Determination of Atrazine, Bromacil, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Diamino Chlorotraizine (DACT), Desmethyl Norflurazone,Tebuthiuron and the metabolites Tebuthiuron-104, Tebuthiuron-106, Tebuthiuron-107 and Tebuthiuron-108 in Well Water by MCX extraction and Liquid Chromatography- triple quadrupole mass spectrometry

1. Scope:

This section method (SM) is applicable to the analysis of Atrazine, Bromacil, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), and Diamino Chlorotraizine (DACT) in well water and river water using ESI/LC/MS/MS. Desmethyl Norflurazon Tebuthiuron, Tebuthiuron-104 , Tebuthiuron-106, Tebuthiuron-107 and Tebuthiuron-108 method detection limit and validation data for well water was added later. The reporting limit varies from 0.01 to 0.05 ppb.

2. Principle:

One conditioned Water Oasis ® MCX Cartridge is connected used to retain the analytes from well water samples. The cartridges are placed under vacuum to eliminate any remaining water. The chemicals are eluted with 5% ammonium hydroxide in methanol. The eluant is then filtered, concentrated, reconstituted in 1:3 methanol/water and analyzed by ESI/LC/MS/MS.

3. Safety:

All general laboratory safety rules for sample preparation and analysis shall be followed.

4. Interferences:

There were no matrix interferences that caused quantitative problems during method development and validation

5. Apparatus and Equipment:

5.1 Nitrogen Evaporator (Meyer N-EVAP Organomation Model #112 or equivalent)
5.2 Balance (Mettler PC 4400 or equivalent)
5.3 Vortex-vibrating mixer
5.4 Solid phase extraction manifold, Supelco Visiprep TM24 or equivalent

5.5 Solid phase extraction manifold accessories: vacuum source, vacuum chamber, vacuum controller, cartridge fittings (tube adapters) and connectors, sample delivery tubing with stainless steel weight, sample collection tubes and rack.
5.6 Sample filtration apparatus
5.7 Liquid Chromatograph equipped with a triple quadrupole (LCMS)

6. **Reagents and Supplies**:

6.1	Diamino Chlorotriazine (DACT)	CAS#3397-62-4
6.2	Deisopropyl Atrazine (ACET)	CAS#11007-28-9
6.3	Deethyl Atrazine (DEA)	CAS#6190-65-4
6.4	Metribuzin	CAS#21087-64-9
6.5	Bromacil	CAS#314-40-9
6.6	Atrazine	CAS#1912-24-9
6.7	Norflurazon	CAS#27314-13-2
6.8	Simazine	CAS#122-34-9
6.9	Hexazinone	CAS#51235-04-2
6.10	Diuron	CAS#330-54-1
6.11	Prometon	CAS#1610-18-0
6.12	Prometryn	CAS#7287-19-6
6.13	Propazine (surrogate)	CAS#139-40-2
6.14	Desmethyl-Norflurazon	CAS#23576-24-1
6.15	Tebuthiuron	CAS#34014-18-1
6.16	Tebuthiuron 108	CAS#
6.17	Tebuthiuron 107	CAS#
6.18	Tebuthiuron 106	CAS#
6.19	Tebuthiuron 104	CAS#

6.20 Methanol, MS grade, Burdick & Jackson or equivalent
6.21 Water, MS grade, Burdick & Jackson or equivalent
6.22 Acetic Acid, HPLC grade
6.23 Ammonium hydroxide, reagent grade or equivalent.
6.24 Elution reagent: 5% ammonium hydroxide in methanol.
6.25 Hydrochloric acid 6 N
6.26 Type I DI water
6.27 Reconstitution reagent: 1:3 methanol/water
6.28 Solid phase extraction cartridges: Waters Oasis® MCX 6 cc (150mg), 60-micron particle size cartridge or a (500mg) cartridge.
6.29 Nylon Acrodisc ®, 0.2 micron, Gelman Sciences
6.30 Syringe and plunger for filtration, 10mL
6.31 Graduated test tube, 15 mL (calibrated at 0.5mL with methanol)
6.32 Fiberglass filters, 1um x 47 mm.

6.33 LCMS Columns:
Analytical column: Waters Acquity UPLC HSS T3 1.8 µm, 2.1 x 100mm column (part # 186003539) or equivalent

7. Standards Preparation:

7.1 A combination stock standard of 0.1 mg/mL for all the triazines except propazine was obtained from the CDFA/CAC Standards Repository. Propazine was received at a concentration of 1 mg/mL and was diluted to 1.0 ug/mL in methanol for spiking as a surrogate. Tebuthiuron and metabolites were received at a concentration of 1 mg/mL and were diluted with the combination triazine standard to 1.0 ug/mL in methanol for spiking.

A combination standard of10 µg/mL was prepared with 1:3 methanol/water from the combination 0.1mg/mL standard, Tebuthiuron, metabolites and propazine standards. The combination working standard was diluted to the following concentrations: 0.025, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 µg/mL in 1:3 methanol/water. These working standards were diluted with blank matrix to prepare the following concentrations: 0.0125, 0.025, 0.05, 0.1, 0.25, 0.5, 1.0 µg/mL for instrument calibration.

7.2 Keep all standards in the designated refrigerator for storage.

7.3 The expiration date of each standard is six months from the preparation date or the expiration date of the stock standards whichever comes first.

8. **Sample Preservation and Storage**:

Store all samples waiting for extraction in a separate refrigerator (32-40 °F).

9. **Test Sample Preparation**:

9.1 Background Preparation

The Department of Pesticide Regulation (DPR) provided the surface and well water for background to be used in method validation and QC.

9.2 Preparation of blank and spike

Matrix blank: Weigh out 500 g of background water and follow the test sample extraction procedure.

Matrix spike: Weigh out 500 g of background water. Spike a client requested amount of herbicides into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.3 Test Sample Extraction

9.3.1 Remove sample from refrigerator and allow them to come to ambient temperature.

9.3.2 Weigh 500 ± 0.5 g of water sample into a 600 mL beaker.

9.3.3 Add 0.1 µg propazine (100 µL of 1 ng/µL spiking solution) as a surrogate to each sample except blank. Note: the volume of methanol in spiking solution added to the sample should be 0.1% or less of the sample volume.

9.3.4 Filter the surface water sample through a 1 µm x 47mm fiberglass filter. Note: no filtration is needed for well water sample.

9.3.5 Adjust pH to 2.5 – 3.0 with 3 N HCL.

9.3.6 An MCX cartridge (150mg) is connected to the vacuum manifold.

9.3.7 Condition the cartridge with total ~15 mL of methanol at a flow rate ~ 8 mL/minutes followed by ~ 15 mL of type I DI water by applying vacuum.

9.3.8 Turn off the vacuum when the type I water has just passed through the cartridge. Refill MCX cartridge with type I water. Attach the sample delivery tubes to the cartridge and place weighted tube ends into water sample.

9.3.9 Allow the sample to pass through the conditioned cartridges by applying vacuum. Adjust the flow rate to ~ 8 mL/minute

9.3.10 After all of the water sample has passed through the cartridges, increase the vacuum to ~ 20 psi for about 2 minutes. Detach the sample delivery tube from MCX cartridge. Shake out any excess water in the cartridge reservoir. Reverse the stacking order of the MCX cartridges on the vacuum manifold.

9.3.11 Place the graduated test tubes into the vacuum manifold.

9.3.12 Elute and collect all chemicals with 15 ± 0.5 mL of 5% ammonium hydroxide in methanol at a flow rate of ~8 mL/minutes.

9.3.13 Concentrate the eluant to ~10 mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen.

9.3.14 Filter the eluant through a 0.2 µm Acrodisc into a 15 mL graduated test tube, which has been calibrated at 0.5 mL. Rinse the test tube with ~ 2 mL of Methanol and filter the rinsate. Add filtered rinsate to eluant. Rinse the filter and syringe and add to eluant.

9.3.15 Concentrate the eluant to ~0.5mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen. Bring to a final volume of 1.0mL with reconstitution reagent (1:3, methanol/water). Vortex for 30 seconds. Transfer the extract into an autosampler vial. Analyzed by ESI/LC/MS/MS.

10. **Instrument Calibration**:

10.1 The calibration standard curve consists of a minimum of three levels for a linear curve and 5 levels for a quadratic curve. The lowest level must be at or below the corresponding reporting limits.

10.2 The LCMS calibration curves were obtained using linear or quadratic regression.

11. **Analysis:**

11.1 Injection Scheme

The instrument may need to be conditioned with a few standards before running the following sequence of Standard Curve, Solvent, Matrix Blank, Matrix Spike, Test Samples and Standard Curve.

11.2 Linear Ion Trap Quadrupole LC/MS/MS Mass Spectrometer

11.2.1 LC Instrument: Shimadzu LC30
Column: Acquity UPLC HSS T3 1.8 µm, 2.1 x 100 mm column
Column Temperature: 40 °C
Mobile Phase: Gradient
Solvent 1: 0.04% Acetic acid in water
Solvent 2: 0.04% Acetic acid in methanol
Gradient:

Time(min)	Flow rate (mL/min)	Solvent 1	Solvent 2
0.50	0.40	95.0	5.0
2.0	0.40	40.0	60.0
8.50	0.40	5.0	95.0
9.50	0.40	5.0	95.0
9.51	0.40	95.0	5.0

Injection Volume: 3.0 µL

11.2.2 Mass Spectrometry and Operating Parameters

Model:	AB Sciex QTRAP Triple Quadrupole
Ion Probe Type:	Electrospray Ionization (ESI)
Ion Mode:	ES+
Source Temp:	150 °C
Curtain Gas:	25.0
Ion Spray Voltage:	4500
Temp:	450
Ion Source Gas 1	50
Ion Source Gas 2	50
Collision Gas:	7.0

Compound	RT	Precursor Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
ACET	3.83	173.9	**95.9**	61	25	10	16
		173.9	103.8	61	29	10	16
Atrazine	5.33	215.8	**174**	56	23	10	22
		215.8	95.9	56	31	10	16
Bromacil	4.76	261	**205**	41	17	10	26
		261	187.9	41	37	10	20
DACT	2.51	145.8	**78.96**	51	23	10	18
		145.8	67.9	51	27	10	16
		145.8	103.9	51	25	10	16
DEA	4.20	187.9	**145.9**	46	23	10	20
		187.9	103.8	46	31	10	18
DMN	5.10	289.9	**269.9**	176	31	10	16
		289.9	145	176	53	10	10
Diuron	5.46	233	**72.0**	56	21	10	12
		233	45.9	56	43	10	12
Hexazinone	4.76	252.9	**171**	46	21	10	22
		252.9	71	46	39	10	18
Metribuzin	4.78	214.9	**187.1**	76	23	10	26
		214.9	48.9	76	47	10	12
Norflurazon	5.44	303.8	**283.9**	101	31	10	36
		303.8	159.9	101	39	10	18
Prometon	5.38	225.9	**184**	81	25	10	24
		225.9	142	81	29	10	18
Prometryn	6.40	241.9	**157.9**	101	31	10	18
		241.9	200	101	25	10	30
Propazine	5.95	229.9	**188**	66	23	10	24
		229.9	145.9	66	31	10	18
Simazine	4.77	201.9	**124**	66	23	10	16
		201.9	103.9	66	31	10	12

Compound	RT	Precursor Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Tebuthiuron 104	4.39	214.9	**171.9**	71	23	10	22
		214.9	115.9	71	33	10	20
Tebuthiuron 106	4.23	200.9	**157.9**	51	21	10	20
		200.9	184	51	21	10	24
Tebuthiuron 108	4.07	157.9	**74.9**	61	25	10	12
		157.9	101.9	61	25	10	12
Tebuthiuron	4.84	228.9	**171.9**	56	23	10	20
		228.9	116	56	35	10	14

Quantitation ions are in bold.

12. **Quality Control**:

12.1 Method Detection Limits (MDL)

Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, seven surface water/well water samples are spiked at 0.010 µg and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL for each analyte using the following equation:

MDL = tS

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicates used to determine the MDL, t=3.143.

The results for the standard deviations and MDL are in Appendix 1.

12.2 Reporting Limit (RL)

Reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The RL is chosen in a range 1-5 times the MDL, as per client agreement. The reporting limit varies from 0.01 to 0.05 ppb

12.3 Method Validation

The method validation consisted of three sample sets. Each set included three levels of fortification and a method blank. The recovery data is shown in Appendix 2. This method is updated to the current instrumentation – AB Sciex 6500 UPLC positive electrospray ionization triple quadrupole mass spectrometry (ES-LC/MS/MS).

12.4 Control Charts and Limits

Control charts were generated using the data from the method verification for each analyte. The upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the % recovery, respectively, shown in Appendix 2.

12.5 Acceptance Criteria

12.5.1 Each set of samples will have a matrix blank and a spiked matrix sample.

12.5.2 The retention time of the analyte must match within ± 0.1 minute of the analyte in the standards within the same sequence.

12.5.3 The recoveries of the matrix spikes shall be within the control limits. When spike recoveries fall outside the control limits, the chemist must investigate the cause. The entire extraction set of samples is re-analyzed. If the spike recoveries fall within the limit, then the results from the re-analyzed samples shall be reported.

12.5.4 The sample shall be diluted if results fall outside of the calibration curve.

12.5.5 Bracketing standard curves should have a percent change ≤20 %.

12.5.6 Presence of both precursor and product ion. The relative abundances of structurally significant ions used for confirmation must be within ± 30% relative when compared to a standard injected during the same run.

13. Calculations:

Quantitation is based on an external standard (ESTD) calculation using either the peak area or height. The LCMS software used a quadratic curve fit, with all levels weighted equally. Alternatively, at the chemist's discretion, concentrations may be calculated using the response factor for the standard whose value is < 30% to the level in the sample.

$$ppb = \frac{(\text{sample peak area or ht}) \times (\text{std conc}) \times (\text{std vol. Injected}) \times (\text{final vol of sample})(1000\ \mu L/mL)}{(\text{std.peak area or ht}) \times (\text{sample vol injected}) \times (\text{sample wt (g)})}$$

14. Reporting Procedure:

Sample results are reported out according to the client's analytical laboratory specification sheets.

15. Discussion and References:

15.1 This method is updated to reflect the new instrumentation being used – Water's UPLC positive electrospray ionization triple quadrupole mass spectrometry (ES-LC/MS/MS). Method verification consisted of three sample sets. Each set included three levels of fortification and a method blank. All spikes and method blanks were processed through the extraction method and analyzed. Since only nine verification data points were used to generate the new control chart, additional QC points will be added as samples are processed. A new control range will be calculated when enough data points have accumulated.

15.2 Information and data pertaining to the Thermo Finnigan, LCQ DECA ion trap MS instrument has been moved to Appendix 3.

15.3 Propazine is used as a surrogate. Add 0.1 µg of propazine to each sample and processed through the entire analytical method. This allows the extraction steps to be monitored.

15.4 The segment durations in the mass spectrometer settings determine the retention time windows for each analyte. As the HPLC column performance may change over time because of irreversible contamination, phase stripping, etc., it may be necessary to adjust these windows before beginning a sequence for the observed retention times of the analytes. Installation of a new guard column or analytical column may also necessitate adjustments of window times. These

retention time windows should be verified before each sequence and adjusted as necessary.

15.5 References:

15.41 SOP # EM 501.4

15.42 SOP # EM 501.5

Appendix 1

The Determination of Method Detection Limit (MDL) and Reporting Limit (RL) in Well Water

Spk\Analyte	DACT	ACET	DEA	Bromacil	Propazine	Diuron
blk	ND	ND	ND	ND	ND	ND
0.01ppb spk 1	0.00767	0.00721	0.00732	0.00736	0.00829	0.00810
0.01ppb spk 2	0.00744	0.01124	0.00707	0.00705	0.00835	0.00780
0.01ppb spk 3	0.00752	0.01142	0.00678	0.00686	0.00763	0.00713
0.01ppb spk 4	0.00825	0.00684	0.00796	0.00773	0.00840	0.00840
0.01ppb spk 5	0.00614	0.00826	0.00606	0.00555	0.00656	0.00610
0.01ppb spk 6	0.00834	0.00865	0.00777	0.00744	0.00798	0.00785
0.01ppb spk 7	0.00705	0.01003	0.00625	0.00620	0.00623	0.00729
SD	0.00075	0.00184	0.00072	0.00077	0.00089	0.00077
MDL	0.00235	0.00580	0.00226	0.00241	0.00280	0.00241
RL	0.05	0.03	0.02	0.02	0.02	0.02
Spk\Analyte	Hexazinone	Metribuzin	Simazine	Prometon	Atrazine	Norflurazon
Blk	ND	ND	ND	ND	ND	ND
0.01ppb spk 1	0.00801	0.00779	0.00733	0.00780	0.00821	0.00754
0.01ppb spk 2	0.00773	0.00750	0.00742	0.00793	0.00805	0.00692
0.01ppb spk 3	0.00697	0.00721	0.00717	0.00761	0.00732	0.00627
0.01ppb spk 4	0.00798	0.00798	0.00723	0.00786	0.00877	0.00743
0.01ppb spk 5	0.00632	0.00628	0.00541	0.00644	0.00662	0.00523
0.01ppb spk 6	0.00782	0.00796	0.00734	0.00764	0.00829	0.00720
0.01ppb spk 7	0.00728	0.00620	0.00547	0.00604	0.00599	0.00666
SD	0.00063	0.00076	0.00091	0.00076	0.00100	0.00080
MDL	0.00197	0.00238	0.00286	0.00240	0.00316	0.00252
RL	0.01	0.05	0.02	0.02	0.02	0.02

Spk\Analyte	Desmethyl Norflurazon	Prometryn	Tebuthiuron
Blk	ND	ND	ND
0.01ppb spk 1	0.00731	0.00828	0.00834
0.01ppb spk 2	0.00711	0.00838	0.00811
0.01ppb spk 3	0.00670	0.00770	0.00769
0.01ppb spk 4	0.00775	0.00861	0.00834
0.01ppb spk 5	0.00598	0.00672	0.00650
0.01ppb spk 6	0.00741	0.00824	0.00832
0.01ppb spk 7	0.00723	0.00651	0.00693
SD	0.00058	0.00084	0.00075
MDL	0.00181	0.00265	0.00236
RL	0.01	0.05	0.05

Spk\Analyte	Metabolite 104	Metabolite 106	Metabolite 107	Metabolite 108
Blk	ND	ND	ND	ND
0.1ppb spk 1	0.0984	0.0902	0.0929	0.0934
0.1ppb spk 2	0.0973	0.0969	0.0954	0.0943
0.1ppb spk 3	0.0906	0.0891	0.0882	0.0888
0.1ppb spk 4	0.0981	0.0957	0.0932	0.0968
0.1ppb spk 5	0.107	0.0959	0.0925	0.0918
0.1ppb spk 6	0.107	0.0994	0.0908	0.0923
0.1ppb spk 7	0.0926	0.0931	0.0921	0.0916
SD	0.00636	0.00371	0.00223	0.00249
MDL	0.02	0.01166	0.007	0.00783

Appendix 2
Triazine Method Validation -Sciex TQ Instrument

Analyte	Spike amount ppb	Set 1 % Recovery	Set 2 % Recovery	Set 3 % Recovery		%
					Mean:	86.7
DACT	0.1	98.9	88.6	94.4	SD:	9.0
	0.5	88.8	76.6	81.6	UCL:	114
	2.0	76.5	77.5	97.5	UWL:	105
					LWL:	68.7
					LCL:	59.7
					Mean:	75.7
ACET	0.1	73.6	74.3	76.4	SD:	8.1
	0.5	75.6	60.0	68.8	UCL:	100
	2.0	84.0	83.0	86.0	UWL:	92
					LWL:	59.5
					LCL:	51.3
					Mean:	78.6
DEA	0.1	80.0	75.6	82.8	SD:	6.8
	0.5	76.6	65.6	72.0	UCL:	99
	2.0	83.0	86.5	85.0	UWL:	92
					LWL:	65.0
					LCL:	58.2
					Mean:	79.6
Bromacil	0.1	79.4	87.7	81.5	SD:	7.3
	0.5	77.6	66.6	71.2	UCL:	102
	2.0	85.5	78.0	88.5	UWL:	94
					LWL:	64.9
					LCL:	57.6
					Mean:	84.5
Diuron	0.1	84.7	83.0	96.3	SD:	7.2
	0.5	82.0	70.4	80.2	UCL:	106
	2.0	90.0	88.5	85.5	UWL:	99
					LWL:	70.2
					LCL:	63.0

					Mean:	89.5
Hexazinone	0.1	83.1	80.7	84.2	SD:	7.0
	0.5	80.2	63.8	68.0	UCL:	111
	2.0	80.0	82.5	78.5	UWL:	104
					LWL:	75.6
					LCL:	68.6
					Mean:	77.3
Metribuzin	0.1	81.8	80.6	83.9	SD:	6.0
	0.5	74.8	64.8	71.2	UCL:	95
	2.0	79.5	80.0	79.00	UWL:	89
					LWL:	65.3
					LCL:	59.2
					Mean:	78.3
Simazine	0.1	80.9	84.7	88.1	SD:	6.6
	0.5	74.6	65.8	72.4	UCL:	98
	2.0	79.0	79.5	80.0	UWL:	92
					LWL:	65.0
					LCL:	58.4
					Mean:	79.6
Prometon	0.1	76.1	84.4	85.0	SD:	4.7
	0.5	78.2	70.8	75.6	UCL:	94
	2.0	81.5	81.5	83.0	UWL:	89
					LWL:	70.1
					LCL:	65.4
					Mean:	85.8
Atrazine	0.1	85.3	81.0	83.5	SD:	5.7
	0.5	76.0	69.4	73.8	UCL:	103
	2.0	78.0	84.5	81.0	UWL:	97.0
					LWL:	74.4
					LCL:	68.7
					Mean:	84
Norflurazon	0.1	87.6	83.8	88.4	SD:	6.3
	0.5	78.4	72.8	76.6	UCL:	103
	2.0	91.0	87.5	87.5	UWL:	96
					LWL:	71.1
					LCL:	64.9

					Mean:	82.4
Desmethyl	0.1	83.0	89.4	85.8	SD:	5.9
Norflurazon	0.5	83.0	69.6	78.6	UCL:	100
	2.0	86.5	86.0	79.5	UWL:	94
					LWL:	70.6
					LCL:	64.7
					Mean:	76.4
Propazine	0.1	79.0	77.5	79.5	SD:	5.5
	0.5	71.6	65.6	71.8	UCL:	93
	2.0	78.5	82.0	82.0	UWL:	87
					LWL:	65.3
					LCL:	59.8
					Mean:	77.8
Prometryn	0.1	81.4	79.5	83.3	SD:	5.0
	0.5	75.8	67.4	73.4	UCL:	93
	2.0	79.0	82.0	78.5	UWL:	88
					LWL:	67.9
					LCL:	62.9
					Mean:	89.4
Tebuthiuron	0.1	84.5	83.4	85.2	SD:	8.34
	0.5	85.6	71.2	73.0	UCL:	114
	2.0	85.0	87.0	77.0	UWL:	106
					LWL:	72.7
					LCL:	64.4

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Revision Log:

Date	What was revised? Why?
9/10/07	Add data for Desmethyl Norflurazon in well water
1/09/09	Add data for Tebuthiuron and metabolites in well water
1/27/20	Removed Waters and Finnigan validation results
1/27/20	Removed Section 11.2 Waters and Finnigan LCMS Instrument conditions Added ABSciex Linear Ion Trap Quadrupole LC/MS/MS Mass Spectrometer
1/27/20	Added Sciex 6500 validation results
5/13/20	Added Sciex MDL results