

1.0 INTRODUCTION

1.1 SCOPE

This method is utilized for the determination of (1) the chlorotriazine compounds atrazine, simazine and propazine and their applicable degradates G-30033, G-28279, and G-28273, (2) ametryn and prometryn and their applicable degradates GS-11354, GS-11355, and GS-26831, (3) S-metolachlor and its corresponding ethanesulfonic (ESA) and oxanillic acid (OA) degradates, and (4) mesotrione in various types of water samples at a lower limit of method validation (LLMV) of 0.05 ppb, except G-28273 which has a LLMV of 0.50 ppb. Thus, in this study the LLMV corresponds to the limit of quantification (LOQ). The limit of detection (LOD) is 10 pg for G-28273 and 1.0 pg for all the other analytes and is defined as the lowest concentration of standard injected (on-column injected amount) and used to construct the respective calibration plots. The types of water samples include laboratory de-ionized, ground, surface and treated (finished) water. However, this method may not be applicable for the listed thiomethyl-containing compounds in some treated (finished) waters due to their inherent chemical instability in the presence of various types of oxidizing agents used for water treatment (e.g., chlorination). The compounds included in this method and their chemical names are shown in Table 1 and their structures are shown in Figure 1. Sample preparation is minimal and final measurement is accomplished using direct aqueous injection (DAI) - electrospray ionization (ESI) - liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS).

The method described in this report represents an extension and improvement to a direct aqueous injection ESI-LC/MS/MS method reported previously¹⁻³. It provides a faster and relatively low cost alternative procedure for monitoring a broader range of analytes and minimizes even further the need for pre-injection sample manipulation without sacrificing meaningful quantification levels and analyte confirmatory capabilities.

1.2 PRINCIPLE

Typically, after thermal equilibration to ambient temperature, an 800 to 1000 μL portion of water sample is transferred to an HPLC vial (no further sample manipulation), followed by analysis using direct aqueous injection-ESI-LC/MS/MS. To achieve maximum instrumental sensitivity for all the targeted analytes when using an instrument with a relative lengthy duty cycle for mode switching (e.g. 700 milliseconds when using an API-4000 instrument), the positive and negative ion mode ESI analyses are performed separately. Thus, two separate injections (& sequences) are required for each sample: one in the positive ion mode and one in the negative ion mode. The LC operating parameters for each injection are identical. Dilution is required for samples containing residue concentration levels greater than 4.0 ppb since this is the upper limit of the calibration plots. Although usually not necessary, water samples can be diluted prior to analysis if suppression is observed and sufficient instrument sensitivity can be maintained at the LLMV (e.g., 500 μL of HPLC grade water can be added to 500 μL of water sample to reduce the observed suppression).

2.0 MATERIALS AND METHODS

2.1 APPARATUS

1. Brinkmann Eppendorf Pipettor Tips, 200 μ L tip, Fisher Scientific Catalog No. 022491334
2. Brinkmann Eppendorf Pipettor Tips, 1000 μ L tip, Fisher Scientific Catalog No. 022491351
3. Brinkmann Eppendorf Pipettor Tips, 5 mL, Fisher Scientific Catalog No. 022491385
4. Brinkmann Eppendorf Pipettor Tips, 10 mL, Fisher Scientific Catalog No. 05-403-119
5. Brinkmann Eppendorf 2100 Research Series Pipettor, range 20 - 200 μ L, Fisher Scientific Catalog No. 05-402-89
6. Brinkmann Eppendorf 2100 Research Series Pipettor, range 100 - 1000 μ L, Fisher Scientific Catalog No. 05-402-90
7. Brinkmann Eppendorf 2100 Research Series Pipettor, range 500 - 5000 μ L, Fisher Scientific Catalog No. 05-402-91
8. Brinkmann Eppendorf 2100 Research Series Pipettor, range 1 - 10 mL, Fisher Scientific Catalog No. 05-403-121
9. Fisher Variable-Speed Touch Mixer, Fisher Scientific, Catalog No. 12-811-10
10. Disposable Pasteur Pipets, 146 mm, Fisher Scientific, Catalog No. 22-230-482
11. Auto-sampler vials, Alltech Associates Inc., Catalog No. 99167
12. Closures for auto-sampler vials, Alltech Associates Inc., Catalog No. 99082
13. HPLC column filter, MAC-MOD Analytical Inc., P/N MMCS210
14. HPLC column: Agilent Zorbax SB-Aq, 4.6 x 50 mm, 3.5 μ m, Agilent Catalog No. 835975-914

Note: Other manufacturers' equivalents of the items listed above can be used but this must be demonstrated by obtaining acceptable procedural recoveries. In general, Class A glass volumetric flasks and pipettes were utilized for standard solution preparation and are not individually listed.

2.2 REAGENTS

1. Water, HPLC grade, Fisher Scientific, Catalog No. W5SK-4
2. Methanol, HPLC grade, Fisher Scientific, Catalog No. A452SK-4
3. Acetonitrile, HPLC grade, Fisher Scientific, Catalog No. A998SK-4
4. Formic Acid, 88%, HPLC grade, Fisher Scientific, Catalog No. A118P-500

Note: Equivalent reagents obtained from other manufacturers can be used instead of the reagents described above; however, it is important to verify the quality of the solvents to insure there are no interfering contaminants.

5. Acetonitrile/HPLC H₂O, 5/95 (v/v); prepared by mixing 50 mL of HPLC grade Acetonitrile and 950 mL of HPLC water.
6. "0.1%" Formic Acid in HPLC H₂O; prepared by mixing 1.0 mL of formic acid with 1000 mL of HPLC grade Water.
7. "0.1%" Formic Acid in HPLC Acetonitrile; prepared by mixing 1.0 mL of formic acid with 1000 mL of HPLC grade acetonitrile.
8. The standards used in this study were supplied by the Analytical and Product Chemistry Department and Chemical Synthesis Group of Syngenta Crop Protection, Inc.

Atrazine
(G-30027) CAS RN: 1912-24-9
 CAS Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-N'-(1-methylethyl)-
 Syngenta standard code: S96-1870
 Purity: 97.9%
 Storage Condition: Frozen

G-30033 CAS RN: 6190-65-4
 CAS Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N-(1-methylethyl)-
 Syngenta standard code: S92-1618
 Purity: 94%
 Storage Condition: Frozen

G-28279 CAS RN: 1007-28-9
 CAS Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-
 Syngenta standard code: S87-1225
 Purity: 96%
 Storage Condition: Frozen

G-28273 CAS RN: 3397-62-4
 CAS Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-
 Syngenta standard code: S87-1195
 Purity: 97%
 Storage Condition: Frozen

Simazine (G-27692)	CAS RN: 122-34-9 CAS Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-diethyl- Syngenta standard code: S86-1071 Purity: 99.7% Storage Condition: Frozen
Propazine (G-30028)	CAS RN: 139-40-2 CAS Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(1-methylethyl)- Syngenta standard code: S04-2866 Purity: 98.5% Storage Condition: Frozen
Ametryn (G-34162)	CAS RN: 834-12-8 CAS Name: 1,3,5-Triazine-2,4-diamine, N-ethyl-N'-(1-methylethyl)-6-(methylthio)- Syngenta standard code: 410430 Purity: 98.3% Storage Condition: Frozen
Prometryn (G-34161)	CAS RN: 7287-19-6 CAS Name: 1,3,5-Triazine-2,4-diamine, N,N'-bis(1-methylethyl)-6-(methylthio)- Syngenta standard code: S89-1411 Purity: 99.7% Storage Condition: Frozen
GS-11354	CAS RN: 4147-57-3 CAS Name: 1,3,5-Triazine-2,4-diamine, N-(1-methylethyl)-6-(methylthio)- Syngenta standard code: S85-0804 Purity: 97% Storage Condition: Frozen
GS-11355	CAS RN: 4147-58-4 CAS Name: 1,3,5-Triazine-2,4-diamine, N-ethyl-6-(methylthio)- Syngenta standard code: DAH-XXXI-29-1 Purity: 98% Storage Condition: Frozen

GS-26831	<p>CAS RN: 5397-01-3 CAS Name: 1,3,5-Triazine-2,4-diamine, 6-(methylthio)- Syngenta standard code: S85-0802 Purity: 99% Storage Condition: Frozen</p>
S-Metolachlor (CGA-77102)	<p>CAS RN: 87392-12-9 CAS Name: Acetamide, 2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl]- Syngenta standard code: S03-2803 Purity: 97.9% Storage Condition: Frozen</p>
Metolachlor-ESA (CGA-354743)	<p>CAS RN: 171118-09-5 CAS Name: Ethanesulfonic acid, 2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxo-, sodium salt Syngenta standard code: DAH-XXVII-76 Purity: 95.9% Storage Condition: Frozen</p>
Metolachlor-OA (CGA-51202)	<p>CAS RN: 152019-73-3 CAS Name: Acetic acid, [(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]oxo- Syngenta standard code: DAH-XXVIII-40 Purity: 99.7% Storage Condition: Frozen</p>
Mesotrione (ZA-1296)	<p>CAS RN: 104206-82-8 CAS Name: 1,3-Cyclohexanedione, 2-[4-(methylsulfonyl)-2-nitrobenzoyl]- Syngenta standard code: S01-2518 Purity: 93.5% Storage Condition: Frozen</p>

2.3 PREPARATION OF ANALYTICAL AND FORTIFICATION STANDARDS

2.3.1 Standard Preparation

Individual stock solutions at the 100 µg/mL concentration level are prepared by dissolving 10.0 mg of each compound into individual 100-mL volumetric flasks followed by dilution to the mark with methanol (5.0 mg of G-28273, G-28279, or G-30033 are used to give 50 µg/mL concentration stock standards due to solubility issues). The amounts weighed for each compound should be corrected for its respective % purity. A mixed standard solution at the 5.0 µg/mL concentration level is prepared by mixing 5.0 mL of each stock standard (10 mL for the G-28273, G-28279, and G-30033 stock standards) into a 100-mL volumetric flask and filling to the mark with HPLC grade methanol. Serial dilutions of this mixed standard solution are prepared in 5/95 (v/v) acetonitrile/HPLC water to create mixed working standards in the appropriate concentration range starting with a standard at half the concentration equivalent to the LLMV and ending at an upper concentration equivalent to 4.0 ppb. These mixed working standards are used for both analytical and fortification purposes.

All standard solutions are stored in amber glass bottles in a refrigerator at approximately 4°C to prevent concentration changes due to photodecomposition of the analytes or solvent evaporation. Fresh mixed working standard solutions are typically prepared every three months and fresh mixed stock standard solutions are prepared every six months. In general, the expiration dates of the mixed stock and working standard solutions are not extended beyond the expiration date of the solid standard unless stability considerations or other pertinent information dictate otherwise.

2.3.2 Fortification

Water samples can be fortified for procedural recovery purposes by judicious choice of working solution concentration and volume. For example, the addition of 1.0-mL of a 0.0005 µg/mL working standard solution to a 9.0-mL aliquot portion of water sample produces a 0.050 ppb fortification of all the analytes. The fortification levels used in each set of analyses can vary but should always include one recovery sample at the 0.050 ppb concentration level (0.50 ppb for G-28273) when necessary to establish the method LLMV or LOQ.

2.4 ANALYTICAL PROCEDURE

2.4.1 Sample Storage and Temperature Re-Equilibration

Water samples are typically received chilled and then stored at refrigerator temperature (4°C) until removed for analysis. The sample should be allowed to re-equilibrate to room temperature before removing and transferring a portion to an injection vial for analysis. If necessary, filter or centrifuge the water sample prior to analysis.

2.4.2 Sample Preparation

1. Transfer approximately 1 mL of water sample into an auto-sampler vial.
2. Load the sample vials onto the injection tray for DAI-ESI-LC/MS/MS analysis.
3. Perform two injection sequences for the positive and negative ESI detections separately.

Note: The water sample should be subjected to centrifugation prior to analysis if the appearance of the water sample is not clear or if particulates are visible. Dilution with HPLC grade water and reanalysis will be required when (1) samples contain residues >4.0 ppb and/or (2) samples show evidence of suppression.

2.5 INSTRUMENTATION FOR DAI-ESI-LC/MS/MS

2.5.1 Description and Operating Conditions

Refer to Table 2 for the ESI-LC/MS/MS operating parameters.

2.5.2 Calibration and Standardization

1. The mass spectrometer should undergo periodic (bi-annual is usually sufficient) mass calibration of both quadrupole analyzers using polyethylene glycols (PEG) of varying molecular weight or manufacturer recommended tuning standards. More frequent mass calibration is required only if drift from the expected masses is excessive.
2. The instrument is tuned by infusing the standard (typically at a concentration of 0.5 ng/ μ L) directly into the source (ESI) at a flow rate of 10 μ L/minute individually. The respective precursor and product ion pairs for each analyte are shown in Table 2.
3. Standardize the system using the conditions listed in Table 2 by injecting 50- μ L portions of standard at different concentration levels over the range of 0.020 to 4.0 pg/ μ L (a calibration range of 1.0 to 200 pg injected). The Analyst data system software allows one to create a calibration plot (e.g. linear regression) from the standard concentrations and the measured peak responses obtained for each analyte. Representative MRM chromatograms at LOD level (the top chromatography trace) are shown in Figure 2.

Note: The standard calibration range can be adjusted depending on the range of analyte concentrations expected. However, the dynamic range should be limited to two orders of magnitude of the lowest standard injected in order to maintain accuracy.

4. During routine monitoring, the sequence of standards injected is typically at the same concentration levels as in the previous set of sample analyses. Thus, after each sequence the results for the new standards are used to update the calibration table for each analyte. After a new calibration table has been generated, the data system is programmed to re-analyze the data files of the sequence and provide the amounts found in the injected sample volumes based on the new calibration curves. Typical calibration plot of atrazine is presented in Figure 3. The “pg found” values can be manually or automatically transferred to an applicable worksheet such that the residue in units of ppb can be calculated using the equations described in Section 2.9.

2.6 INTERFERENCES

Interferences are generally not significant due to the highly selective nature of MS/MS analysis. If suppression or enhancement issues are encountered, the samples can be diluted further prior to injection.

2.7 CONFIRMATORY TECHNIQUES

Analysis using MS/MS is confirmatory.

2.8 MODIFICATIONS AND POTENTIAL PROBLEMS

1. Average procedural recoveries may fluctuate due to varying quantities of dissolved water sample components, but average recoveries should fall within the range of 70-120%.
2. The quality of the calibration plot can deteriorate if the ESI source becomes too dirty. Thus, inspection of each calibration plot needs to be performed in order to maintain accurate and reliable quantification of each set of samples.
3. The chromatographic conditions employed were not designed to resolve the stereoisomers in racemic mixtures.

2.9 DETERMINATION OF SAMPLE RESIDUES

2.9.1 Samples

Calibrate the instrument with injections of at least five (or more) concentration levels of the mixed standard solutions and generate a calibration curve for each analyte. Quality control (QC) standards are injected intermittently throughout the set to evaluate system stability. The data system uses the calibration plot and the respective peak responses (e.g., area, height) to calculate the amount of analyte in a sample. If the analyte response in the sample exceeds 10% of the response for the highest concentration standard injected, the sample should be diluted and re-injected.

2.9.2 Procedural Recoveries

Each set of sample analyses is validated by acquiring procedural recovery data within EPA's acceptance criteria of mean recoveries from 70 to 120% and standard deviations of $\leq 20\%$. Recovery samples are corrected for control values when detected.

2.9.3 Calculations

Calculate the concentration of analytes in units of parts per billion (ppb) from equation (1):

$$(1) \quad \text{ppb of analyte} = \frac{\text{picogram of analyte found (pg)}}{\text{amount of sample injected (mg)}} \times \frac{1}{R}$$

where R is the recovery factor expressed in decimal form (i.e., 1.0 = 100%) and is calculated from equation (3). For $R > 1$, use a factor of 1.0.

The amount of sample injected is calculated from equation (2).

$$(2) \quad \text{amount of sample injected} = V_1 \left(\frac{1 \text{ mL}}{1000 \mu\text{L}} \right) \left(\frac{1 \text{ g}}{1 \text{ mL}} \right) \left(\frac{1000 \text{ mg}}{1 \text{ g}} \right)$$

where grams of sample extracted is the grams of sample used in extraction (for water, 1.0 mL = 1.0 g), V_1 is the volume (μL) of sample injected.

The recovery factor, expressed as a percentage (R%), is calculated from fortification experiments and is presented in equation (3).

$$(3) \quad R\% = \left(\frac{\text{ppb of analyte found} - \text{ppb of analyte found in control}}{\text{ppb of analyte added}} \right) \times 100$$

3.0 RESULTS AND DISCUSSION

3.1 Test Systems

Four types of water were evaluated in this study: deionized, ground (well), surface and treated (finished) waters. The deionized (Picopure purification system) water used in this study was collected in Syngenta laboratory L-2021. The ground (well) and treated water (finished tap water) used in this validation study were collected from two separate residential water supplies. The surface water was collected from a local municipality reservoir. No further treatments of any kind were made to these samples prior to use in this validation. After collection, the water samples were stored in amber glass bottles under refrigerated temperature conditions.

4.0 CONCLUSION

Analytical Method T001681-06 is a valid and accurate procedure for the determination of atrazine, simazine, propazine, G-30033, G-28279, G-28273, ametryn, prometryn, GS-11354, GS-11355, GS-26831, S-metolachlor, metolachlor-ESA, metolachlor-OA and mesotrione in ground, surface, and de-ionized water at a LLMV of 0.050 ppb (0.50 ppb for G-28273). This method is also valid and accurate for the analysis of treated (finished) water for atrazine, simazine, propazine, G-30033, G-28279, G-28273, S-metolachlor, metolachlor-ESA and metolachlor-OA. Water samples containing oxidizing agents (e.g., finished tap water) are not expected to contain ametryn, prometryn, GS-11354, GS-11355, GS-26831, or mesotrione since these sulfur containing compounds are oxidized to other, yet unknown, species.

The method is very cost effective since no sample manipulation, other than transfer to an injection vial, is required prior to instrumental analysis. About 100 injections can be performed overnight (within 12 hours period).

TABLES AND FIGURES SECTION

TABLE 1. CHEMICAL NAME, CAS, AND OTHER RELEVANT INFORMATION FOR THE ANALYTES

Common Name	CAS Name	CAS RN	MW	MF
Atrazine	1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-N'-(1-methylethyl)-	1912-24-9	215.7	C ₈ H ₁₄ ClN ₅
G-30033	1,3,5-Triazine-2,4-diamine, 6-chloro-N-(1-methylethyl)-	6190-65-4	187.6	C ₆ H ₁₀ ClN ₅
G-28279	1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-	1007-28-9	173.6	C ₅ H ₈ ClN ₅
G-28273	1,3,5-Triazine-2,4-diamine, 6-chloro-	3397-62-4	145.6	C ₃ H ₄ ClN ₅
Simazine (G-27692)	1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-diethyl-	122-34-9	201.7	C ₇ H ₁₂ ClN ₅
Propazine (G-30028)	1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(1-methylethyl)-	139-40-2	229.7	C ₉ H ₁₆ ClN ₅
Ametryn (G-34162)	1,3,5-Triazine-2,4-diamine, N-ethyl-N'-(1-methylethyl)-6-(methylthio)-	834-12-8	227.3	C ₉ H ₁₇ N ₅ S
Prometryn (G-34161)	1,3,5-Triazine-2,4-diamine, N,N'-bis(1-methylethyl)-6-(methylthio)-	7287-19-6	241.4	C ₁₀ H ₁₉ N ₅ S
GS-11354	1,3,5-Triazine-2,4-diamine, N-(1-methylethyl)-6-(methylthio)-	4147-57-3	199.3	C ₇ H ₁₃ N ₅ S
GS-11355	1,3,5-Triazine-2,4-diamine, N-ethyl-6-(methylthio)-	4147-58-4	185.3	C ₆ H ₁₁ N ₅ S
GS-26831	1,3,5-Triazine-2,4-diamine, 6-(methylthio)-	5397-01-3	157.2	C ₄ H ₇ N ₅ S
S-Metolachlor (CGA-77102)	Acetamide, 2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl]-	87392-12-9	283.8	C ₁₅ H ₂₂ ClNO ₂
Metolachlor-ESA (CGA-354743)	Ethanesulfonic acid, 2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxo-, sodium salt	171118-09-5	351.4	C ₁₅ H ₂₂ NNaO ₅ S
Metolachlor-OA (CGA-51202)	Acetic acid, [(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]oxo-	152019-73-3	279.3	C ₁₅ H ₂₁ NO ₄
Mesotrione (ZA-1296)	1,3-Cyclohexanedione, 2-[4-(methylsulfonyl)-2-nitrobenzoyl]-	104206-82-8	339.3	C ₁₄ H ₁₃ NO ₇ S

TABLE 2. DAI-ESI-LC/MS/MS OPERATING PARAMETERS

HPLC: Perkin Elmer Series 200
 Column: Zorbax SB-AQ, 4.6 x 50 mm, 3.5 µm particle size (Agilent P/N 835975-914)
 Column Filter: ColumnSaver (MAC-MOD P/N MMCS210)
 Flow rate: 0.50 mL/min (see details below)
 Column Temperature: 25°C
 Injection volume: 50 µL
 Mobile Phase: A = 0.1% Formic Acid in Water,
 B = 0.1% Formic Acid in Acetonitrile

<u>Time (min.)</u>	<u>% A</u>	<u>% B</u>	
0.0	95	5	<p>Linear Gradient @ 0.5 mL/min</p> <p>Stay at 95%B @ 0.5 mL/min</p> <p>Step to 5%B @ 1.0 mL/min</p> <p>Stay at 5%B @ 0.5 mL/min</p>
2.0	5	95	
3.0	5	95	
4.0	95	5	
6.0	95	5	

Concentration range used for calibration plots: 1.0 pg – 200 pg injected
 Calibration standard solution in 5/95 Acetonitrile/H₂O: 4.0, 2.0, 1.0, 0.5, 0.2, 0.1, 0.05 and 0.02 pg/µL

Note: the calibration standard range can be adjusted depending on the targeted range of analysis, however, the dynamic range should be limited to two orders of magnitude of the lowest standard injected in order to maintain the accuracy of the analysis.

MS/MS Conditions & Parameters on API 4000

Instrumentation: Applied Biosystems/MDS Sciex
 API 4000 triple quadrupole
 Software: Analyst Version 1.4.1
 Ionization: Electrospray (Positive and Negative mode)
 Desolvation Temperature (TEM): 700°C
 IonSpray Voltage: 5500 volts in positive mode
 4500 volts in negative mode

**TABLE 2. DAI-ESI-LC/MS/MS OPERATING PARAMETERS
(Continued)**

Acquisition parameters:

CUR: 10	Scan Type: MRM
GS1: 50	Polarity: Positive and Negative
GS2: 50	Resolution Q1: Unit
CAD: 2	Resolution Q2: Unit
EP: +10/-10 (+/- mode)	Ion Source: Turbo Spray

MRM Transition and Corresponding Parameters for the Analytes

Analyte	MRM Transition ¹	Ion Mode	Dwell (msec)	DP	CE	CXP	Retention Time (min.) ²
G-28273	145.7 > 104.0	+	40	52	27	12	1.91
GS-26831	158.2 > 110.0	+	40	60	25	10	1.85
G-28279	174.2 > 96.2	+	40	75	24	8	2.16
GS-11355	186.1 > 96.0	+	40	80	30	9	2.01
G-30033	188.3 > 104.0	+	40	40	35	8	2.29
GS-11354	200.3 > 158.0	+	40	70	24	14	2.10
Simazine	202.1 > 132.1	+	40	53	27	8	2.48
Atrazine	216.1 > 174.2	+	40	70	25	11	2.60
Ametryn	228.2 > 186.1	+	40	65	25	20	2.28
Prometryn	242.0 > 158.2	+	40	70	32	12	2.38
Propazine	230.2 > 145.9	+	40	66	31	12	2.70
S-Metolachlor	284.2 > 176.3	+	40	55	40	17	2.87
Metolachlor-ESA	328.2 > 121.0	-	100	-114	-32	-9	2.35
Metolachlor-OA	278.1 > 206.3	-	100	-62	-16	-9	2.44 – 2.57 ³
Mesotrione	338.0 > 290.8	-	100	-45	-10	-17	2.55

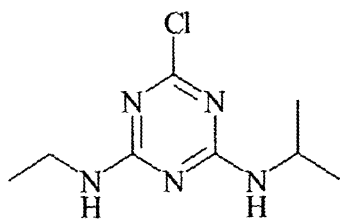
¹ If significant interferences are encountered during sample analysis, alternate product ions can be used for each MRM transition by optimizing the cone voltage and collision energy for the newly selected ion.

² The retention time may vary depend upon chromatographic conditions and systems.

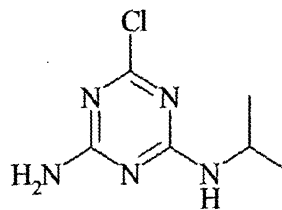
³ Typically two peaks; integrate both peaks for quantification.

Note: The optimum operating parameters of each ESI-LC/MS/MS system must be established prior to routine analysis and may differ from those shown here due to differences in instrumentation and differences by manufacturer.

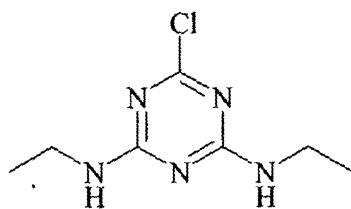
FIGURE 1. STRUCTURE OF ANALYTES



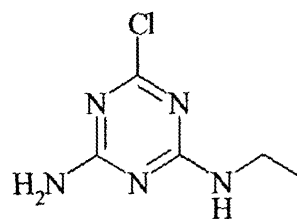
Atrazine
MW 215.7



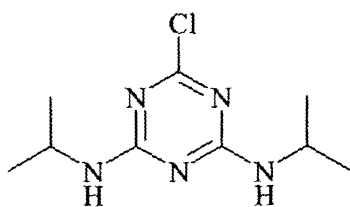
G-30033
MW 187.6



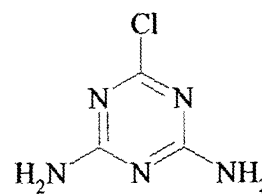
Simazine
MW 201.7



G-28279
MW 173.6

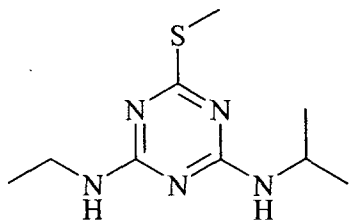


Propazine
MW 229.7

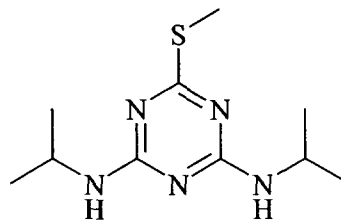


G-28273
MW 145.6

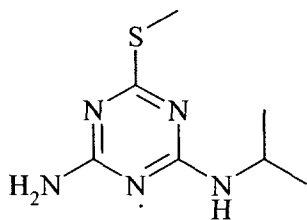
FIGURE 1. STRUCTURE OF ANALYTES(Continued)



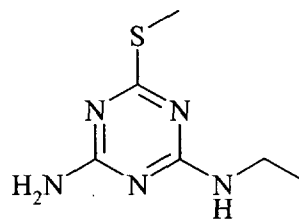
Ametryn
MW 227.3



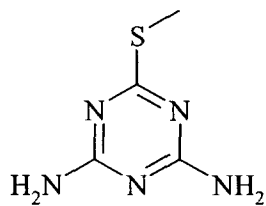
Prometryn
MW 241.4



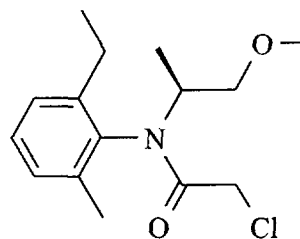
GS-11354
MW 199.3



GS-11355
MW 185.3

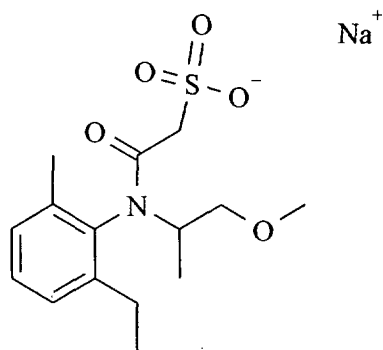


GS-26831
MW 157.2

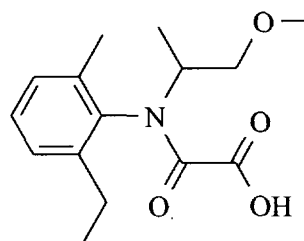


S-Metolachlor
MW 283.8

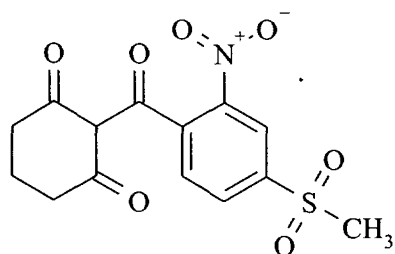
FIGURE 1. STRUCTURE OF ANALYTES (Continued)



Metolachlor-ESA
MW 351.4



Metolachlor-OA
MW 279.3



Mesotrione
MW 339.3

Note: The metolachlor-ESA standard was supplied as a salt form.