Designation: D7645 – 16

Standard Test Method for Determination of Aldicarb, Aldicarb Sulfone, Aldicarb Sulfoxide, Carbofuran, Methomyl, Oxamyl, and Thiofanox in Water by Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D7645; 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 procedure covers the determination of aldicarb, aldicarb sulfone, aldicarb sulfoxide, carbofuran, methomyl, oxamyl, and thiofanox (referred to collectively as carbamates in this test method) in water by direct injection using liquid chromatography (LC) and detected with tandem mass spectrometry (MS/MS). These analytes are qualitatively and quantitatively determined by this test method. This test method adheres to multiple reaction monitoring (MRM) mass spectrometry.

1.2 The Detection Verification Level (DVL) and Reporting Range for the carbamates are listed in Table 1.

1.2.1 The DVL is required to be at a concentration at least 3 times below the Reporting Limit (RL) and have a signal/noise ratio greater than 3:1. Fig. 1 displays the signal/noise ratios of the primary single reaction monitoring (SRM) transitions, and Fig. 2 displays the confirmatory SRM transitions at the DVLs for the carbamates.

1.2.2 The reporting limit is the concentration of the Level 1 calibration standard as shown in Table 2 for the carbamates.

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

1.4 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

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
D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
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

2.2 *Other Documents:*[3]

EPA Publication SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods
EPA Method 531 Measurement of *N*-Methyl Carbamoyloximes and *N*-Methyl Carbamates in Drinking Water by Direct Aqueous Injection HPLC with Post Column Derivatization
EPA Method 531.2 Measurement of *N*-Methylcarbamoyloximes and *N*-Methylcarbamates in Water by Direct Aqueous Injection HPLC with Postcolumn Derivatization

[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.

[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 1 Detection Verification Level and Reporting Range

Analyte	DVL (ng/L)	Reporting Range (µg/L)
Aldicarb	250	1-100
Aldicarb Sulfone	250	1-100
Aldicarb Sulfoxide	250	1-100
Carbofuran	250	1-100
Methomyl	250	1-100
Oxamyl	250	1-100
Thiofanox	250	1-100

EPA Method 538 Determination of Selected Organic Contaminants in Drinking Water by Direct Aqueous Injection-Liquid Chromatography/Tandem Mass Spectrometry (DAI-LC/MS/MS)

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 *carbamates, n*—in this test method, aldicarb, aldicarb sulfone, aldicarb sulfoxide, carbofuran, methomyl, oxamyl, and thiofanox collectively.

3.2.2 *detection verification level, DVL, n*—a concentration that has a signal/noise ratio greater than 3:1 and is at least 3 times below the Reporting Limit (RL).

3.2.3 *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. The IRM shall be obtained from a different lot of material than is used for calibration.

3.3 *Acronyms:*

3.3.1 *CCC, n*—Continuing Calibration Check

3.3.2 *IC, n*—Initial Calibration

3.3.3 *LC, n*—Liquid Chromatography

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

3.3.5 *MeOH, n*—Methanol

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

3.3.7 *MRM, n*—Multiple Reaction Monitoring

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

3.3.9 *NA, adj*—Not Available

3.3.10 *ND, n*—non-detect

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

3.3.12 *PPB, n*—parts per billion

3.3.13 *PPT, n*—parts per trillion

3.3.14 *QA, adj*—Quality Assurance

3.3.15 *QC, adj*—Quality Control

3.3.16 *RL, n*—Reporting Limit

3.3.17 *RSD, n*—Relative Standard Deviation

3.3.18 *RT, n*—Retention Time

3.3.19 *SDS, n*—Safety Data Sheets

3.3.20 *SRM, n*—Single Reaction Monitoring

3.3.21 *SS, n*—Surrogate Standard

3.3.22 *TC, n*—Target Compound

3.3.23 *µM, n*—micromolar, 1×10^{-6} moles/L

3.3.24 *VOA, n*—Volatile Organic Analysis

4. Summary of Test Method

4.1 This is a performance-based method, and modifications are allowed to improve performance.

4.2 For carbamate analysis, samples are shipped to the lab acidified between 0°C and 6°C and analyzed within 14 days of collection. In the lab, the samples are spiked with surrogates, filtered using a syringe driven filter unit, and analyzed directly by LC/MS/MS.

4.3 The carbamates, methomyl-$^{13}C_2$,^{15}N (surrogate) and carbofuran-$^{13}C_6$ (surrogate) are identified by retention time and two SRM transitions. The target analytes and surrogate are quantitated using the primary SRM transitions utilizing an external calibration. The final report issued for each sample lists the concentration of carbamates and the surrogate recoveries.

5. Significance and Use

5.1 This test method has been developed by U.S. EPA Region 5 Chicago Regional Laboratory (CRL).

5.2 The *N*-methyl carbamate (NMC) pesticides: aldicarb, carbofuran, methomyl, oxamyl, and thiofanox have been identified by EPA as working through a common mechanism. These affect the nervous system by reducing the ability of enzymes. Enzyme inhibition was the primary toxicological effect of regulatory concern to EPA in assessing the NMC's food, drinking water, and residential risks. In most of the country, NMC residues in drinking water sources are at levels that are not likely to contribute substantially to the multi-pathway cumulative exposure. Shallow private wells extending through highly permeable soils into shallow, acidic ground water represent what the EPA believes to be the most vulnerable drinking water. Aldicarb sulfone and aldicarb sulfoxide are breakdown products of aldicarb and should also be monitored due to their toxicological effects.[4]

5.3 This test method has been investigated for use with reagent, surface, and drinking water for the selected carbamates: aldicarb, aldicarb sulfone, aldicarb sulfoxide, carbofuran, methomyl, oxamyl, and thiofanox.

6. Interferences

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other apparatus producing discrete artifacts or elevated baselines. All of these materials are demonstrated to be free from interferences by analyzing laboratory reagent blanks under the same conditions as samples.

[4] Additional information about Carbamate pesticides area available from United States Environmental Protection Agency (EPA), http://www.epa.gov.

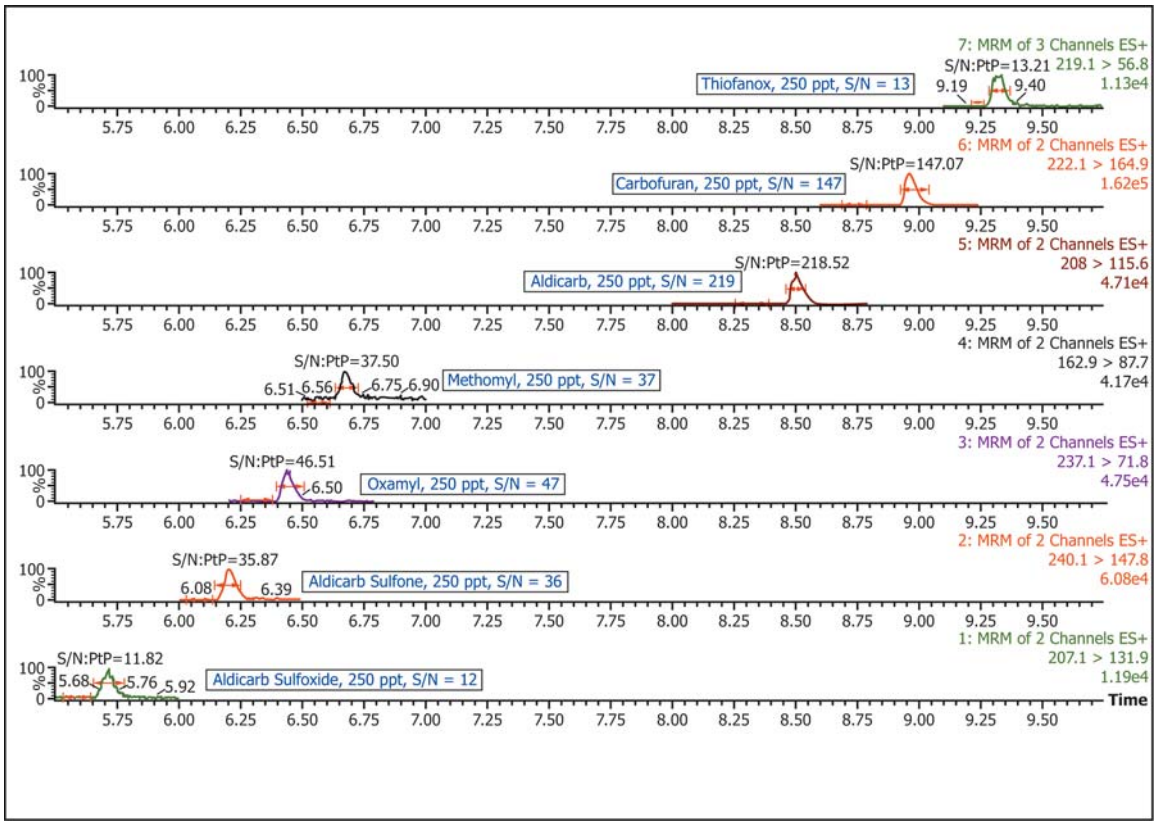

FIG. 1 Example Primary SRM Chromatograms Signal/Noise Ratios

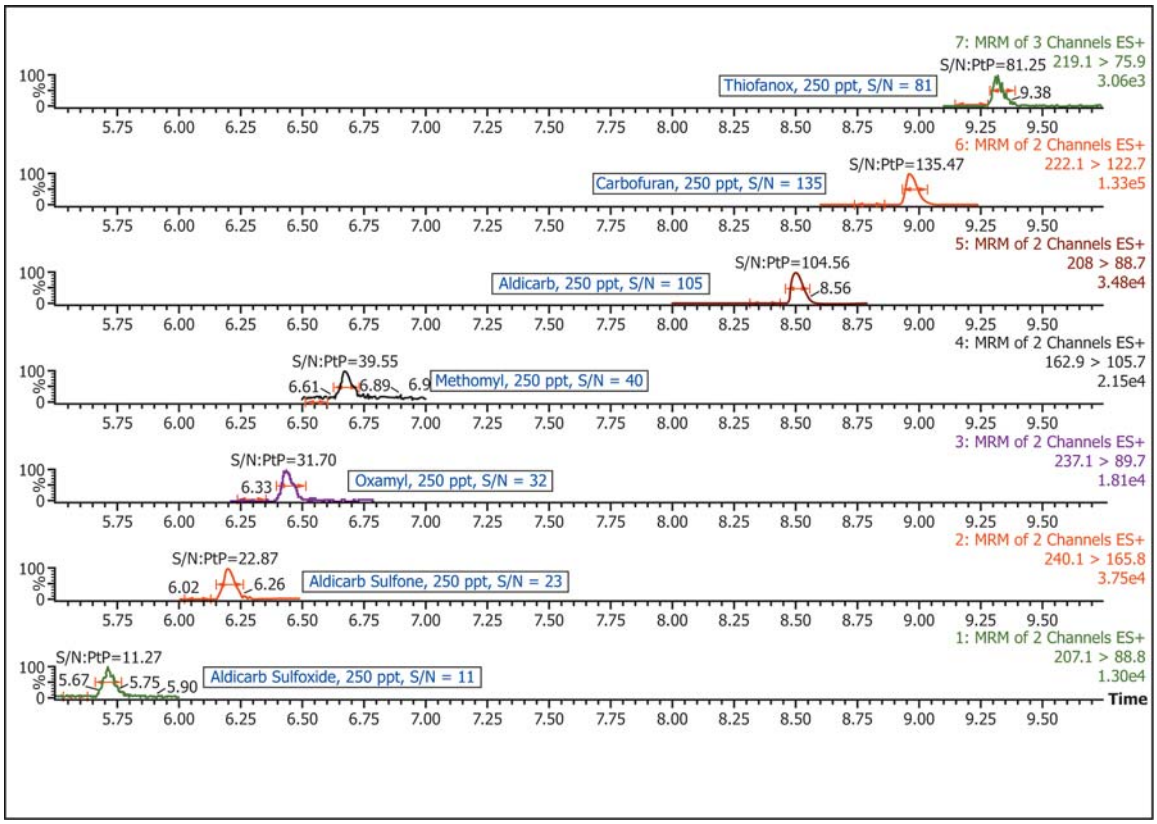

FIG. 2 Example Confirmatory SRM Chromatograms Signal/Noise Ratios

TABLE 2 Concentrations of Calibration Standards (PPB)

Analyte/Surrogate	LV 1	LV 2	LV 3	LV 4	LV 5	LV 6	LV 7	LV 8
Aldicarb	1	5	10	25	35	50	75	100
Aldicarb Sulfone	1	5	10	25	35	50	75	100
Aldicarb Sulfoxide	1	5	10	25	35	50	75	100
Carbofuran	1	5	10	25	35	50	75	100
Methomyl	1	5	10	25	35	50	75	100
Oxamyl	1	5	10	25	35	50	75	100
Thiofanox	1	5	10	25	35	50	75	100
Carbofuran-$^{13}C_6$ (Surrogate)	1	5	10	25	35	50	75	100
Methomyl-$^{13}C_2$, ^{15}N (Surrogate)	1	5	10	25	35	50	75	100

6.2 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 to 30 minutes. All glassware is subsequently cleaned with acetone followed by methanol.

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

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

7. Apparatus

7.1 *LC/MS/MS System:*

7.1.1 *Liquid Chromatography (LC) System*—A complete LC system is needed to analyze samples.[5] This should include a sample injection system, a solvent pumping system capable of mixing solvents, a sample compartment capable of maintaining required temperature and a temperature controlled column compartment. A system that is capable of performing at the flows, pressures, controlled temperatures, sample volumes, and requirements of the standard may be used.

7.1.2 *Analytical Column*[6]—A C18 column was used to develop this test method.

7.2 *Tandem Mass Spectrometer (MS/MS) System*—A MS/MS system capable of MRM analysis.[7] Any system that is capable of performing at the requirements in this standard may be used.

7.3 *Filtration Device:*

7.3.1 *Hypodermic syringe*—A lock tip glass syringe capable of holding a syringe-driven filter unit or similar may be used.

7.3.1.1 A 25-mL lock tip glass syringe size is recommended since a 25-mL sample size is used in this test method.

7.3.2 *Filter unit*[8]—PVDF filter units were used to filter the samples.

8. Reagents and Materials

8.1 *Purity of Reagents*—High Performance Liquid Chromatography (HPLC) pesticide residue analysis and spectrophotometry grade chemicals shall be used in all tests. Unless indicated otherwise, it is intended that all reagents shall conform to the Committee on Analytical Reagents of the American Chemical Society.[9] 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 shall 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 *Gases*—Ultrapure nitrogen and argon.

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

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

8.6 Acetone (CAS # 67-64-1).

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

8.8 Acetic Acid (Glacial, CAS # 64-19-7).

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

8.10 Aldicarb Sulfone (CAS # 1646-88-4).

8.11 Aldicarb Sulfoxide (CAS # 1646-87-3).

8.12 Carbofuran (CAS # 1563-66-2).

8.13 Oxamyl (CAS # 23135-22-0).

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

8.15 Thiofanox (CAS # 39196-18-4).

[5] An ACQUITY UltraPerformance Liquid Chromatography (UPLC) (a trademark of Waters Technologies Corporation in Wilmington, DE) System was used to develop this test method. All parameters in this test method are based on this system and may vary depending on your instrument.

[6] Waters ACQUITY UPLC (a trademark of Waters Technologies Corporation in Wilmington, DE) BEH C18, 2.1 × 100 mm, 1.7 µm particle size 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] A Quattro Premier XE (a trademark of Waters Technologies Corporation in Wilmington, DE) tandem quadrupole mass spectrometer was used to develop this test method. All parameters in this test method are based on this system and may vary depending on your instrument.

[8] A Millex HV Syringe Driven Filter Unit PVDF 0.22 µm (Millipore Corporation, Catalog #SLGV033NS; Millex is a trademark of Merck KGAA, Darmstadt, Germany) has been found suitable for use for this test method, any filter unit may be used that meets the performance of this test method may be used.

[9] Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D.C. For Suggestions on the testing of reagents not listed by the American Chemical Society, see Annual Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulators, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.16 Methomyl-$^{13}C_2$,^{15}N (acetohydroxamate-$^{13}C_2$,^{15}N, CAS # (unlabeled) 16752-77-5).

8.17 Carbofuran-$^{13}C_6$ (Ring- $^{13}C_6$, CAS # (unlabeled) 1563-66-2).

9. Hazards

9.1 Normal laboratory safety applies to this test 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 test method.

10. Sampling

10.1 *Sampling and Preservation*—Grab samples should be collected in ≥25 mL pre-cleaned amber glass bottles with Teflon[10]-lined caps demonstrated to be free of interferences. All samples are acidified with glacial acetic acid to pH ≤3.8 upon collection. A few drops or less of glacial acetic acid is required per 40 mL water sample collected. Chlorinated drinking water samples are also dechlorinated with ascorbic acid; 10 mg of ascorbic acid is added to each 40 mL volume of water prior to collection. Drinking water samples must be dechlorinated upon collection. Aldicarb oxidizes when residual chlorine is present in the sample. This test method is based on a 25 mL sample size per analysis. If different sample sizes are used, spiking solution amounts and preservatives will need to be modified. Conventional sampling practices should be followed. Refer to Guide D3856 and Practices D3694. Store samples between 0°C and 6°C from the time of collection until analysis. Analyze the sample within 14 days of collection.

NOTE 1—Less sample volume is acceptable, but the spike amounts and sample preservatives must be adjusted accordingly.

10.1.1 EPA Method 531.2 demonstrated that carbamates are more stable under acidic conditions. Potassium dihydrogen citrate buffer is used in Method 531.2 to bring the pH to ~3.8, but this buffer is incompatible with LC/MS/MS. Therefore, the pH adjustment is accomplished with acetic acid in this test method. EPA Method 531.2 demonstrated that carbamates under acidic conditions are stable for at least 28 days. EPA Method 531 demonstrated that oxamyl and methomyl are stable for at least 70 days at pH 3 ± 0.2. Holding time is dependent upon your individual matrix and will vary. Practice D4841 may be used to conduct a holding time study on your individual matrix.

11. Preparation of LC/MS/MS

11.1 *LC Chromatograph Operating Conditions:*[5]

11.1.1 Injection volumes of all calibration standards and samples are made at 50 µL volume using a full loop injection. If a 50 µL volume loop is installed in the LC, a "full loop" mode is the preferred technique when performing fast, qualitative analyses. This mode should be used whenever accuracy and precision are the primary concerns. The first sample analyzed after the calibration curve is a blank to ensure there is no carry-over. The gradient conditions for the liquid chromatograph are shown in Table 3.

TABLE 3 Gradient Conditions for Liquid Chromatography

Time (min)	Flow (µL/min)	Percent 95 % Water/ 5 % Methanol, 5 mM NH_4CO_2H	Percent 95 % Methanol/ 5 % Water, 5 mM NH_4CO_2H
0.0	300	100	0
2.0	300	100	0
3.0	300	95	5
5.0	300	85	15
10.0	300	0	100
11.5	300	0	100
12.0	300	100	0
14.0	300	100	0

11.2 *LC Sample Manager Conditions:*

11.2.1 *Wash Solvents*—Weak wash is 2.4 mL of 95 % water/5 % methanol. Strong wash is 1.2 mL of methanol. The strong wash solvent is needed to eliminate carry-over between injections of carbamate samples. The weak wash is used to remove the strong wash solvent. Instrument manufacturer specifications should be followed in order to eliminate sample carry-over.

11.2.2 *Temperatures*—Column, 30°C; Sample compartment, 15°C.

11.2.3 *Seal Wash*—Solvent: 50 Acetonitrile/50 Water; Time: 5 minutes.

11.3 *Mass Spectrometer Parameters:*[7]

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 your instrument. Each peak requires at least 10 scans per peak for adequate quantitation. This test method contains two surrogates, which are isotopically labeled methomyl and carbofuran, and seven carbamates, which are split up into seven MRM acquisition functions to optimize sensitivity. Variable parameters regarding retention times, SRM transitions, and cone and collision energies are shown in Table 4. Mass spectrometer parameters used in the development of this test method are listed below:

The instrument is set in the Electrospray positive source setting.
Capillary Voltage: 3.5 kV
Cone: Variable depending on analyte (Table 4)
Extractor: 2 Volts
RF Lens: 0.1 Volts
Source Temperature: 120°C
Desolvation Temperature: 375°C
Desolvation Gas Flow: 800 L/hr
Cone Gas Flow: 25 L/hr
Low Mass Resolution 1: 14.5
High Mass Resolution 1: 14.5
Ion Energy 1: 0.5
Entrance Energy: –1
Collision Energy: Variable depending on analyte (Table 4)
Exit Energy: 0
Low Mass Resolution 2: 14.5
High Mass resolution 2: 14.5
Ion Energy 2: 0.7
Multiplier: 650
Gas Cell Pirani Gauge: 7.0×10^{-3} Torr
Inter-Channel Delay: 0.005 seconds
Inter-Scan Delay: 0.005 seconds
Dwell: 0.075 seconds

12. Calibration and Standardization

12.1 The mass spectrometer must be calibrated in accordance with manufacturer specifications before analysis. In

[10] Teflon is a trademark of The Chemours Company, LLC, in Wilmington, DE.

TABLE 4 Retention Times, SRM Ions, and Analyte-Specific Mass Spectrometer Parameters

Analyte	Primary/ Confirmatory	Retention Time (min)	Cone Voltage (Volts)	Collision Energy (eV)	SRM Mass Transition (Parent > Product)	Primary/ Confirmatory SRM Area Ratio
Aldicarb	Primary	8.50	10	7	208.0 > 115.6	1.4
	Confirmatory		10	16	208.0 > 88.7	
Aldicarb Sulfone	Primary	6.20	13	13	240.1 > 147.8	1.6
	Confirmatory		13	11	240.1 > 165.8	
Aldicarb Sulfoxide	Primary	5.72	16	6	207.1 > 131.9	1.1
	Confirmatory		16	14	207.1 > 88.8	
Carbofuran	Primary	8.96	22	12	222.1 > 164.9	1.2
	Confirmatory		22	20	222.1 > 122.7	
Methomyl	Primary	6.68	15	10	162.9 > 87.7	1.8
	Confirmatory		15	10	162.9 > 105.7	
Oxamyl	Primary	6.44	11	11	237.1 > 71.8	2.6
	Confirmatory		11	7	237.1 > 89.7	
Thiofanox	Primary	9.32	12	8	219.1 > 56.8	4.8
	Confirmatory		12	5	219.1 > 75.9	
Carbofuran-$^{13}C_6$ (Surrogate)	Primary	8.96	22	11	228.1 > 170.9	1.3
	Confirmatory		22	21	228.1 > 128.8	
Methomyl-$^{13}C_2$,^{15}N (Surrogate)	Primary	6.68	18	8	165.8 > 90.7	1.7
	Confirmatory		18	9	165.8 > 108.7	

order to obtain accurate analytical values through using this test method within the confidence limits, the following procedures must be followed when performing the test method. Prepare all solutions in the lab using Class A volumetric glassware.

12.2 *Calibration and Standardization*—To calibrate the instrument, analyze eight calibration standards containing the eight concentration levels of the carbamates, methomyl-$^{13}C_2$, ^{15}N and carbofuran-$^{13}C_6$ prior to analysis as shown in Table 2. A calibration stock standard solution is prepared from standard materials or they are purchased as certified solutions. Stock Standard Solution A containing the carbamates and surrogates is prepared at Level 8 concentration and aliquots of that solution are diluted to prepare Levels 1 through 7. The following steps will produce standards with the concentration values shown in Table 2. 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 Prepare Stock Standard Solution A (Level 8) by adding to a 50 mL volumetric flask individual solutions of the following: 100 µL of aldicarb, aldicarb sulfone, aldicarb sulfoxide, carbofuran, methomyl, oxamyl, and thiofanox, each at 50 ppm in methanol and 50 µL of methomyl-$^{13}C_2$,^{15}N in methanol and carbofuran-$^{13}C_6$ in 1,4-dioxane each at 100 ppm, dilute to 50 mL with water. The preparation of the Level 8 standard can be accomplished using different volumes and concentrations of stock solutions as is accustomed in the individual laboratory. Depending on the prepared stock concentrations, the solubility at that concentration will have to be ensured.

12.2.2 Aliquots of Solution A are then diluted with water to prepare the desired calibration levels in 2-mL amber glass LC vials. The calibration vials must be used within 24 hours to ensure optimum results. Stock calibration standards are routinely replaced every 7 days if not previously discarded for quality control failure. Calibration standards are not filtered.

12.2.3 Inject each standard and obtain its chromatogram. An external calibration technique is used to monitor the primary and confirmatory SRM transitions of each analyte. Calibration software is utilized to conduct the quantitation of the target analytes and surrogates using the primary SRM transition. The ratios of the primary/confirmatory SRM transition area counts are given in Table 4 and will vary depending on the individual tuning conditions. The primary/confirmatory SRM transition area ratio must be within 35 % of the individual labs' accepted primary/confirmatory SRM transition area ratio. The primary SRM transition of each analyte is used for quantitation and the confirmatory SRM transition for confirmation. This gives added confirmation by isolating the parent ion, forming two product ions via fragmentation, and relating it to the retention time in the calibration standard.

12.2.4 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 ppt or ppb units, as long as the analyst is consistent. Concentrations may be calculated using the data system software to generate linear regression or quadratic calibration curves. Forcing the calibration curve through the origin is not recommended.

12.2.5 Linear calibration may be used if the coefficient of determination, r^2, is >0.98 for the analyte. 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. If one of the calibration standards other than the high or low point causes the r^2 of the curve to be <0.98, this point must be re-injected or a new calibration curve must be regenerated. If the low and/or high point is excluded, minimally a six point curve is acceptable but the reporting range must be modified to reflect this change.

12.2.6 Quadratic calibration may be used if the coefficient of determination, r^2, is >0.99 for the analyte. 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. If one of the calibration standards causes the curve to be <0.99, this point must be re-injected or a new calibration curve must be regenerated. Minimally a six point curve is acceptable using a

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

12.2.6.1 An initial eight point curve over the calibration range is an option in the event that the low or high point, or both, must be excluded to obtain a coefficient of determination >0.99. In this event, the reporting range must be modified to reflect this change.

12.2.7 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.

12.2.8 A midpoint calibration check standard must be analyzed at the end of each batch of 20 samples or within 24 hours after the initial calibration curve was generated. This end calibration check should be the same calibration standard 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 analytes and surrogates. If the results are not within these criteria, the problem must be corrected and either all samples in the batch must be re-analyzed against a new calibration curve or the affected results must be 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, 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 analytes and surrogates, 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., a precision and bias study must be performed to demonstrate laboratory capability.

12.3.1 Analyze at least four replicates of a sample solution containing the carbamates and surrogates at a concentration in the calibration range of Levels 5 to 7. The Level 6 concentration of the eight-point calibration curve was used to set the QC acceptance criteria in this test method. The matrix and chemistry should be similar to the solution used in this test method. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment 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 5.

12.3.3 This study should be repeated until the single operator precision and mean recovery are within the limits in Table 5. 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 5 were generated from a single-laboratory. Data from reagent, surface, and drinking water matrices are shown in Section 16, Precision and Bias. It is recommended that the laboratory generate their own in-house QC acceptance criteria which meets or exceeds the criteria in this standard. References on how to generate QC acceptance criteria are Practices D2777, D5847, E2554, or Method 8000B in EPA Publication SW-846.

12.4 *Surrogate Spiking Solution:*

12.4.1 A surrogate spiking 50 % methanol/50 % 1,4-dioxane solution containing methomyl-$^{13}C_2$,^{15}N and carbofuran-$^{13}C_6$ is added to all samples. A stock surrogate spiking solution is prepared at 50 ppm. Spiking 25 µL of this spiking solution into a 25 mL water sample results in a concentration of 50 ppb of the surrogate in the sample. The result obtained for the surrogate recovery must fall within the limits of Table 5. If the limits are not met, the affected results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.4.1.1 The surrogate spiking solution was prepared by adding 1.0 mL of a 100 ppm solution of methomyl-$^{13}C_2$,^{15}N in methanol to 1.0 mL of a 100 ppm solution of carbofuran-$^{13}C_6$ in 1,4-dioxane and stored in a 4 mL amber glass vial with a Teflon lined cap. Surrogate spiking solutions are routinely replaced every 14 days if not previously discarded for quality control failure.

TABLE 5 QC Acceptance Criteria

Analyte	Test Conc. (µg/L)	Initial Demonstration of Performance			Lab Control Sample	
		Recovery (%)		Precision	Recovery (%)	
		Lower Limit	Upper Limit	Maximum % RSD	Lower Limit	Upper Limit
Aldicarb	50	65	128	30	65	128
Aldicarb Sulfone	50	68	127	30	68	127
Aldicarb Sulfoxide	50	75	118	30	75	118
Carbofuran	50	39	142	30	39	142
Methomyl	50	67	127	30	67	127
Oxamyl	50	59	143	30	59	143
Thiofanox	50	71	129	30	67	133
Carbofuran-$^{13}C_6$ (Surrogate)	50	40	164	30	40	164
Methomyl-$^{13}C_2$,^{15}N (Surrogate)	50	90	129	30	84	135

12.5 *Method Blank:*

12.5.1 Analyze a reagent water blank with each batch of 20 or fewer samples. The concentration of the carbamates found in the blank must be below the DVL. If the concentrations of the carbamates are found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.6 *Laboratory Control Sample (LCS):*

12.6.1 To ensure that the test method is in control, analyze a LCS prepared with the carbamates at a concentration in the calibration range of Levels 4 to 6. The LCS is prepared following the analytical method and analyzed with each batch of 20 samples or less. Prepare a stock matrix spiking solution in methanol containing the carbamates each at 50 ppm. Spike 25 µL of this stock solution into 25 mL of water to yield a concentration of 50 ppb for the carbamates in the sample. The result obtained for the LCS must fall within the limits in Table 5. Matrix spiking solutions are routinely replaced every 14 days if not previously discarded for quality control failure.

12.6.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all samples in the batch must be re-analyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.7 *Matrix Spike (MS):*

12.7.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch of 20 or fewer samples by spiking the sample with a known concentration of carbamates and following the analytical method. Prepare a stock matrix spiking solution in methanol containing the carbamates at 50 ppm. Spike 25 µL of this stock solution into 25 mL of water to yield a concentration of 50 ppb of the carbamates in the sample.

12.7.2 If the spiked concentration plus the background concentration exceeds that of the Level 8 calibration standard, the sample must be diluted to a level near the midpoint of the calibration curve.

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

$$P = 100\,\frac{\left|A\left(V_s+V\right)-BV_s\right|}{CV} \tag{1}$$

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.

12.7.4 The percent recovery of the spike shall fall within the limits in Table 6. If the percent recovery is not within these limits, a matrix interference may be present in the selected sample. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

TABLE 6 MS/MSD QC Acceptance Criteria

Analyte	Test Conc. (µg/L)	MS/MSD		
		Recovery (%)		Precision
		Lower Limit	Upper Limit	Maximum RPD (%)
Aldicarb	50	72	118	30
Aldicarb Sulfone	50	72	135	30
Aldicarb Sulfoxide	50	81	125	30
Carbofuran	50	39	142	30
Methomyl	50	67	127	30
Oxamyl	50	59	143	30
Thiofanox	50	67	133	30
Carbofuran-$^{13}C_6$ (Surrogate)	50	53	157	30
Methomyl-$^{13}C_2$,^{15}N (Surrogate)	50	74	141	30

12.7.5 The matrix spike/matrix spike duplicate (MS/MSD) limits in Table 6 were generated by a single-laboratory using surface and drinking water samples from the data in Section 16, Precision and Bias. The matrix variation between the different waters may have a tendency to generate significantly wider control limits than those generated by a single-laboratory in one water matrix. It is recommended that the laboratory generate their own in-house QC acceptance criteria which meets or exceeds the criteria in this standard.

12.7.5.1 The laboratory should generate their own in-house QC acceptance criteria after the analysis of 15–20 matrix spike samples of a particular surface water matrix. References on how to generate QC acceptance criteria are Practices D5847, D2777, E2554, or Method 8000B in EPA Publication SW-846.

12.8 *Duplicate:*

12.8.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch of 20 or fewer samples. If the sample contains the analyte at a level greater than 5 times the detection limit of the method, the sample and duplicate may be analyzed unspiked; otherwise, an MSD should be used.

12.8.2 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 6.

$$RPD = \frac{\left|MSR-MSDR\right|}{\left(MSR+MSDR\right)\div 2}\times 100 \tag{2}$$

where:

RPD = relative percent difference,
MSR = matrix spike recovery, and
$MSDR$ = matrix spike duplicate recovery.

12.8.3 If the result exceeds the precision limit, the batch must be re-analyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13. Procedure

13.1 This test method is based upon a 25-mL sample size per analysis. The samples must be analyzed within 14 days of collection. If the samples are above 6°C when received or during storage, or not analyzed within 14 days of collection,

the data is qualified estimated and noted in the case narrative that accompanies the data.

13.2 In the laboratory, a 25-mL Class A glass volumetric flask is used to measure a 25-mL aliquot of the sample. Every sample is then spiked with the surrogates as described in Section 12. The laboratory control and matrix spike samples are then spiked with the target compounds as described in Section 12. The samples are then shaken in order to mix the spike solutions throughout the water sample.

13.3 For every sample, the entire 25 mL volume is filtered through the filtration device described in section 7.3 into a 40 mL pre-cleaned amber glass vial with a Teflon-lined cap. A new filter unit is used for each sample.

13.3.1 The syringe must be cleaned between each filtration. It is the analyst's responsibility to ensure that the syringe is clean. A suggested method for cleaning the syringe between filtrations is to first rinse with at least 5 syringe volumes of water, followed by at least 3 volumes of acetone, then 3 volumes of methanol, and a final rinse with water.

13.4 An aliquot of each filtered sample is placed into 2-mL amber glass LC vials for analysis.

13.5 Once a passing calibration curve is generated the analysis of samples may begin. An order of analysis may be method blank(s), laboratory control sample(s), sample(s), duplicate(s), matrix spike sample(s) followed by an end calibration check standard.

14. Calculation or Interpretation of Results

14.1 For quantitative analysis of the carbamates and surrogates, the SRM transitions are identified by comparison of retention times in the sample to those of the standards. External calibration curves are used to calculate the amounts of carbamates and surrogates. Calculate the concentration in mg/L (ppb) for each analyte. The individual carbamates may be reported if present at or above the reporting limit. If the concentration of the analyte is determined to be above the calibration range, the sample is diluted with reagent water to obtain a concentration near the mid-point of the calibration range and re-analyzed. This test method uses two surrogates, methomyl-$^{13}C_2$,^{15}N and carbofuran-$^{13}C_6$, to monitor performance. The surrogate recoveries are provided with all data generated from this test method.

14.1.1 Both surrogates are used to monitor the performance of aldicarb, aldicarb sulfone, aldicarb sulfoxide, oxamyl and thiofanox. If both surrogates meet the quality control criteria in this test method, the data may be reported unqualified for all analytes if all other quality control in this test method are acceptable. If one or both of the surrogates do not meet the quality control criteria of the test method, the data is qualified for these five analytes.

14.1.2 Methomyl-$^{13}C_2$,^{15}N is used as the surrogate for methomyl. Carbofuran-$^{13}C_6$ is used as the surrogate for carbofuran. If the surrogate recovery does not meet the quality control criteria of the test method, the data is qualified for the appropriate analyte.

15. Report

15.1 Determine the results in units of µg/L (ppb) in a water sample. Calculate the concentration in the sample using the linear or quadratic calibration curve generated. All data that does not meet the specifications in the test method must be appropriately qualified.

16. Precision and Bias

16.1 The determination of precision and bias was conducted through EPA and generated applicable data to determine the precision and bias as described in Practice D2777.

16.2 This test method was tested by CRL on reagent water. The samples were spiked with the carbamates to obtain a 50 ppb concentration of each and a 50 ppb concentration of surrogates as described in Section 12. Table 7 contains the recoveries and standard deviation (SD) for the surrogates and target compounds.

16.3 This test method was tested by CRL on Chicago River water. The samples were spiked with target compounds across the calibration range as Youden pairs and surrogates as described in Section 12. Table 8 contains the recoveries for the surrogates and target compounds.

16.4 This test method was tested by CRL on Lake Michigan water. The samples were spiked with target compounds across the calibration range as Youden pairs and surrogates as described in Section 12. Table 9 contains the recoveries for the surrogates and target compounds.

TABLE 7 Single-Laboratory Recovery Data in Reagent Water

Precision and Accuracy Samples	Measured ppb from 50 ppb Spikes								
	Aldicarb	Aldicarb Sulfone	Aldicarb Sulfoxide	Carbofuran	Methomyl	Oxamyl	Thiofanox	Carbofuran-$^{13}C_6$ (Surrogate)	Methomyl-$^{13}C_2$,^{15}N (Surrogate)
1	49.9	49.7	50.5	49.7	50.5	50.6	50.9	50.8	52.2
2	49.4	49.7	50.3	49.2	49.8	49.7	50.7	51.7	52.5
3	51.3	51.0	51.0	50.6	51.0	51.0	52.5	52.7	53.8
4	46.8	47.9	50.6	47.7	47.7	49.4	49.2	49.7	53.2
5	46.8	48.0	51.9	48.2	47.9	48.4	48.3	49.7	53.6
6	45.9	48.4	51.9	47.7	47.1	48.3	48.9	49.4	53.2
7	46.0	48.1	51.2	47.5	54.9	48.9	50.4	48.2	52.7
Average Recovery:	48.0	49.0	51.1	48.7	49.8	49.5	50.1	50.3	53.0
Average % Recovery:	96.0	97.9	102.1	97.3	99.7	98.9	100.2	100.6	106.0
Standard Deviation:	2.1	1.2	0.7	1.2	2.7	1.0	1.4	1.5	0.6
% Relative SD	4.5	2.4	1.3	2.4	5.4	2.1	2.8	3.0	1.1

TABLE 8 Single-Laboratory Recovery Data in Chicago River Water

Sample	Youden Pair	Target Compound Spike (ppb)	Aldicarb (ppb)	Aldicarb % Recovery	Aldicarb Sulfone (ppb)	Aldicarb Sulfone % Recovery	Aldicarb Sulfoxide (ppb)	Aldicarb Sulfoxide % Recovery	Carbofuran (ppb)	Carbofuran % Recovery	Surrogate Carbofuran-$^{13}C_6$ (ppb)	Carbofuran-$^{13}C_6$ % Recovery
Blank											54.5	108.9
Sample 1	1	1.5	1.4	94.0	1.4	93.3	1.3	88.0	1.2	82.0	54.3	108.6
Sample 2		1.8	1.7	95.0	1.8	97.2	1.7	92.2	1.5	81.1	53.8	107.5
Sample 3	2	40.0	38.3	95.8	38.5	96.3	37.2	93.0	37.6	93.9	48.5	97.1
Sample 4		48.0	46.2	96.1	45.9	95.6	44.0	91.6	45.4	94.6	47.6	95.3
Sample 5	3	75.0	74.2	98.9	72.9	97.2	67.3	89.8	76.0	101.4	45.9	91.9
Sample 6		90.0	89.5	99.4	87.6	97.4	78.2	86.9	92.6	102.8	45.2	90.3

Sample	Youden Pair	Target Compound Spike (ppb)	Methomyl (ppb)	Methomyl % Recovery	Oxamyl (ppb)	Oxamyl % Recovery	Thiofanox (ppb)	Thiofanox % Recovery	Surrogate Methomyl-$^{13}C_2$,^{15}N (ppb)	Methomyl-$^{13}C_2$,^{15}N % Recovery
Blank									48.7	97.4
Sample 1	1	1.5	1.3	86.0	1.4	94.7	1.2	78.0	48.5	97.0
Sample 2		1.8	1.5	84.4	1.7	93.3	1.5	83.9	48.1	96.2
Sample 3	2	40.0	37.6	94.0	38.0	95.1	40.2	100.5	48.3	96.6
Sample 4		48.0	45.8	95.3	45.3	94.4	45.2	94.1	47.8	95.5
Sample 5	3	75.0	77.5	103.3	71.2	94.9	73.3	97.7	48.5	97.1
Sample 6		90.0	97.8	108.7	85.5	95.0	88.9	98.8	48.2	96.4

TABLE 9 Single-Laboratory Recovery Data in Lake Michigan Water

Sample	Youden Pair	Target Compound Spike (ppb)	Aldicarb (ppb)	Aldicarb % Recovery	Aldicarb Sulfone (ppb)	Aldicarb Sulfone % Recovery	Aldicarb Sulfoxide (ppb)	Aldicarb Sulfoxide % Recovery	Carbofuran (ppb)	Carbofuran % Recovery	Surrogate Carbofuran-$^{13}C_6$ (ppb)	Carbofuran-$^{13}C_6$ % Recovery
Blank											53.3	106.7
Sample 1	1	1.5	1.3	83.3	1.4	92.0	1.7	114.7	1.2	77.3	53.5	106.9
Sample 2		1.8	1.5	83.3	1.6	89.4	1.9	107.2	1.4	75.6	53.3	106.6
Sample 3	2	40.0	35.0	87.6	38.0	94.9	43.5	108.7	37.3	93.2	47.9	95.8
Sample 4		48.0	41.9	87.2	44.6	93.0	52.1	108.5	44.8	93.4	48.3	96.6
Sample 5	3	75.0	66.3	88.4	68.9	91.8	77.7	103.6	73.2	97.6	44.1	88.1
Sample 6		90.0	80.1	89.0	82.0	91.1	87.7	97.4	89.9	99.9	41.7	83.4

Sample	Youden Pair	Target Compound Spike (ppb)	Methomyl (ppb)	Methomyl % Recovery	Oxamyl (ppb)	Oxamyl % Recovery	Thiofanox (ppb)	Thofanox % Recovery	Surrogate Methomyl-$^{13}C_2$,^{15}N (ppb)	Methomyl-$^{13}C_2$,^{15}N % Recovery
Blank									52.3	104.5
Sample 1	1	1.5	1.2	81.3	1.4	92.0	1.1	70.7	52.9	105.8
Sample 2		1.8	1.4	78.9	1.6	90.0	1.3	72.8	51.0	101.9
Sample 3	2	40.0	36.4	90.9	38.9	97.1	36.1	90.3	51.1	102.2
Sample 4		48.0	44.3	92.3	45.2	94.2	44.5	92.6	52.1	104.3
Sample 5	3	75.0	72.6	96.7	71.2	95.0	69.2	92.2	50.2	100.4
Sample 6		90.0	90.2	100.2	83.1	92.4	79.0	87.8	46.2	92.4

16.5 This test method was tested by CRL on Florida Everglades water. The samples were spiked with target compounds across the calibration range as Youden pairs and surrogates as described in Section 12. Table 10 contains the recoveries for the surrogates and target compounds.

16.6 This test method was tested by CRL on chlorine fortified Chicago drinking water. The drinking water was fortified with Clorox [11]) bleach to 2.2 ppm free chlorine. After the addition of ascorbic acid, the free chlorine concentration was less than the detection limit (100 ppb) of the chlorine meter.[12] The samples were spiked with target compounds across the calibration range as Youden pairs and surrogates as described in Section 12. Table 11 contains the recoveries for the surrogates and target compounds.

16.7 This test method was tested by CRL on Madison, WI, drinking water. The free chlorine residual was determined to be 290 ppb in the native tap water sample before dechlorinating with ascorbic acid. After the addition of ascorbic acid, the free chlorine concentration was less than the detection limit (100 ppb) of the chlorine meter. The samples were spiked with target compounds across the calibration range as Youden pairs and surrogates as described in Section 12. Table 12 contains the recoveries for the surrogates and target compounds.

16.8 This test method was tested by CRL on Miami, FL, drinking water. The free chlorine residual was determined to be 310 ppb in the native tap water sample before dechlorinating with ascorbic acid. After the addition of ascorbic acid, the free chlorine concentration was less than the detection limit (100 ppb) of the chlorine meter. The samples were spiked with target compounds across the calibration range as Youden pairs and surrogates as described in Section 12. Table 13 contains the recoveries for the surrogates and target compounds.

[11] Clorox is a trademark of the Clorox Company in Oakland, CA.

[12] A Hach Pocket Colorimeter II (a trademark of the Hach Company in Loveland, CO) was used to measure free chlorine.

TABLE 10 Single-Laboratory Recovery Data in Florida Everglades Water

Sample	Youden Pair	Target Compound Spike (ppb)	Aldicarb (ppb)	Aldicarb % Recovery	Aldicarb Sulfone (ppb)	Aldicarb Sulfone % Recovery	Aldicarb Sulfoxide (ppb)	Aldicarb Sulfoxide % Recovery	Carbofuran (ppb)	Carbofuran % Recovery	Surrogate Carbofuran-$^{13}C_6$ (ppb)	Carbofuran-$^{13}C_6$ % Recovery
Blank											58.6	117.2
Sample 1	1	1.5	1.5	98.0	1.6	105.3	1.5	100.7	1.3	85.3	59.9	119.8
Sample 2		1.8	1.7	95.0	1.8	99.4	1.7	92.8	1.5	84.4	59.3	118.5
Sample 3	2	40.0	42.4	106.1	43.1	107.7	40.1	100.1	42.1	105.3	54.2	108.5
Sample 4		48.0	51.9	108.2	52.8	109.9	48.5	101.1	51.1	106.4	54.2	108.4
Sample 5	3	75.0	85.7	114.3	84.2	112.3	74.5	99.4	89.0	118.7	52.2	104.3
Sample 6		90.0	100.0	111.2	99.2	110.2	82.4	91.5	107.2	119.1	46.5	93.0

Sample	Youden Pair	Target Compound Spike (ppb)	Methomyl (ppb)	Methomyl % Recovery	Oxamyl (ppb)	Oxamyl % Recovery	Thiofanox (ppb)	Thiofanox % Recovery	Surrogate Methomyl-$^{13}C_2$,^{15}N (ppb)	Methomyl-$^{13}C_2$,^{15}N % Recovery
Blank									52.1	104.2
Sample 1	1	1.5	1.4	94.7	1.5	102.7	1.4	93.3	53.9	107.7
Sample 2		1.8	1.7	92.2	1.8	99.4	1.6	90.0	53.4	106.8
Sample 3	2	40.0	44.8	111.9	44.3	110.7	45.0	112.4	55.0	110.1
Sample 4		48.0	55.0	114.5	53.6	111.6	54.2	113.0	56.8	113.5
Sample 5	3	75.0	96.7	129.0	84.2	112.3	84.3	112.4	56.3	112.7
Sample 6		90.0	122.3	135.9	96.5	107.2	97.7	108.5	51.0	101.9

TABLE 11 Single-Laboratory Recovery Data in Fortified Chicago Drinking Water

Sample	Youden Pair	Target Compound Spike (ppb)	Aldicarb (ppb)	Aldicarb % Recovery	Aldicarb Sulfone (ppb)	Aldicarb Sulfone % Recovery	Aldicarb Sulfoxide (ppb)	Aldicarb Sulfoxide % Recovery	Carbofuran (ppb)	Carbofuran % Recovery	Surrogate Carbofuran-$^{13}C_6$ (ppb)	Carbofuran-$^{13}C_6$ % Recovery
Blank											48.1	96.3
Sample 1	1	1.5	1.2	78.7	1.2	81.3	1.3	87.3	1.0	64.7	49.7	99.3
Sample 2		1.8	1.5	82.2	1.5	85.0	1.7	91.7	1.3	71.1	49.6	99.2
Sample 3	2	40.0	30.7	76.8	31.6	79.1	35.3	88.3	31.8	79.6	44.3	88.7
Sample 4		48.0	36.6	76.2	37.6	78.4	43.5	90.7	38.6	80.4	43.6	87.2
Sample 5	3	75.0	54.7	73.0	56.0	74.6	67.0	89.3	59.6	79.4	40.4	80.8
Sample 6		90.0	65.2	72.5	69.1	76.8	85.7	95.2	75.2	83.6	39.2	78.4

Sample	Youden Pair	Target Compound Spike (ppb)	Methomyl (ppb)	Methomyl % Recovery	Oxamyl (ppb)	Oxamyl % Recovery	Thiofanox (ppb)	Thiofanox % Recovery	Surrogate Methomyl-$^{13}C_2$,^{15}N (ppb)	Methomyl-$^{13}C_2$,^{15}N % Recovery
Blank									51.2	102.3
Sample 1	1	1.5	1.1	72.0	1.2	79.3	1.1	70.0	54.1	108.2
Sample 2		1.8	1.3	74.4	1.5	83.9	1.4	78.9	53.6	107.2
Sample 3	2	40.0	30.3	75.8	33.0	82.4	32.1	80.2	51.5	103.0
Sample 4		48.0	37.3	77.8	38.9	81.0	40.1	83.6	51.5	102.9
Sample 5	3	75.0	56.8	75.8	58.2	77.7	58.4	77.8	50.6	101.2
Sample 6		90.0	70.8	78.7	71.9	79.9	71.9	79.9	51.1	102.2

16.9 *Multi-Laboratory Validation*—The test method has been tested by six laboratories using reagent water. Each lab spiked seven replicates of the target analytes at the reporting limit (1 ppb) and four replicates spiked at the laboratory control spike level (50 ppb) each with the appropriate surrogate spike as described in 12.4. Further validation of the test method consisted of acidified, as described in Section 10, unknown reagent water samples prepared and shipped by EPA and analyzed by volunteer laboratories during a laboratory emergency response full scale exercise conducted by EPA that required a quick turn-around time, within 48 hours. Five laboratories submitted data in a timely manner that met the exercise requirements. Tables 14-16 show the multi-laboratory data.

17. Quality Control

17.1 A crucial part of a test method is quality control. A laboratory should follow their in-house QA/QC procedures and should meet or exceed the criteria given in this test method. The quality-control criteria are given in the various test method sections. Section 10 contains the sampling and preservation requirements and Section 12 contains the majority of quality control requirements when following this test method. Section 12 includes requirements for calibration, precision and bias study to demonstrate laboratory capability, initial demonstration of performance, surrogate, method blank, reporting limit check, laboratory control, matrix spike and duplicate sample requirements. An IRM should be incorporated into the analysis periodically to verify that standard concentrations are comparable between sources. The IRM criteria should be based upon the laboratories QA/QC policies and the individual data quality objectives.

18. Keywords

18.1 carbamates; liquid chromatography; mass spectrometry; water

TABLE 12 Single-Laboratory Recovery Data in Madison, WI, Drinking Water

Sample	Youden Pair	Target Compound Spike (ppb)	Aldicarb (ppb)	Aldicarb % Recovery	Aldicarb Sulfone (ppb)	Aldicarb Sulfone % Recovery	Aldicarb Sulfoxide (ppb)	Aldicarb Sulfoxide % Recovery	Carbofuran (ppb)	Carbofuran % Recovery	Surrogate Carbofuran-$^{13}C_6$ (ppb)	Carbofuran-$^{13}C_6$ % Recovery
Blank											58.8	117.5
Sample 1	1	1.5	1.5	97.3	1.5	102.7	1.4	94.0	1.2	82.0	58.6	117.2
Sample 2		1.8	1.8	97.2	1.9	103.9	1.7	96.7	1.5	85.0	58.5	117.1
Sample 3	2	40.0	39.9	99.7	41.9	104.8	39.1	97.7	39.8	99.4	53.2	106.3
Sample 4		48.0	47.1	98.1	49.0	102.0	46.6	97.1	47.8	99.6	52.0	104.1
Sample 5	3	75.0	74.0	98.7	77.6	103.4	73.8	98.4	80.1	106.9	50.0	100.0
Sample 6		90.0	88.3	98.1	92.9	103.2	88.9	98.7	97.2	108.0	47.6	95.1

Sample	Youden Pair	Target Compound Spike (ppb)	Methomyl (ppb)	Methomyl % Recovery	Oxamyl (ppb)	Oxamyl % Recovery	Thiofanox (ppb)	Thiofanox % Recovery	Surrogate Methomyl-$^{13}C_2$,^{15}N (ppb)	Methomyl-$^{13}C_2$,^{15}N % Recovery
Blank									54.9	109.9
Sample 1	1	1.5	1.4	92.0	1.5	99.3	1.3	84.7	55.9	111.8
Sample 2		1.8	1.7	93.3	1.9	102.8	1.6	86.7	55.5	111.1
Sample 3	2	40.0	40.9	102.2	42.1	105.3	39.3	98.2	55.8	111.6
Sample 4		48.0	49.6	103.3	49.7	103.5	46.8	97.4	55.7	111.4
Sample 5	3	75.0	83.1	110.8	78.1	104.1	74.1	98.8	55.9	111.8
Sample 6		90.0	102.4	113.8	92.1	102.3	86.7	96.4	54.6	109.2

TABLE 13 Single-Laboratory Recovery Data in Miami, FL, Drinking Water

Sample	Youden Pair	Target Compound Spike (ppb)	Aldicarb (ppb)	Aldicarb % Recovery	Aldicarb Sulfone (ppb)	Aldicarb Sulfone % Recovery	Aldicarb Sulfoxide (ppb)	Aldicarb Sulfoxide % Recovery	Carbofuran (ppb)	Carbofuran % Recovery	Surrogate Carbofuran-$^{13}C_6$ (ppb)	Carbofuran-$^{13}C_6$ % Recovery
Blank											57.8	115.5
Sample 1	1	1.5	1.5	101.3	1.6	106.7	1.6	107.3	1.5	101.3	58.8	117.6
Sample 2		1.8	1.8	101.1	1.9	107.2	1.9	105.0	1.6	86.7	59.3	118.5
Sample 3	2	40.0	40.3	100.7	42.2	105.5	42.3	105.7	40.1	100.2	52.9	105.8
Sample 4		48.0	47.4	98.8	50.0	104.2	52.8	109.9	48.8	101.8	52.1	104.2
Sample 5	3	75.0	72.6	96.8	77.8	103.7	82.3	109.7	79.8	106.4	48.5	97.0
Sample 6		90.0	87.4	97.1	90.2	100.2	96.6	107.3	98.5	109.4	43.2	86.3

Sample	Youden Pair	Target Compound Spike (ppb)	Methomyl (ppb)	Methomyl % Recovery	Oxamyl (ppb)	Oxamyl % Recovery	Thiofanox (ppb)	Thiofanox % Recovery	Surrogate Methomyl-$^{13}C_2$,^{15}N (ppb)	Methomyl-$^{13}C_2$,^{15}N % Recovery
Blank									58.2	116.4
Sample 1	1	1.5	2.2	147.3	1.7	110.7	1.7	112.7	58.6	117.2
Sample 2		1.8	1.8	97.2	1.9	106.1	1.7	96.7	60.4	120.9
Sample 3	2	40.0	41.6	103.9	43.1	107.8	41.4	103.6	59.2	118.3
Sample 4		48.0	50.4	105.0	51.0	106.3	48.5	100.9	60.1	120.2
Sample 5	3	75.0	81.8	109.1	78.8	105.0	77.1	102.8	59.0	118.1
Sample 6		90.0	101.3	112.5	91.0	101.2	90.8	100.9	53.7	107.3

TABLE 14 Multi-Laboratory Recovery Data from Reagent Water

Analyte	Spike Conc. (ppb)	# Results	# Labs	Bias			Precision			
				Mean Recovery (%)	Min Recovery (%)	Max Recovery (%)	Overall SD	Pooled Within-Lab DS	Overall RSD (%)	Pooled Within-Lab RSD (%)
Aldicarb	1	42	6	97.4	41.6	145.4	0.26	0.08	26.8	7.1
Aldicarb	50	24	6	96.6	71.8	114.8	6.14	2.29	12.7	5.0
Aldicarb Sulfone	1	42	6	103.2	77.9	118.0	0.09	0.05	8.7	5.4
Aldicarb Sulfone	50	24	6	97.3	74.5	111.6	5.70	1.86	11.7	4.0
Aldicarb Sulfoxide	1	42	6	86.3	32.4	112.0	0.25	0.07	29.4	9.3
Aldicarb Sulfoxide	50	24	6	96.4	76.9	109.1	4.50	2.34	9.3	5.1
Carbofuran	1	42	6	75.6	13.8	111.0	0.33	0.03	44.2	7.3
Carbofuran	50	24	6	90.5	45.1	109.2	9.64	1.90	21.3	5.2
Methomyl	1	42	6	91.7	36.0	129.0	0.26	0.04	28.8	5.2
Methomyl	50	24	6	97.2	72.8	114.0	5.99	2.41	12.3	5.2
Oxamyl	1	42	6	101.2	75.0	135.0	0.19	0.06	19.1	5.9
Oxamyl	50	24	6	100.7	77.5	126.0	7.99	2.17	15.9	4.7
Thiofanox	1	42	6	109.9	70.2	165.0	0.20	0.13	18.4	12.4
Thiofanox	50	24	6	100.1	75.8	118.8	7.34	5.16	14.7	11.3
Carbofuran-$^{13}C_6$	50	64	6	102.2	50.8	147.0	12.01	4.32	23.5	6.9
Methomyl-$^{13}C_2$,^{15}N	50	64	6	109.8	80.6	130.9	5.80	4.89	10.6	9.0

TABLE 15 Multi-Laboratory Target Analyte Recovery Data from an EPA Emergency Response Exercise

Analyte	Sample Number	Youden Pair	Spike Conc. (ppb)	# Labs	Measured Mean Conc. (ppb)	Total SD	Bias (%)	Single Operator SD (ppb)	Recovery (%)
Aldicarb	CAR-1		0	5	0.0				
Aldicarb	CAR-2		0	5	0.0				
Aldicarb	CAR-3	1	4	5	3.7	0.31	–7.1	0.15	92.9
Aldicarb	CAR-4		4.8	5	4.5	0.44	–5.4		94.6
Aldicarb	CAR-5	2	40	5	37.7	4.05	–5.7	1.60	94.4
Aldicarb	CAR-6		48	5	44.6	5.02	–7.0		93.0
Aldicarb	CAR-7	3	60	5	55.0	8.68	–8.4	2.02	91.6
Aldicarb	CAR-8		72	5	67.7	9.26	–6.0		94.0
Aldicarb Sulfone	CAR-1		0	5	0.0				
Aldicarb Sulfone	CAR-2		0	5	0.0				
Aldicarb Sulfone	CAR-3	1	4	5	4.4	0.50	10.4	0.24	110.4
Aldicarb Sulfone	CAR-4		4.8	5	5.3	0.72	10.3		110.3
Aldicarb Sulfone	CAR-5	2	40	5	43.9	5.28	9.7	2.73	109.7
Aldicarb Sulfone	CAR-6		48	5	50.5	8.29	5.2		105.2
Aldicarb Sulfone	CAR-7	3	60	5	64.9	10.32	8.2	4.07	108.2
Aldicarb Sulfone	CAR-8		72	5	75.0	15.83	4.2		104.2
Aldicarb Sulfoxide	CAR-1		0	5	0.0				
Aldicarb Sulfoxide	CAR-2		0	5	0.0				
Aldicarb Sulfoxide	CAR-3	1	4	5	4.3	0.36	7.4	0.37	107.4
Aldicarb Sulfoxide	CAR-4		4.8	5	5.5	0.23	14.0		114.0
Aldicarb Sulfoxide	CAR-5	2	40	5	43.7	2.33	9.3	2.45	109.4
Aldicarb Sulfoxide	CAR-6		48	5	50.4	5.58	5.0		105.0
Aldicarb Sulfoxide	CAR-7	3	60	5	66.5	5.07	10.8	5.27	110.8
Aldicarb Sulfoxide	CAR-8		72	5	73.6	9.98	2.2		102.3

TABLE 16 Multi-Laboratory Surrogate Recovery from an EPA Emergency Response Exercise

Analyte	Spike Conc. (ppb)	Mean Measured Conc. (ppb)	Total SD (ppb)	Bias (%)	Single Operator SD (ppb)	Recovery (%)
Carbofuran-$^{13}C_6$	50	54.3	10.7	8.5	4.6	108.5
Methomyl-$^{13}C_2$,^{15}N	50	52.3	9.7	4.6	6.0	104.6