



Designation: D7600 – 16 (Reapproved 2017)

Standard Test Method for Determination of Aldicarb, Carbofuran, Oxamyl and Methomyl by Liquid Chromatography/Tandem Mass Spectrometry¹

This standard is issued under the fixed designation D7600; 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, carbofuran, oxamyl and methomyl (referred to collectively as carbamates in this test method) in surface 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 This test method has been developed by U.S. EPA Region 5 Chicago Regional Laboratory (CRL).

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

1.4 The Detection Verification Level (DVL) and Reporting Range for the carbamates are listed in [Table 1](#).

1.4.1 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.

1.4.2 The reporting limit is the concentration of the Level 1 calibration standard as shown in [Table 2](#) for the carbamates.

1.5 *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.*

1.6 *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 Recom-*

mendations 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](#)
- [D3694 Practices for Preparation of Sample Containers and for Preservation of Organic 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](#)

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, carbofuran, oxamyl and methomyl 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

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	100	1–100
Carbofuran	100	1–100
Oxamyl	100	1–100
Methomyl	100	1–100

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 *MDL*, *n*—Method Detection Limit

3.3.6 *MeOH*, *n*—Methanol

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

3.3.8 *MRM*, *n*—Multiple Reaction Monitoring

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

3.3.10 *NA*, *adj*—Not Available

3.3.11 *ND*, *n*—non-detect

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

3.3.13 *PPB*, *n*—parts per billion

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 *RSD*, *n*—Relative Standard Deviation

3.3.19 *RT*, *n*—Retention Time

3.3.20 *SDS*, *n*—Safety Data Sheets

3.3.21 *SRM*, *n*—Single Reaction Monitoring

3.3.22 *SS*, *n*—Surrogate Standard

3.3.23 *TC*, *n*—Target Compound

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

3.3.25 *VOA*, *n*—Volatile Organic Analysis

4. Summary of Test Methods

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 between 0°C and 6°C and analyzed within 7 days of collection. In the lab, the samples are spiked with surrogate, filtered using a syringe-driven filter unit and analyzed directly by LC/MS/MS.

4.3 Aldicarb, carbofuran, oxamyl, methomyl, and 4-bromo-3,5-dimethylphenyl-*N*-methylcarbamate (BDMC, 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 aldicarb, carbofuran, oxamyl, methomyl and the BDMC surrogate recovery.

5. Significance and Use

5.1 The *N*-methyl carbamate (NMC) pesticides: aldicarb, carbaryl, carbofuran, formetanate hydrochloride, methiocarb, methomyl, oxamyl, pirimicarb, propoxur, and thiodicarb have been identified by EPA as working through a common mechanism. They affect the nervous system by reducing the ability of the enzyme cholinesterase. Cholinesterase 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.⁴

5.2 This test method has been investigated for use with reagent and surface water for the selected carbamates: aldicarb, carbofuran, oxamyl, and methomyl.

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.

6.2 All glassware is washed in hot water with a detergent, 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, then 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 that are co-extracted from 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 in order 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

⁴ Additional information about carbamate pesticides can be found on the Internet at <http://www.epa.gov>.

⁵ A Waters Alliance High Performance Liquid Chromatography (HPLC) System (a trademark of the Waters Corporation, Milford, MA), or equivalent, was found suitable for use. The multi-laboratory study included Agilent and Waters LC systems.

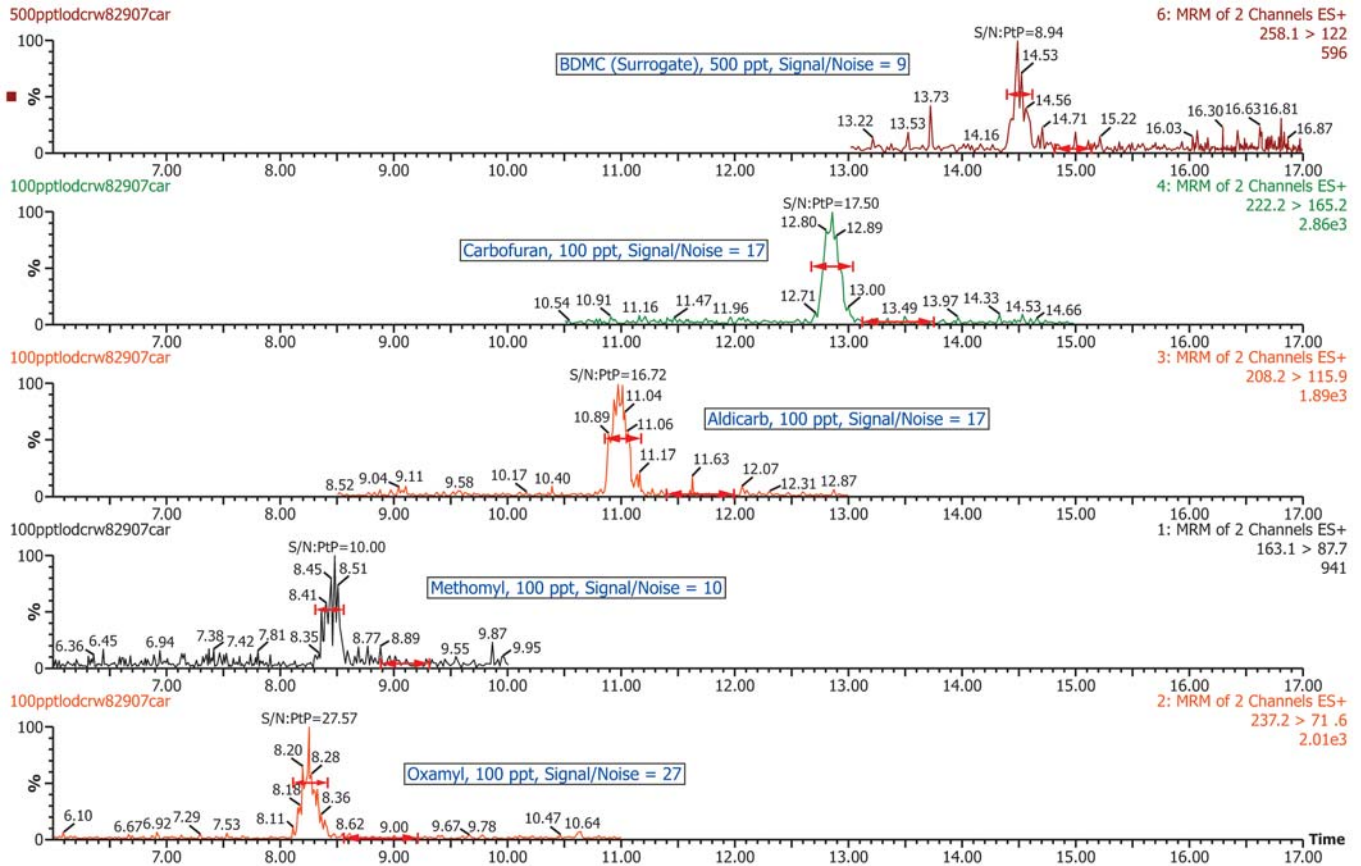


FIG. 1 Example Primary SRM Chromatograms Signal/Noise Ratios

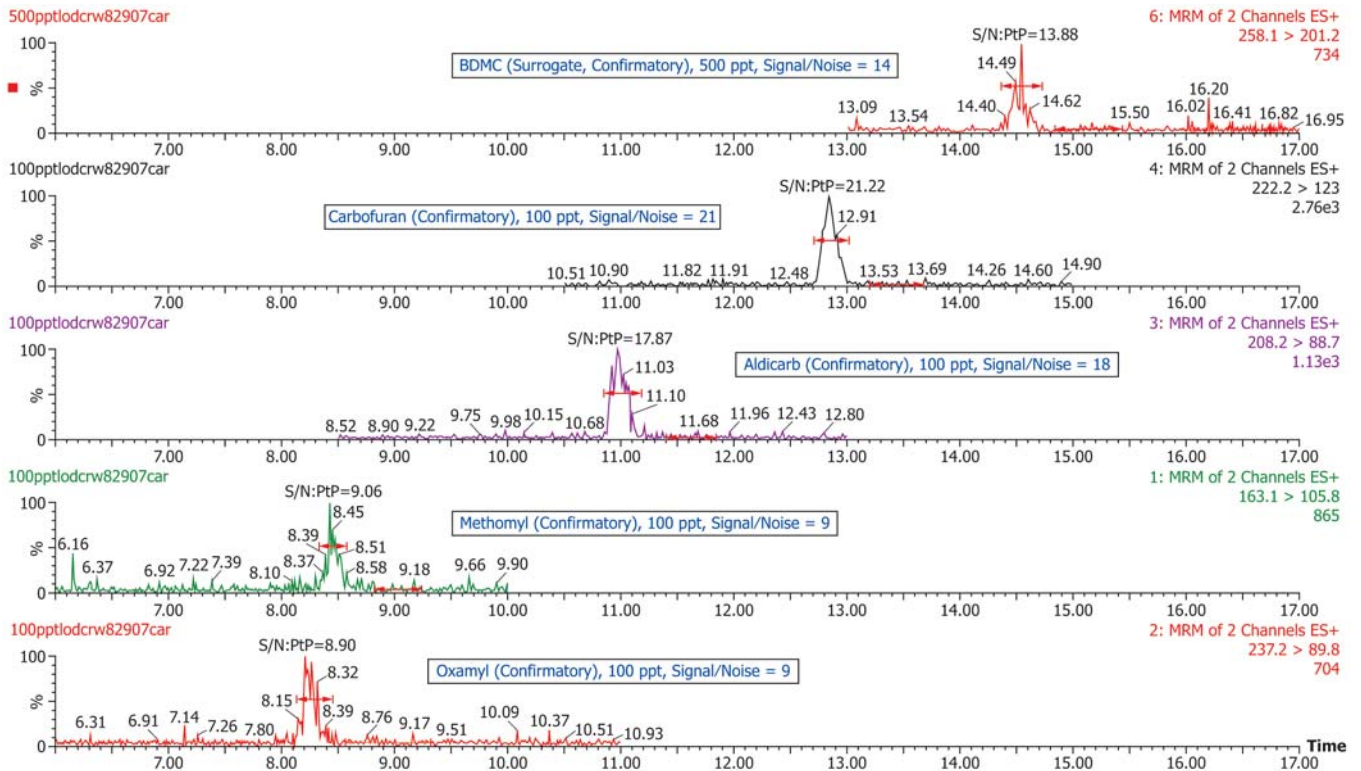


FIG. 2 Example Confirmatory SRM Chromatograms Signal/Noise Ratios