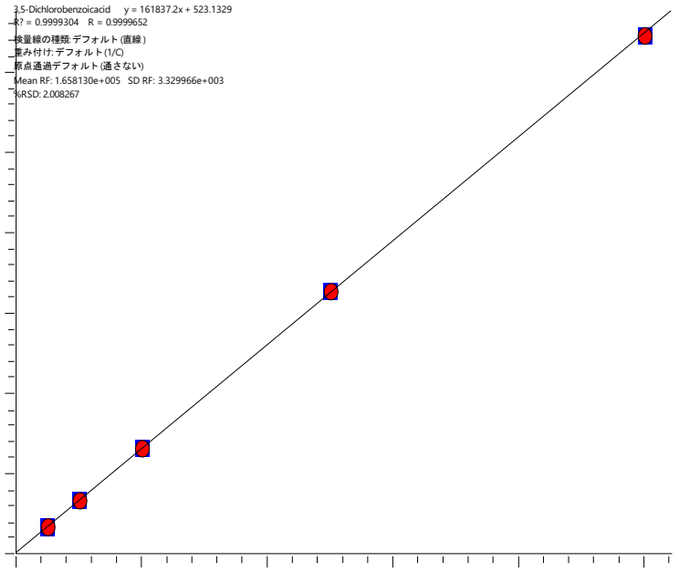
2,4,5-TP (0.01µg/L)



Baygon (0.01µg/L)

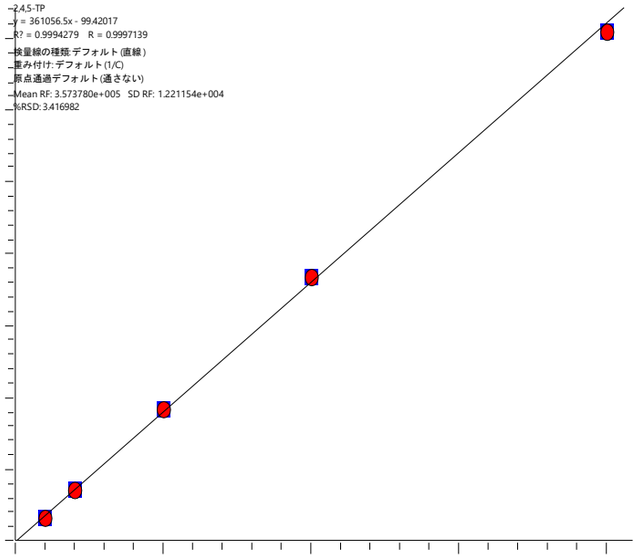
Example calibration curves under the optimized conditions

0.05, 0.1, 0.2, 0.5, 1.0 µg/L



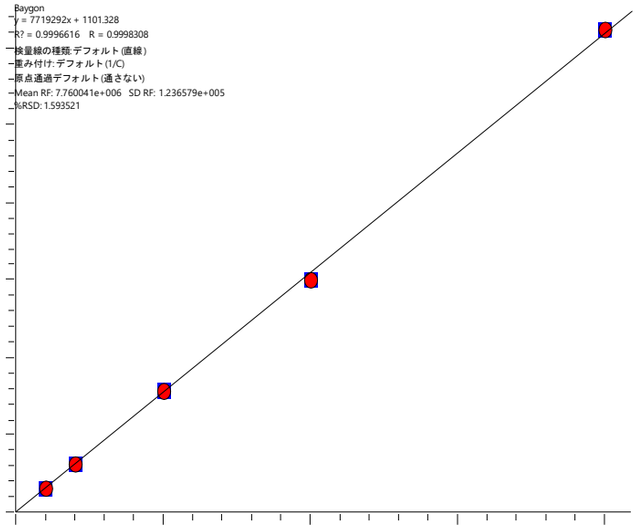
3,5-Dichlorobenzoicacid

0.01, 0.02, 0.05, 0.1, 0.2 µg/L



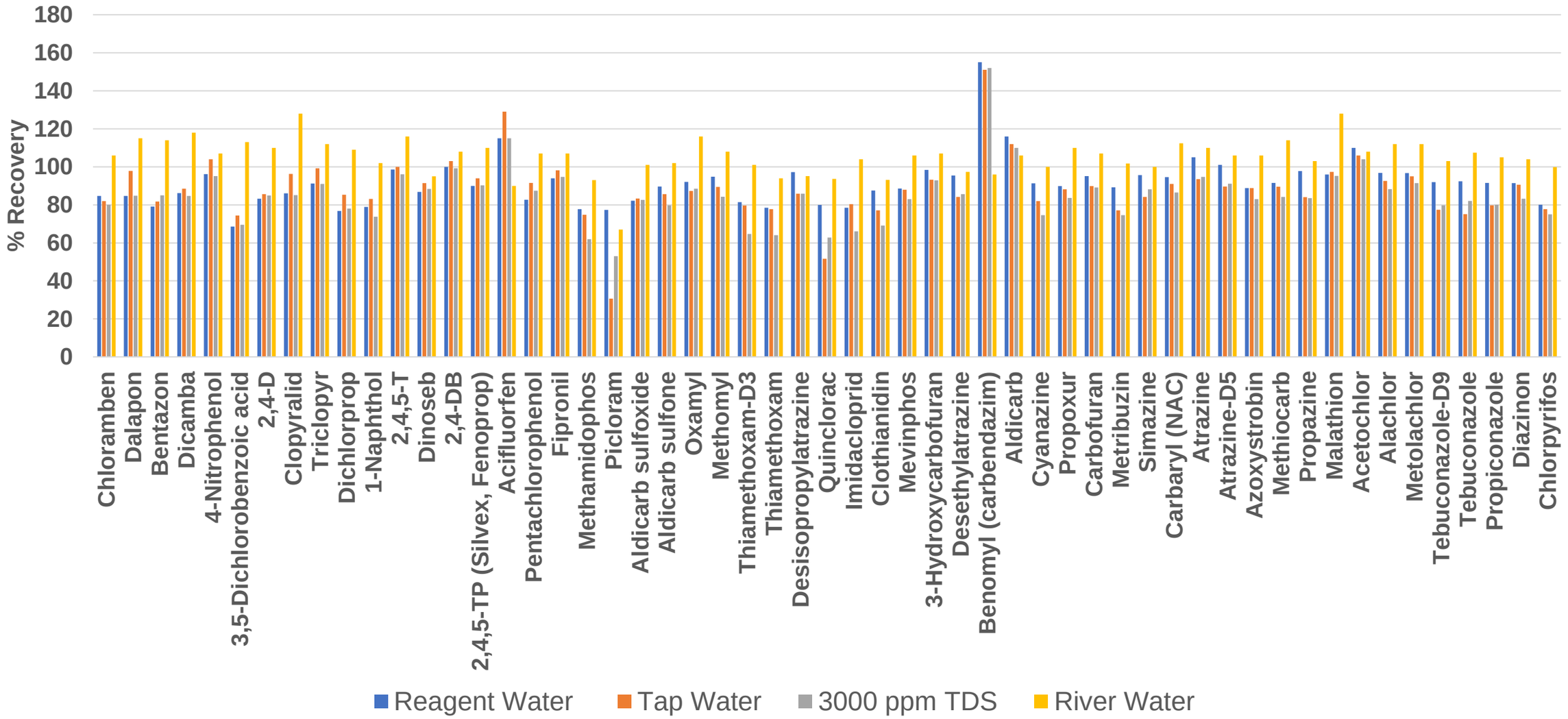
2,4,5-TP

0.01, 0.02, 0.05, 0.1, 0.2 µg/L

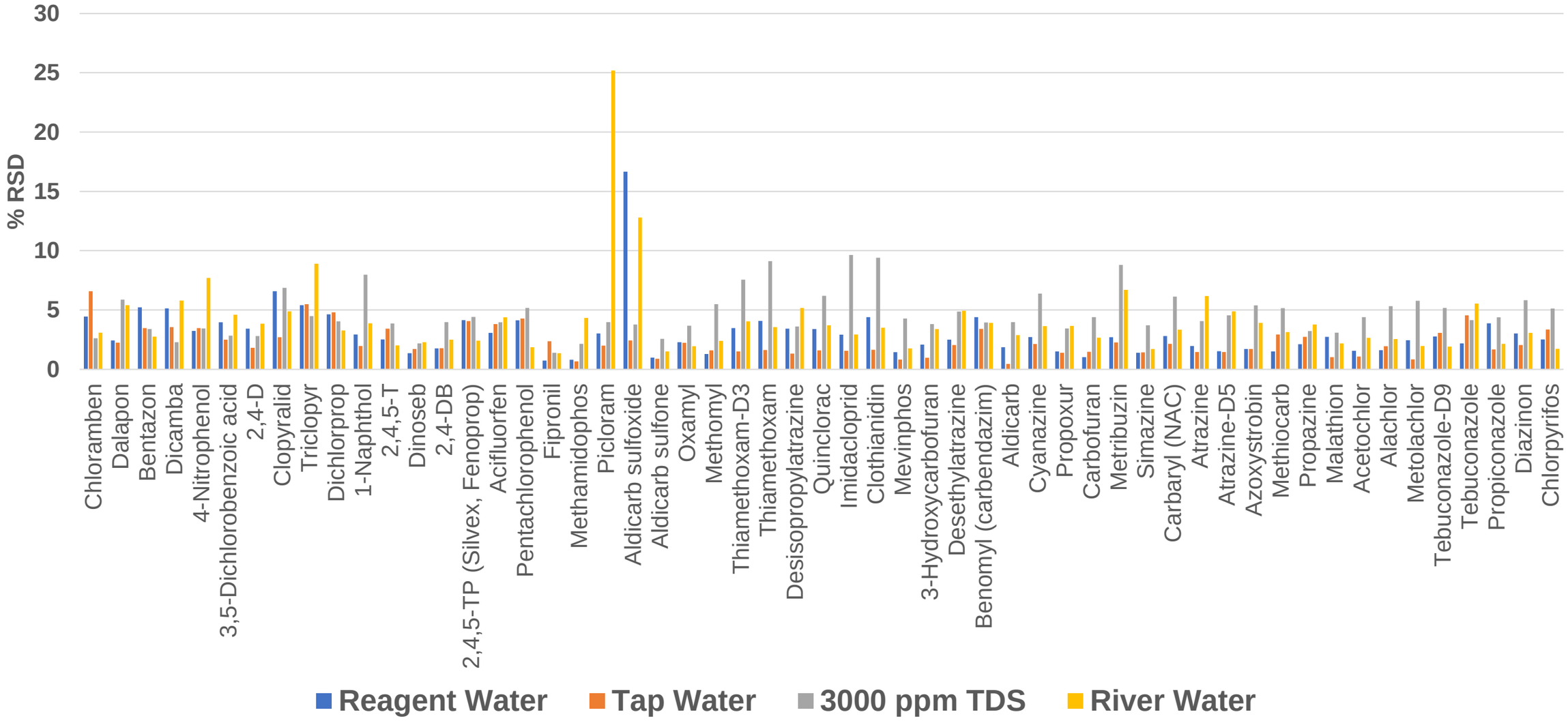


Baygon

Recovery of mid-level spiked target compounds in various matrices



% RSD of Mid-level spiked target compounds in various matrices



Advantages of the proposed method for analysis of polar pesticides and herbicides

- Fewer interferences
- Detection limits suitable for regulation
- Only one instrument needed
- No solvent extractions, or derivatizations
- No second column confirmation (needed for GC methods)
- Same instrument can be used for other analytes (PPCP, Cyanotoxins, PFAS)

Thank You, for more information on this new ASTM method, contact:

- wclipps@shimadzu.com
- Or visit www.ssi.shimadzu.com