Designation: D8025 – 23

Standard Test Method for Determination of Select Pesticides in Water by Multiple Reaction Monitoring Liquid Chromatography Tandem Mass Spectrometry[1]

This standard is issued under the fixed designation D8025; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers a method for analysis of selected pesticides in a water matrix by filtration followed with liquid chromatography/electrospray ionization tandem mass spectrometry analysis. The samples are prepared in 20 % methanol, filtered, and analyzed by liquid chromatography/tandem mass spectrometry. This method was developed for an agricultural run-off study, not for low level analysis of pesticides in drinking water. This method may be modified for lower level analysis. The analytes are qualitatively and quantitatively determined by this method. This method adheres to multiple reaction monitoring (MRM) mass spectrometry.

1.2 A full collaborative study to meet the requirements of Practice D2777 has not been completed. This standard contains single-operator precision and bias based on single-operator data. Publication of standards that have not been fully validated is done to make the current technology accessible to users of standards, and to solicit additional input from the user community.

1.3 A reporting limit check sample (RLCS) is analyzed during every batch to ensure that if an analyte was present in a sample at or near the reporting limit it would be positively identified and accurately quantitated within set quality control limits. A method detection limit (MDL) study was not done for this method, the method detection limits would be much lower than the reporting limits in this method and would be irrelevant. A RLCS was determined to be more applicable for this standard. If this method is adapted to report much lower or near the MDL then a MDL study would be warranted.

1.4 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 The Reporting Range for the target analytes are listed in Table 1.

1.5.1 The reporting limit in this test method is the minimum value below which data are documented as non-detects. The reporting limit is calculated from the concentration of the Level 1 calibration standard as shown in Table 6 after taking into account an 8 mL water sample volume and a final diluted sample volume of 10 mL (80 % water/20 % methanol).

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

E2554 Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

TABLE 1 Reporting Range

Analyte	Reporting Ranges, (ng/L)
2,4-D	250–10 000
Acetochlor	250–10 000
Alachlor	250–10 000
Aldicarb	250–10 000
Atrazine	62.5–2 500
Desethylatrazine	62.5–2 500
Desisopropylatrazine	125–5 000
Azoxystrobin	31.2–1 250
Bentazon	250–10 000
Carbaryl	250–10 000
Chlorpyrifos	250–10 000
Clopyralid	25 000–1 000 000
Clothianidin	62.5–2 500
Diazinon	62.5–2 500
Dicamba	12 500–500 000
Fipronil	250–10 000
Imidacloprid	62.5–2 500
Malathion	125–5 000
Methomyl	250–10 000
Metolachlor	62.5–2 500
Metribuzin	125–5 000
Picloram	6 250–250 000
Propiconazole	62.5–2 500
Simazine	62.5–2 500
Tebuconazole	62.5–2 500
Thiamethoxam	62.5–2 500
Triclopyr	1 250–5 000

2.2 *Other Document:*

EPA publication SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods[3]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *batch QC, n*—all the quality control samples and standards included in an analytical procedure.

3.2.2 *independent reference material, IRM, n*—a material of known purity and concentration obtained either from the National Institute of Standards and Technology (NIST) or other reputable supplier.

3.2.2.1 *Discussion*—The IRM must be obtained from a different lot of material than is used for calibration.

3.2.3 *reporting limit, RL, n*—the minimum concentration below which data are documented as non-detects.

3.2.4 *reporting limit check sample, RLCS, n*—a sample used to ensure that if the analyte was present at the reporting limit, it would be confidently identified.

3.3 *Acronyms:*

3.3.1 *CCC, n*—Continuing Calibration Check

3.3.2 *CRW, n*—Chicago River Water

3.3.3 *IC, n*—Initial Calibration

3.3.4 *LC, n*—Liquid Chromatography

3.3.5 *LCS/LCSD, n*—Laboratory Control Sample/Laboratory Control Sample Duplicate

3.3.6 *MDL, n*—Method Detection Limit

3.3.7 *MeOH, n*—Methanol

3.3.8 *mM, n*—millimolar, 1×10^{-3} moles/L

3.3.9 *MRM, n*—Multiple Reaction Monitoring

3.3.10 *MS/MSD, n*—Matrix Spike/Matrix Spike Duplicate

3.3.11 *NA, adj*—Not Available

3.3.12 *ND, n*—non-detect

3.3.13 *P&A, n*—Precision and Accuracy

3.3.14 *ppt, n*—parts-per-trillion

3.3.15 *QA, adj*—Quality Assurance

3.3.16 *QC, adj*—Quality Control

3.3.17 *RL, n*—Reporting Limit

3.3.18 *RLCS, n*—Reporting Limit Check Sample

3.3.19 *RSD, n*—Relative Standard Deviation

3.3.20 *RT, n*—Retention Time

3.3.21 *SDS, n*—Safety Data Sheets

3.3.22 *SRM, n*—Single Reaction Monitoring

3.3.23 *SS, n*—Surrogate Standard

3.3.24 *TC, n*—Target Compound

3.3.25 *VOA, n*—Volatile Organic Analysis

4. Summary of Test Method

4.1 The operating conditions presented in this standard have been successfully used in the determination of the select pesticides in water; however, this standard is intended to be performance based and alternative operating conditions can be used to perform this method provided data quality objectives are attained.

4.2 For pesticide analysis, samples are shipped to the lab on ice and analyzed within 14 days of collection. A sample (8 mL) is transferred to an amber VOA vial, an isotopically labeled pesticide surrogate mix is added to all samples followed by a pesticide spike solution which is added only to the Reporting Limit Check Samples, Laboratory Control and Matrix Spike samples before the addition of methanol. Then 2 mL of methanol is added to each sample and hand shaken or vortexed for 1 min. The samples are then filtered through a PTFE membrane syringe driven filter unit and then analyzed by LC/MS/MS. All concentrations reported only to the reporting limit.

4.3 The analysis of the sample requires two separate analysis methods, one using the LC gradient conditions in Table 2 with the Methanol/Water/Ammonium Formate and the second using the LC gradient conditions in Table 3 with the Methanol/Water/Formic acid. Each analysis set is to be analyzed separately in two different complete sample sequences which includes the exact same samples and may even include the same calibration level standards. The only analytes reported from the formic acid run conditions are 2,4-D, Clopyralid,

[3] Available from National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA, 22161 or at http://www.epa.gov/epawaste/hazard/testmethods/index.htm

TABLE 2 Gradient Conditions for Neutral Liquid Chromatography

Time (min)	Flow (mL/min)	Percent 95 % Water: 5 % Methanol	Percent Methanol	Percent 200 mM Ammonium Formate (95 % Water: 5 % Methanol)
0	0.3	95	0	5
1.5	0.3	95	0	5
9	0.3	0	95	5
12	0.3	0	95	5
13	0.3	95	0	5
16	0.3	95	0	5

TABLE 3 Gradient Conditions for Acidic Liquid Chromatography

Time (min)	Flow (mL/min)	Percent 95 % Water: 5 % Methanol	Percent Methanol	Percent 4 % Formic Acid (95 % Water: 5 % Methanol)
0	0.3	95	0	5
1.5	0.3	95	0	5
6	0.3	0	95	5
9	0.3	0	95	5
10	0.3	95	0	5
13	0.3	95	0	5

Dicamba, Picloram, Triclopyr, 2,4-D (Ring-D3) and Dicamba-D3, the rest of the analytes are reported from the ammonium formate analysis run.

4.4 The pesticides are identified by comparing the single reaction monitoring (SRM) transition and its confirmatory SRM transitions if correlated to the known standard SRM transition (Tables 4 and 5) and quantitated utilizing an external calibration. The final report issued for each sample lists the concentration of pesticides, if detected, or RL, if not detected, in ng/L and surrogate recovery.

5. Significance and Use

5.1 Pesticides may be used in various agricultural and household products. These products may enter waterways at low levels through run-off or misuse near water resources. Hence, there is a need for quick, easy and robust method to determine pesticide concentration in water matrices for understanding the sources and concentration levels in affected areas.

5.2 This method has been single-laboratory validated in reagent water and surface waters (Tables 12-14).

6. Interferences

6.1 All glassware is washed in hot water with detergent and rinsed in hot water followed by distilled water. The glassware is then dried and heated in an oven at 250 °C for 15 min to 30 min. All glassware is subsequently rinsed or sonicated, or both, with acetone, n-propanol, acetonitrile, or a combination thereof.

6.2 All reagents and solvents should be pesticide residue purity or higher to minimize interference problems.

6.3 Matrix interferences may be caused by contaminants in the sample. The extent of matrix interferences can vary considerably depending on variations in the sample matrices.

7. Apparatus

7.1 *LC/MS/MS System:*

7.1.1 *Liquid Chromatography System*—A complete LC system is required in order to analyze samples, this should include a sample injection system, an autosampler, a solvent pumping system capable of mixing solvents, a sample compartment capable of maintaining required temperature and a temperature controlled column compartment. A LC system that is capable of performing at the flows, pressures, controlled temperatures, sample volumes, and requirements of the standard must be used.

7.1.2 *Analytical Column*[4]—A reverse phase C18 particle column was used to develop this test method. Any column that achieves adequate resolution may be used. The retention times and order of elution may change depending on the column used and need to be monitored.

7.2 *Tandem Mass Spectrometer System*—A MS/MS system capable of multiple reaction monitoring (MRM) analysis or any system that is capable of meeting the requirements in this standard must be used. Electrospray ionization is utilized for this standard.

7.3 *Adjustable Volume Pipettes*—10 µL, 20 µL, 100 µL, 1000 µL, 5 mL, and 10 mL.

7.3.1 *Discussion*—Any pipette may be used providing the data generated meets the performance of the standard.

7.3.2 *Pipette Tips*—Polypropylene pipette tips free of release agents or low retention coating of various sizes.

7.4 *Class A Volumetric Glassware.*

7.5 *Filtration Device:*

7.5.1 *Hypodermic Syringe*—A luer-lock tip glass syringe capable of holding a syringe driven filter unit.

[4] A Waters Acquity (a trademark of the Waters Corporation, Milford, MA) UPLC BEH C18, 2.1 mm × 100 mm and 1.7 µm particle size column was used, if you are aware of an alternative column that meets the performance of the standard, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

TABLE 4 SRM Ions and Analyte-Specific Mass Spectrometer Parameters

Chemical	Primary/ Confirmatory	MRM Transition	ESI Mode Neg/Pos	Cone (V)	Collision (eV)
2,4-D[A]	Primary	218.9→160.9	Neg	20	14
	Confirmatory	220.9→162.9			14
Acetochlor	Primary	270.1→224.1	Pos	20	10
	Confirmatory	270.1→148			18
Alachlor	Primary	270.1→162	Pos	30	12
	Confirmatory	270.1→238.1			18
Aldicarb	Primary	213→88.9	Pos	20	16
	Confirmatory	213→116			12
Atrazine	Primary	216.1→174	Pos	20	18
	Confirmatory	216.1→95.9			24
Desethylatrazine	Primary	188→146	Pos	30	16
	Confirmatory	188→78.8			22
Desisopropylatrazine	Primary	174→96	Pos	30	16
	Confirmatory	174→78.8			16
Azoxystrobin	Primary	404.2→372.2	Pos	20	14
	Confirmatory	404.2→344.2			24
Bentazon	Primary	239→197	Pos	20	20
	Confirmatory	239→175			20
Carbaryl	Primary	202.1→145	Pos	10	10
	Confirmatory	202.1→127			25
Chlorpyrifos	Primary	350→197.9	Pos	30	20
	Confirmatory	350→322			11
Clopyralid[A]	Primary	189.9→145.9	Neg	5	10
	Confirmatory	191.9→147.9			10
Clothianidin	Primary	250→169	Pos	20	15
	Confirmatory	250→131.9			11
Diazinon	Primary	305.1→169	Pos	30	20
	Confirmatory	305.1→153			20
Dicamba[A]	Primary	218.9→174.9	Neg	10	8
	Confirmatory	220.9→176.9			8
Fipronil	Primary	435→330	Pos	30	15
	Confirmatory	435→318			23
Imidacloprid	Primary	256.1→209.1	Pos	30	17
	Confirmatory	256.1→175			23
Malathion	Primary	331.1→127	Pos	20	12
	Confirmatory	331.1→285			6
Methomyl	Primary	163→87.9	Pos	10	10
	Confirmatory	163→105.9			11
Metolachlor	Primary	284.1→252.1	Pos	30	16
	Confirmatory	284.1→176.1			25
Metribuzin	Primary	215.1→187.1	Pos	30	16
Picloram[A]	Primary	240.9→196.9	Neg	10	11
	Confirmatory	238.9→194.9			11
Propiconazole	Primary	342.1→158.9	Pos	30	22
	Confirmatory	342.1→205			17
Simazine	Primary	202→132	Pos	40	17
	Confirmatory	202→124			17
Tebuconazole	Primary	308.2→70	Pos	40	20
	Confirmatory	308.2→125			28
Thiamethoxam	Primary	292.1→211.1	Pos	20	12
	Confirmatory	292.1→131.9			20
Triclopyr[A]	Primary	253.9→195.9	Neg	10	12
	Confirmatory	253.9→217.9	Neg	10	6
		Surrogates			
2,4-D (Ring-D3)[A]	Primary	221.9→163.8	Neg	20	14
Atrazine (ethyl-D5)	Primary	221.1→179	Pos	20	17
Desethylatrazine (iso-propyl-D7)	Primary	195→146.9	Pos	20	18
Desisopropylatrazine (ethyl-D5)	Primary	179→100.9	Pos	30	18
Bentazon -D7	Primary	246.1→182	Pos	20	20
Carbofuran (Ring-13C6)	Primary	228.1→171	Pos	20	12
Clothianidin -D3	Primary	253→131.9	Pos	20	15
Diazinon (Diethyl-D10)	Primary	315.2→170	Pos	30	20
Dicamba -D3[A]	Primary	223.9→179.9	Neg	10	8
Imidacloprid -D4	Primary	260.1→213.1	Pos	30	15
Methomyl (Acetohydroxamate-13C2 15N)	Primary	166→90.8	Pos	10	8
Simazine (Diethyl-D10)	Primary	212.1→134	Pos	40	18
Tebuconazole (tert-Butyl-D9)	Primary	317.2→69.9	Pos	40	20
Thiamethoxam -D3	Primary	295→214.1	Pos	30	12

[A] Indicates analyzed under acidic LC conditions.

TABLE 5 SRM Ions, Retention times and SRM Ion Ratios

Chemical	Primary/ Confirmatory	MRM Transition	Retention Time Minutes	Primary/Confirmatory SRM Area Ratio
2,4-D[A]	Primary	218.9→160.9	7.6	1.5
	Confirmatory	220.9→162.9		
Acetochlor	Primary	270.1→224.1	10.3	2.5
	Confirmatory	270.1→148		
Alachlor	Primary	270.1→162	10.3	0.4
	Confirmatory	270.1→238.1		
Aldicarb	Primary	213→88.9	8	2.1
	Confirmatory	213→116		
Atrazine	Primary	216.1→174	9.2	3.6
	Confirmatory	216.1→95.9		
Desethylatrazine	Primary	188→146	7.6	5.4
	Confirmatory	188→78.8		
Desisopropylatrazine	Primary	174→96	6.6	1.3
	Confirmatory	174→78.8		
Azoxystrobin	Primary	404.2→372.2	9.6	3.7
	Confirmatory	404.2→344.2		
Bentazon	Primary	239→197	6.4	1.1
	Confirmatory	239→175		
Carbaryl	Primary	202.1→145	8.8	3.6
	Confirmatory	202.1→127		
Chlorpyrifos	Primary	350→197.9	11.4	1.8
	Confirmatory	350→322		
Clopyralid[A]	Primary	189.9→145.9	5.2	1.5
	Confirmatory	191.9→147.9		
Clothianidin	Primary	250→169	6.9	1.6
	Confirmatory	250→131.9		
Diazinon	Primary	305.1→169	10.6	1.6
	Confirmatory	305.1→153		
Dicamba[A]	Primary	218.9→174.9	7.1	1.5
	Confirmatory	220.9→176.9		
Fipronil	Primary	435→330	10.3	5.7
	Confirmatory	435→318		
Imidacloprid	Primary	256.1→209.1	6.9	1.1
	Confirmatory	256.1→175		
Malathion	Primary	331.1→127	9.9	1.2
	Confirmatory	331.1→285		
Methomyl	Primary	163→87.9	6.1	1.8
	Confirmatory	163→105.9		
Metolachlor	Primary	284.1→252.1	10.3	2.4
	Confirmatory	284.1→176.1		
Metribuzin	Primary	215.1→187.1	8.5	NA
Picloram[A]	Primary	240.9→196.9	5.9	1
	Confirmatory	238.9→194.9		
Propiconazole	Primary	342.1→158.9	10.6	7.2
	Confirmatory	342.1→205		
Simazine	Primary	202→132	7.6	5.4
	Confirmatory	202→124		
Tebuconazole	Primary	308.2→70	10.5	11.2
	Confirmatory	308.2→125		
Thiamethoxam	Primary	292.1→211.1	6.3	4
	Confirmatory	292.1→131.9		
Triclopyr[A]	Primary	253.9→195.9	7.8	2.9
	Confirmatory	253.9→217.9		
Surrogates				
2,4-D (Ring-D3)[A]	Primary	221.9→163.8	7.6	NA
Atrazine (ethyl-D5)	Primary	221.1→179	9.2	NA
Desethylatrazine (iso-propyl-D7)	Primary	195→146.9	7.6	NA
Desisopropylatrazine (ethyl-D5)	Primary	179→100.9	6.6	NA
Bentazon -D7	Primary	246.1→182	6.4	NA
Carbofuran (Ring-13C6)	Primary	228.1→171	8.6	NA
Clothianidin -D3	Primary	253→131.9	6.9	NA
Diazinon (Diethyl-D10)	Primary	315.2→170	10.6	NA
Dicamba -D3[A]	Primary	223.9→179.9	7.1	NA
Imidacloprid -D4	Primary	260.1→213.1	6.9	NA
Methomyl (Acetohydroxamate-13C2, 15N)	Primary	166→90.8	6.1	NA
Simazine (Diethyl-D10)	Primary	212.1→134	7.6	NA
Tebuconazole (tert-Butyl-D9)	Primary	317.2→69.9	10.5	NA
Thiamethoxam -D3	Primary	295→214.1	6.3	NA

[A] Indicates analyzed under acidic LC conditions.

7.5.2 A 10 mL Lock Tip Glass Syringe size is recommended since a 10 mL prepared sample size is used in this test method. If a smaller volume syringe is used, do not wash out the syringe or change filters while filtering the same sample if multiple refills of the syringe are required in order to filter the 10 mL prepared sample.

7.5.3 *Filter Unit*[5]—PTFE filter units were used to filter the samples.

7.6 *Vials*—2-mL autosampler vials (LC vials) with pre-slit PTFE/silicone septa or equivalent.

7.7 *Sonicator.*

7.8 *Oven*—Capable to achieve 250 °C.

7.9 *VOA Vials*—Amber, 40 mL.

8. Reagents and Materials

8.1 *Purity of Reagents*—High Performance Liquid Chromatography (HPLC) pesticide residue analysis and spectrophotometry grade chemicals must be used in all tests. Unless indicated otherwise, it is intended that all reagents must conform to the Committee on Analytical Reagents of the American Chemical Society.[6] Other reagent grades may be used provided they are first determined to be of sufficiently high purity to permit their use without affecting the accuracy of the measurements.

8.2 *Purity of Water*—Unless otherwise indicated, references to water must be understood to mean reagent water conforming to Type 1 of Specification D1193. It must be demonstrated that this water does not contain contaminants at concentrations sufficient to interfere with the analysis.

8.3 All prepared solutions are routinely replaced every year if not previously discarded for quality control failure.

8.4 *Gases*—Ultrapure nitrogen and argon.

8.5 Formic Acid (CAS # 64-18-6).

8.6 Acetonitrile (CAS # 75-05-8).

8.7 Methanol (CAS # 67-56-1).

8.8 Ammonium Formate (CAS # 540-69-2).

8.9 2-Propanol (isopropyl alcohol, CAS # 67-63-0).

8.10 2,4-Dichlorophenoxyacetic acid (2,4-D, CAS # 94-75-7).

8.11 Acetochlor (CAS # 34256-82-1).

8.12 Alachlor (CAS # 15972-60-8).

8.13 Aldicarb (CAS # 116-06-3).

8.14 Atrazine (CAS # 1912-24-9).

8.15 Desethylatrazine (CAS # 6190-65-4).

8.16 Desisopropylatrazine (CAS # 1007-28-9).

8.17 Azoxystrobin (CAS # 131860-33-8).

8.18 Bentazon (CAS # 25057-89-0).

8.19 Carbaryl (CAS # 63-25-2).

8.20 Chlorpyrifos (CAS # 2921-88-2).

8.21 Clopyralid (CAS # 1702-17-6).

8.22 Clothianidin (CAS # 210880-92-5).

8.23 Diazinon (CAS # 333-41-5).

8.24 Dicamba (CAS # 1918-00-9).

8.25 Fipronil (CAS # 120068-37-3).

8.26 Imidacloprid (CAS # 138261-41-3).

8.27 Malathion (CAS # 121-75-5).

8.28 Methomyl (CAS # 16752-77-5).

8.29 Metolachlor (CAS # 51218-45-2).

8.30 Metribuzin (CAS # 21087-64-9).

8.31 Picloram (CAS # 1918-02-1).

8.32 Propiconazole (CAS # 60207-90-1).

8.33 Simazine (CAS # 122-34-9).

8.34 Tebuconazole (CAS # 107534-96-3).

8.35 Thiamethoxam (CAS # 153719-23-4).

8.36 Triclopyr (CAS # 55335-06-3).

8.37 *Isotopically Labeled Pesticide Standards (Surrogates)*—There are not isotopically labeled surrogates for every target analyte. The labeled surrogate only mimics its unlabeled target analyte. The isotopically labeled carbofuran was chosen to mimic carbaryl. (Note—P&A data show that the labeled carbofuran is not a good surrogate for carbaryl even though they are structurally similar.) Surrogates may be added or deleted from the below list if new ones become available or if the existing ones are not readily available. The surrogate list is long and expensive to maintain. If surrogates are not available at the time of analysis it will be mentioned in the case narrative that accompanies the data, if extra surrogates are added this will also be mentioned in the case narrative (CAS #'s are for the unlabeled native analyte).

8.37.1 2,4-Dichlorophenoxyacetic acid (2,4-D (Ring-D3), CAS # 94-75-7).

8.37.2 Atrazine (ethyl-D5, CAS # 1912-24-9).

8.37.3 Desethylatrazine (iso-propyl-D7, CAS # 6190-65-4).

8.37.4 Desisopropylatrazine (ethyl-D5, CAS # 1007-28-9).

8.37.5 Bentazon (D7, CAS # 25057-89-0).

8.37.6 Carbofuran (Ring-13C6, CAS # 1563-66-2).

8.37.7 Clothianidin (D3, CAS # 210880-92-5).

8.37.8 Diazinon (diethyl-D10, CAS # 333-41-5).

8.37.9 Dicamba (D3, CAS # 1918-00-9).

8.37.10 Imidacloprid (D4, CAS # 138261-41-3).

8.37.11 Methomyl (Acetohydroxamate-13C2, 15N, CAS # 16752-77-5).

[5] A Millipore IC Millex-LG PTFE/0.2µm membrane syringe driven membrane filter unit (Millex is a trademark of Merck KGAA, Darmstadt, Germany) was used, if you are aware of an alternative filter that meets the performance of the standard, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[6] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.37.12 Simazine (diethyl-D10, CAS # 122-34-9).
8.37.13 Tebuconazole (tert-Butyl-D9, CAS # 107534-96-3).
8.37.14 Thiamethoxam (D3, CAS # 153719-23-4).

9. Hazards

9.1 Normal laboratory safety applies to this method. Analysts should wear safety glasses, gloves, and lab coats when working in the lab. Analysts should review the Safety Data Sheets (SDS) for all reagents used in this method.

10. Sampling and Preservation

10.1 Grab samples are collected in amber glass containers with inert-lined caps, such as, 40 mL amber VOA vials. As part of the overall quality assurance program for this test method, field blanks exposed to the same field conditions as samples are collected and analyzed according to this standard to assess the potential for field contamination, refer to Guide D3856 as a guide for sampling. This test method is based upon an 8 mL sample size per analysis. If different sample sizes are used, spiking solution amounts may need to be modified. EPA publication SW-846 may be used as a sampling guide. Samples must be shipped with a trip blank and between freezing and 6 °C.

10.2 Once received the sample temperature is taken and should be less than 6 °C. If the receiving temperature is greater than 6 °C, the sample temperature is noted in the case narrative accompanying the data. Samples should be stored refrigerated between 0 °C and 6 °C from the time of collection until analysis.

10.3 The samples should be analyzed within 14 days of collection. No holding time study has been done on water matrices tested in this test method. Holding time may vary depending on the matrix and individual laboratories should determine the holding time in their matrix, refer to Practice D4841.

11. Preparation of LC/MS/MS

11.1 *LC Chromatograph Operating Conditions:*

11.1.1 Injections of all standards and samples are made at a 25 µL or 50 µL volume. Other injection volumes may be used to optimize conditions. Standards and sample extracts must be in a 80:20 water:methanol solution. In the case of extreme concentration differences amongst samples, it is wise to analyze a blank after a concentrated sample and before a dilute sample to minimize carry-over of analytes from injection to injection. However, there should not be carry-over between samples. The LC utilized to develop this test method has a flow through LC needle design. The gradient conditions for the two liquid chromatography analysis runs are shown in Tables 2 and 3. The primary SRM transition chromatograms at the lowest calibration level are shown in the Appendix, Figs. X1.1-X1.5.

11.2 *LC Auto Sampler Conditions:*

11.2.1 *Needle Wash Solvent*—60 % acetonitrile/40 % 2-propanol. 8 s wash time before and after injection. Instrument manufacturer's specifications should be followed in order to eliminate sample carry-over.

11.2.2 *Temperatures*—Column, 35 °C; Sample compartment, 15 °C.

11.2.3 *Seal Wash*—Solvent: 50 % methanol/50 % water; Time: 5 min.

11.3 *Mass Spectrometer Parameters:*

11.3.1 To acquire the maximum number of data points per SRM channel while maintaining adequate sensitivity, the tune parameters may be optimized according to the instrument used. Each peak requires at least 10 scans per peak for adequate quantitation. Variable parameters regarding SRM transitions, and cone and collision energies are shown in Table 4. Mass spectrometer parameters used in the development of this method are listed below.

11.3.2 The instrument is set in the Electrospray source setting. The values for the following parameters are shown here for information only. These conditions should be checked and optimized when required.

Methanol/Water/Ammonium Formate Analysis Run Conditions

Capillary Voltage: 1 kV in both ESI modes
Cone: Variable depending on analyte
Source Offset (V) 10
Source Temperature: 150 °C
Desolvation Gas Temperature: 500 °C
Desolvation Gas Flow: 900 L/h
Cone Gas Flow: 150 L/h
Collision Gas Flow: 0.15 mL/min
Low Mass Resolution 1: 2.7
High Mass Resolution 1: 14.7
Ion Energy 1: 0.5
Entrance Energy: 1
Collision Energy: Variable depending on analyte
Exit Energy: 1
Low Mass Resolution 2: 2.8
High Mass resolution 2: 14.7
Ion Energy 2: 1.5
Gain: 1.0
Multiplier: 535
Inter-Scan Delay: 0.003 s
Polarity Switching Inter-scan Delay: 0.020 s

Methanol/Water/Formic Acid Analysis Run Conditions

Capillary Voltage: Positive mode 2 kV, Negative mode 0.75 kV
Cone: Variable depending on analyte
Source Offset (V) 10
Source Temperature: 150 °C
Desolvation Gas Temperature: 300 °C
Desolvation Gas Flow: 1000 L/h
Cone Gas Flow: 300 L/h
Collision Gas Flow: 0.15 mL/min
Low Mass Resolution 1: 2.7
High Mass Resolution 1: 14.7
Ion Energy 1: 0.5
Entrance Energy: 1
Collision Energy: Variable depending on analyte
Exit Energy: 1
Low Mass Resolution 2: 2.8
High Mass resolution 2: 14.7
Ion Energy 2: 1.5
Gain: 1.0
Multiplier: 535
Inter-Scan Delay: 0.003 s
Polarity Switching Inter-scan Delay: 0.020 s

12. Calibration and Standardization

12.1 The mass spectrometer must be calibrated as per manufacturer's specifications before analysis. Analytical values satisfying test method criteria have been achieved using the following procedures. Prepare all solutions in the lab using Class A volumetric glassware.

12.2 *Calibration and Standardization*—To generate a calibration curve, analyze seven calibration standards of the pesticide compounds prior to sample analysis as shown in Table 6. Calibration stock standard solution is prepared from the target and surrogate spike solutions directly to ensure consistency. Stock standard Solution A containing the pesticides is prepared at Level 7 concentration and aliquots of that solution are diluted to prepare Levels 1 through 6. The following steps will produce 1 mL calibration standards with the concentration values shown in Table 6. The analyst is responsible for recording initial component weights carefully when working with pure materials and correctly carrying the weights through the dilution calculations.

12.2.1 At a minimum, five calibration levels are required when using a linear calibration curve and six calibration levels are required when using a quadratic calibration curve. An initial seven point curve may be used to allow for the dropping of the lower level calibration point if the individual laboratory's instrument can't achieve low detection limits. This should allow for at least a five or six point calibration curve to be obtained.

12.2.2 Calibration stock standard Solution A (Level 7, Table 6) is prepared from the target and surrogate spike solutions directly to ensure consistency. 1.25 mL of the surrogate spike and 1.25 mL of the pesticide Target Spike Solution is added to a 50 mL volumetric flask and brought up to 50 mL volume with 80:20 water and methanol solution. This stock standard Solution A (Level 7, Table 6) is diluted to prepare Levels 1 through 6 as shown in Tables 6 and 7. The preparation of the Level 7 standard can be accomplished using appropriate volumes and concentrations of stock solutions as per a particular laboratory's standard procedure.

12.2.3 Aliquots of Solution A are then diluted with 80:20 water:methanol to prepare the 1 mL desired calibration levels in 2 mL amber glass LC vials, as described in Table 7. The calibration vials must be used within 24 h to ensure optimum results. Calibration standards are not filtered.

12.2.4 Inject each standard and obtain its chromatogram. An external calibration technique is used to monitor the primary and confirmatory SRM transitions of the pesticides and surrogates. Calibration software is utilized to conduct the quantitation of the analytes using the primary SRM transition. The ratios of the primary/confirmatory SRM transitions area counts are given in Table 5 and will vary depending on the individual tuning conditions. The primary/confirmatory SRM transitions area ratio must be within 35 % of the individual labs' accepted primary/confirmatory SRM transitions area ratio. The primary SRM transition of the analytes are used for quantitation and the confirmatory SRM transitions for confirmation. This gives added confirmation by isolating the parent ion, forming product ions via fragmentation, and relating it to the retention time in the calibration standard. Metribuzin and the surrogates only have a primary SRM transition.

12.2.5 Depending on sensitivity and matrix interference issues dependent on sample type, a confirmatory SRM transition may be substituted as the primary SRM transition for quantitation during analysis. This must be explained in a narrative accompanying the data. New primary/confirmatory ion ratios will then be determined if switching the SRM transitions used to quantitate and confirm. The new primary/confirmatory SRM transitions area ratio is required to be within 35 % of the individual labs' new primary/confirmatory SRM transitions area ratio.

12.2.6 The calibration software manual should be consulted to use the software correctly. The quantitation method is set as an external calibration using the peak areas in ng/L units. Concentrations may be calculated using the data system software to generate linear regression or quadratic calibration curves. Forcing the calibration curve through the origin (X=0, Y=0) is not recommended. Curves should be evaluated using relative error or relative standard error.[7]

12.2.7 Linear calibration may be used if the point of origin is excluded and a fit weighting of 1/X is used in order to give more emphasis to the lower concentrations. Each calibration

[7] Management and Technical Requirements for Laboratories Performing Environmental Analysis; Module 4: Quality Systems for Chemical Testing; The NELAC Institute, 2017.

TABLE 6 Concentrations of Calibration Standards (ng/L)

Pesticide and Surrogate Concentrations (ng/L)	LV1	LV2	LV3	LV4	LV5	LV6	LV7
Azoxystrobin	25	50	100	200	400	800	1 000
Atrazine, Desethylatrazine, Clothianidin, Diazinon, Imidacloprid, Metolachlor, Propiconazole, Simazine, Tebuconazole, Thiamethoxam, Atrazine (ethyl-D5), Desethylatrazine (iso-propyl-D7), Clothianidin-D3, Diazinon (diethyl-D10), Imidacloprid-D4, Simazine (diethyl-D10), Tebuconazole (tert-Butyl-D9), Thiamethoxam-D3	50	100	200	400	800	1 600	2 000
Desisopropylatrazine, Malathion, Metribuzin, Desisopropylatrazine (ethyl-D5)	100	200	400	800	1 600	3 200	4 000
2,4-D, Acetochlor, Alachlor, Aldicarb, Bentazon, Carbaryl, Chlorpyrifos, Fipronil, Methomyl, 2,4-D (Ring-D3), Bentazon-D7, Carbofuran (Ring-13C6), Methomyl (Acetohydroxamate-13C2, 15N)	200	400	800	1600	3 200	6 400	8 000
Triclopyr	1 000	2 000	4 000	8 000	16 000	32 000	40 000
Picloram	5 000	10 000	20 000	40 000	80 000	160 000	200 000
Dicamba, Dicamba-D3	10 000	20 000	40 000	80 000	160 000	320 000	400 000
Clopyralid	20 000	40 000	80 000	160 000	320 000	640 000	800 000

TABLE 7 Preparation of Calibration Standards

Solution	LV1	LV2	LV3	LV4	LV5	LV6	LV7
A[A]	25 µL	50 µL	100 µL	200 µL	400 µL	800 µL	1000 µL
B[B]	975 µL	950 µL	900 µL	800 µL	600 µL	200 µL	0 µL

[A] Solution A: Level 7 stock solution prepared according to 12.2 and at Table 6 concentrations.
[B] Solution B: 80 % Water : 20 % Methanol.

point used to generate the curve must have a calculated percent deviation less than 25 % from the generated curve.

12.2.8 Quadratic calibration may be used if the point of origin is excluded, and a fit weighting of 1/X is used in order to give more emphasis to the lower concentrations. Each calibration point used to generate the curve must have a calculated percent deviation less than 25 % from the generated curve.

12.2.9 The retention time window of the SRM transitions must be within 5 % of the retention time of the analyte in a midpoint calibration standard. If this is not the case, re-analyze the calibration curve to determine if there was a shift in retention time during the analysis and the sample needs to be re-injected. If the retention time is still incorrect in the sample, refer to the analyte as an unknown.

12.2.10 A midpoint calibration check standard must be analyzed at the end of each batch of 30 samples or within 24 h after the initial calibration curve was generated, the criteria in the individual labs' quality system may be more restrictive pertaining to the number of samples. This end calibration check should come from the same calibration standard solution that was used to generate the initial curve. The results from the end calibration check standard must have a percent deviation less than 30 % from the calculated concentration for the target analyte. If the results are not within these criteria, corrective action including re-occurrence minimization is performed and either all samples in the batch are re-analyzed against a new calibration curve or the affected results are qualified with an indication that they do not fall within the performance criteria of the test method. If the analyst inspects the vial containing the end calibration check standard and notices that the sample evaporated affecting the concentration or other anomaly, a new end calibration check standard may be made and analyzed. If this new end calibration check standard has a percent deviation less than 30 % from the calculated concentration for the target analyte, the results may be reported unqualified.

12.3 If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., an instrument qualification study including reporting limit check sample (RLCS), calibration range determination and precision and bias determination must be performed to demonstrate laboratory capability.

12.3.1 Analyze at least four replicates of a spiked water sample containing the pesticides at a prepared sample concentration in the calibration range of Levels 3–6. A Level 4 prepared sample concentration was used to set the QC acceptance criteria in this method. The matrix and chemistry should be similar to the matrix used in this test method. Each replicate must be taken through the complete analytical test method including any sample manipulation and preparation steps.

12.3.2 Calculate the mean (average) percent recovery and relative standard deviation (RSD) of the four values and compare to the acceptable ranges of the QC acceptance criteria for the Initial Demonstration of Performance in Table 8.

12.3.3 This study should be repeated until the single operator precision and mean recovery are within the limits in Table 8. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

12.3.3.1 The QC acceptance criteria for the Initial Demonstration of Performance in Table 8 were generated from the single-laboratory data shown in the Precision and Bias Section 16. Data from reagent water and surface water are shown in the Precision and Bias Section 16. It is recommended that each laboratory determine in-house QC acceptance criteria which meet or exceed the criteria in this standard. References generating QC acceptance criteria are ASTM Practices D2777, D5847, E2554 and Method 8000 in EPA publication SW-846.

12.4 *Surrogate Spiking Solution:*

12.4.1 A surrogate spiking solution containing fourteen isotopically-labeled pesticides (listed in Section 8) are added to all samples. 50 µL of a methanolic solution containing the surrogates and concentrations are listed in Table 9, Concentrations in Surrogate Spike Solution, is added to all 8 mL samples to achieve the concentration in the sample listed in Table 9, Concentration in Water Sample.

12.4.2 The result obtained for the surrogates must fall within the limits in Table 8.

12.4.3 There are fourteen surrogates for this analysis. The isotopically-labeled surrogate represents the unlabeled native analyte. Carbofuran (Ring-13C6) represents carbaryl in this standard. No qualifications based on surrogate recovery need to be made for the analytes that do not have representative surrogates. It is left to the analyst's judgment to qualify data based upon non-representative surrogates. The user of the data must also make decisions based on all QC available. If the result is not within these limits, sample analysis is halted until corrective action resolving the problem has been performed. Impacted samples in the batch are either re-analyzed, or the results are flagged with a qualifier stating that they do not fall within the performance criteria of the test method.

12.5 *Method Blank:*

12.5.1 A method blank for every 30 samples is prepared in 8 mL of reagent water, which is taken through the sample preparation Section 13, to investigate for contamination during sample preparation. The concentration of target analytes in the blank must be at less than 25 % of the reporting limit or the data must be qualified as having a blank issue and the reporting

TABLE 8 QC Acceptance Criteria

NOTE 1—Table 8 data is preliminary until a multi-lab validation study is completed.

Analyte	Spiked Sample Conc. (ng/L)	Initial Demonstration of Performance			Laboratory Control Sample	
		Recovery (%)		Precision	Recovery (%)	
		Lower Limit	Upper Limit	Maximum % RSD	Lower Limit	Upper Limit
2,4-D	2 000	70	130	30	70	130
Acetochlor	2 000	70	130	30	70	130
Alachlor	2 000	70	130	30	70	130
Aldicarb	2 000	70	130	30	70	130
Atrazine	500	70	130	30	70	130
Desethylatrazine	500	70	130	30	70	130
Desisopropylatrazine	1 000	70	130	30	70	130
Azoxystrobin	250	70	130	30	70	130
Bentazon	2 000	70	130	30	70	130
Carbaryl	2 000	50	130	30	50	130
Chlorpyrifos	2 000	50	130	30	50	130
Clopyralid	200 000	70	130	30	70	130
Clothianidin	500	70	130	30	70	130
Diazinon	500	70	130	30	70	130
Dicamba	100 000	70	130	30	70	130
Fipronil	2 000	60	130	30	60	130
Imidacloprid	500	70	130	30	70	130
Malathion	1 000	40	130	30	40	130
Methomyl	2 000	70	130	30	70	130
Metolachlor	500	70	130	30	70	130
Metribuzin	1 000	70	130	30	70	130
Picloram	50 000	70	130	30	70	130
Propiconazole	500	50	130	30	50	130
Simazine	500	70	130	30	70	130
Tebuconazole	500	70	130	30	70	130
Thiamethoxam	500	70	130	30	70	130
Triclopyr	10 000	70	130	30	70	130
Surrogates	NA	NA	NA	NA	NA	NA
2,4-D (Ring-D3)	2 000	70	130	30	70	130
Atrazine (ethyl-D5)	500	70	130	30	70	130
Desethylatrazine (iso-propyl-D7)	500	70	130	30	70	130
Desisopropylatrazine (ethyl-D5)	1 000	70	130	30	70	130
Bentazon -D7	2 000	70	130	30	70	130
Carbofuran (Ring-13C6)	2 000	70	130	30	70	130
Clothianidin-D3	500	70	130	30	70	130
Diazinon-(diethyl-D10)	500	70	130	30	70	130
Dicamba-D3	100 000	70	130	30	70	130
Imidacloprid-D4	500	70	130	30	70	130
Methomyl (Acetohydroxamate-13C2, 15N)	2 000	70	130	30	70	130
Simazine (diethyl-D10)	500	70	130	30	70	130
Tebuconazole (tert-Butyl-D9)	500	70	130	30	70	130
Thiamethoxam-D3	500	70	130	30	70	130

TABLE 9 Surrogate Spike Concentrations

Surrogate	Concentration in Surrogate Spike Solution (µg/L)	Concentration in Water Sample (ng/L)
Atrazine (ethyl-D5), Desethylatrazine (iso-propyl-D7), Clothianidin-D3, Diazinon (diethyl-D10), Imidacloprid-D4, Simazine (diethyl-D10), Tebuconazole (tert-Butyl-D9), Thiamethoxam-D3	80	500
Desisopropylatrazine (ethyl-D5)	160	1000
2,4-D (Ring-D3), Bentazon-D7, Carbofuran (Ring-13C6), Methomyl (Acetohydroxamate-13C2, 15N)	320	2000
Dicamba-D3	16 000	100 000

limit must be raised to at least 3 times above the blank contamination concentration.

12.6 *Reporting Limit Check Sample (RLCS):*

12.6.1 Each batch or within the 24 h analysis window a reporting limit check sample must be analyzed. The reporting limit check sample is processed like a Laboratory Control Sample just spiked at or near (1 to 2 times) the reporting limit. The concentration of the RLCS may be reported below the reporting limit since the spike is at or near the reporting limit. This sample is to ensure if the analytes were present at the reporting limit that they would be identified. The recovery limits for the RLCS are 35 % to 150 %, if any analytes are outside of these limits the QC exceedance is explained in a narrative accompanying the data or the batch is re-prepared and analyzed. A continued failure must be explained, investigated and should be corrected.

12.6.2 To prepare the RLCS, 8 mL of reagent water is added to a 40 mL VOA vial. The sample is spiked with 6.25 µL of the target spike solution (see 12.7). The sample is then prepared as described in Section 13.

12.7 *Laboratory Control Sample (LCS):*

12.7.1 Analyze at least one LCS with the pesticides at a mid-level prepared sample concentration. The concentration of pesticides at a prepared sample concentration in the calibration range of Levels 3–6 should be used. The LCS is prepared following the analytical method and analyzed with each batch of 30 samples or less. Each MS/MSD or LCS/LCSD sample is spiked with target pesticides (listed in Section 8) to achieve the concentrations in Table 10, Concentrations in Water Sample. For example, 50 µL of a methanolic pesticide Target Spike Solution shown in Table 10 is spiked into each 8 mL water sample. (The target analyte spiking solution is prepared from intermediate solutions which are prepared from neat standards.) The concentrated stock standard concentration can vary when preparing from neat material. To prepare the LCS, 8 mL of reagent water is added to a 40 mL VOA vial. The sample is spiked with 50 µL of a target spike solution and then taken through the sample preparation Step in Section 13.

12.7.2 The result obtained for the LCS must fall within the limits in Table 8.

12.7.3 If the result is not within these limits, sample analysis is halted until corrective action resolving the problem has been performed. Impacted samples in the batch are either re-analyzed, or the results are flagged with a qualifier stating that they do not fall within the performance criteria of the test method.

12.8 *Matrix Spike (MS):*

12.8.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch of 30 or fewer samples by spiking the sample with a known concentration of pesticides and following the analytical method. The target spike solution from the LCS 12.7 is used for the spike solution. Spike 50 µL of this stock solution into 8 mL of the site sample to yield the various concentrations in the spike sample as shown in section 12.7. The sample is then taken through the sample preparation step in Section 13.

12.8.2 If the spiked concentration plus the background concentration exceeds that of the Level 7 calibration standard, the sample must be diluted using 80 % water/20 % methanol to a level near the midpoint of the calibration curve.

12.8.3 Calculate the percent recovery of the spike (*P*) using Eq 1:

TABLE 10 Target Spike Concentrations

Analyte	Concentration in Target Spike Solution (µg/L)	Concentration in Water Sample (ng/L)
Azoxystrobin	40	250
Atrazine, Desethylatrazine, Clothianidin, Diazinon, Imidacloprid, Metolachlor, Propiconazole, Simazine, Tebuconazole, Thiamethoxam	80	500
Desisopropylatrazine, Malathion, Metribuzin	160	1000
2,4-D, Acetochlor, Alachlor, Aldicarb, Bentazon, Carbaryl, Chlorpyrifos, Fipronil, Methomyl	320	2000
Triclopyr	1600	10 000
Picloram	8000	50 000
Dicamba	16 000	100 000
Clopyralid	32 000	200 000

$$P = 100\frac{|A(V_S + V) - BV_S|}{CV} \quad (1)$$

where:

A = concentration found in spiked sample,
B = concentration found in unspiked sample,
C = concentration of analyte in spiking solution,
V_S = volume of sample used,
V = volume of spiking solution added, and
P = percent recovery.

12.8.4 The percent recovery of the spike must fall within the limits in Table 11. If the percent recovery is not within these limits, a matrix interference may be present. Under these circumstances either all samples in the batch may be analyzed by a test method not affected by the matrix interference, or the results must be qualified indicating that they do not fall within the performance criteria of the test method. It has been found that in some cases the matrix spike concentration may be minimal compared to the concentration in the native sample. If this is the case, the sample may be spiked at a higher level or the generated data may be reported explaining in the narrative accompanying the data that the spike was negligible compared to the native concentration found in the sample.

12.8.5 The matrix spike/matrix spike duplicate (MS/MSD) limits in Table 11 were generated by a single-laboratory study using the data in the Precision and Bias Section 16. The limits in Table 11 are preliminary until a multi-lab validation study is completed. The matrix variation between different waters may have a tendency to generate significantly wider control limits than those generated for this Standard. It is recommended that each laboratory determine in-house QC acceptance criteria meeting or exceeding the criteria stated in this standard.

12.8.5.1 Each laboratory should generate its own in-house QC acceptance criteria after the analysis of 15–20 matrix spike samples of a particular water matrix. References on generating QC acceptance criteria are ASTM Practices D5847, D2777, E2554 and Method 8000 in EPA publication SW-846.

12.9 *Duplicate:*

12.9.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch of 30 or fewer samples. If the sample contains the analyte at a level greater than 5 times the reporting limit of the method, the sample and duplicate may be analyzed unspiked; otherwise, a matrix spike/matrix spike duplicate should be used.

12.9.2 Calculate the relative percent difference (RPD) between the duplicate values or MS/MSD values as shown in Eq 2. Compare to the RPD limit in Table 11.

$$\text{RPD} = \frac{|[\text{MS}] - [\text{MSD}]|}{([\text{MS}] + [\text{MSD}])/2} \times 100 \quad (2)$$

where:

RPD = relative percent difference,
MS = measured concentration in the matrix spike QC sample (to calculate duplicate RPD use—sample concentration), and
MSD = measured concentration in the matrix spike duplicate QC sample (to calculate duplicate RPD use—sample duplicate concentration).