



Designation: D7597 – 16 (Reapproved 2017)

Standard Test Method for Determination of Diisopropyl Methylphosphonate, Ethyl Hydrogen Dimethylamidophosphate, Ethyl Methylphosphonic Acid, Isopropyl Methylphosphonic Acid, Methylphosphonic Acid and Pinacolyl Methylphosphonic Acid in Water by Liquid Chromatography/Tandem Mass Spectrometry¹

This standard is issued under the fixed designation D7597; 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 diisopropyl methylphosphonate (DIMP), ethyl hydrogen dimethylamidophosphate (EHDMAP), ethyl methylphosphonic acid (EMPA), isopropyl methylphosphonic acid (IMPA), methylphosphonic acid (MPA) and pinacolyl methylphosphonic acid (PMPA) (referred to collectively as organophosphonates in this test method) in surface water by direct injection using liquid chromatography (LC) and detected with tandem mass spectrometry (MS/MS) using electrospray ionization (ESI). These analytes are qualitatively and quantitatively determined by this test method. This test method adheres to single reaction monitoring (SRM) 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 organophosphonates are listed in [Table 1](#).

1.4.1 The DVL is required to be at a concentration at least three times below the reporting limit (RL) and have a signal/noise ratio greater than 3:1. [Fig. 1](#) displays the signal/noise ratios at the DVLs for the organophosphonates in the ESI positive mode and [Fig. 2](#) in the ESI negative mode.

1.4.2 The reporting limit is the concentration of the Level 1 calibration standard as shown in [Table 2](#) for the organophosphonates except for MPA in the ESI negative mode which is at Level 2 due to not meeting the DVL criteria at the lower

concentration level. The DVL for MPA in the ESI negative mode is at 20 $\mu\text{g/L}$, which forces a raised reporting limit. However, the multi-laboratory validation required a spike of all target analytes at Level 1 concentrations. The mean recovery for MPA in the ESI negative mode at this level was 98.7 % as shown in [Table 3](#). If your instrument's sensitivity can meet the requirements in this test method, MPA may have a 50 $\mu\text{g/L}$ reporting limit.

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 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](#)
- [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](#)

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 Detection Verification Level and Reporting Range

Analyte	ESI Mode	DVL (µg/L)	Reporting Range (µg/L)
Diisopropyl methylphosphonate	Positive	1	5–150
Ethyl hydrogen dimethylamidophosphate	Negative	0.25	5–150
Ethyl hydrogen dimethylamidophosphate	Positive	0.25	5–150
Ethyl methylphosphonic acid	Negative	5	50–1500
Ethyl methylphosphonic acid	Positive	5	50–1500
Isopropyl methylphosphonic acid	Negative	10	50–1500
Isopropyl Methylphosphonic acid	Positive	5	50–1500
Methylphosphonic acid	Negative	20	100–1500
Methylphosphonic acid	Positive	10	50–1500
Pinacolyl methylphosphonic acid	Negative	5	50–1500
Pinacolyl methylphosphonic acid	Positive	5	50–1500

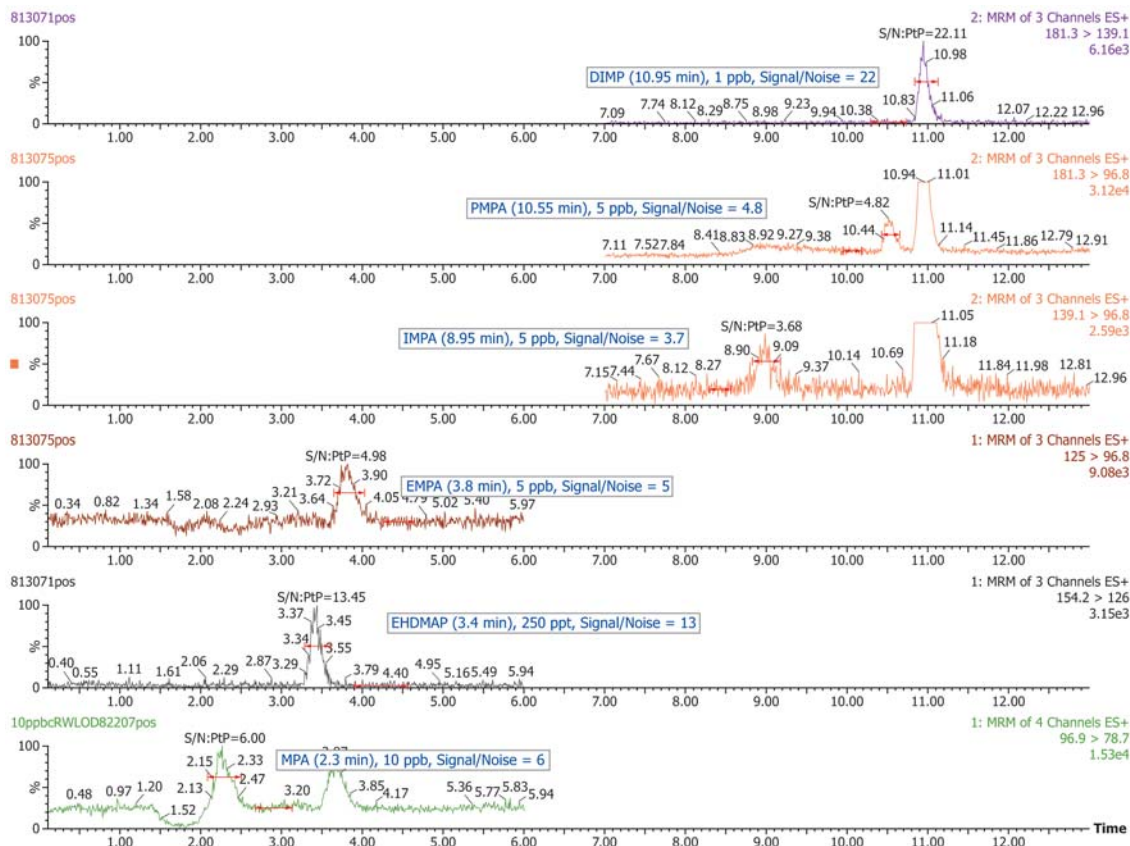


FIG. 1 Example ESI Positive Mode SRM Chromatograms Signal/Noise Ratios

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 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).

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

3.2.3 organophosphonates, *n*—in this test method, diisopropyl methylphosphonate (DIMP), ethyl hydrogen dimethylamidophosphate (EHDMPA), ethyl methylphosphonic acid (EMPA), isopropyl methylphosphonic acid (IMPA), methylphosphonic acid (MPA) and pinacolyl methylphosphonic acid (PMPA).

³ Available from United States Environmental Protection Agency (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

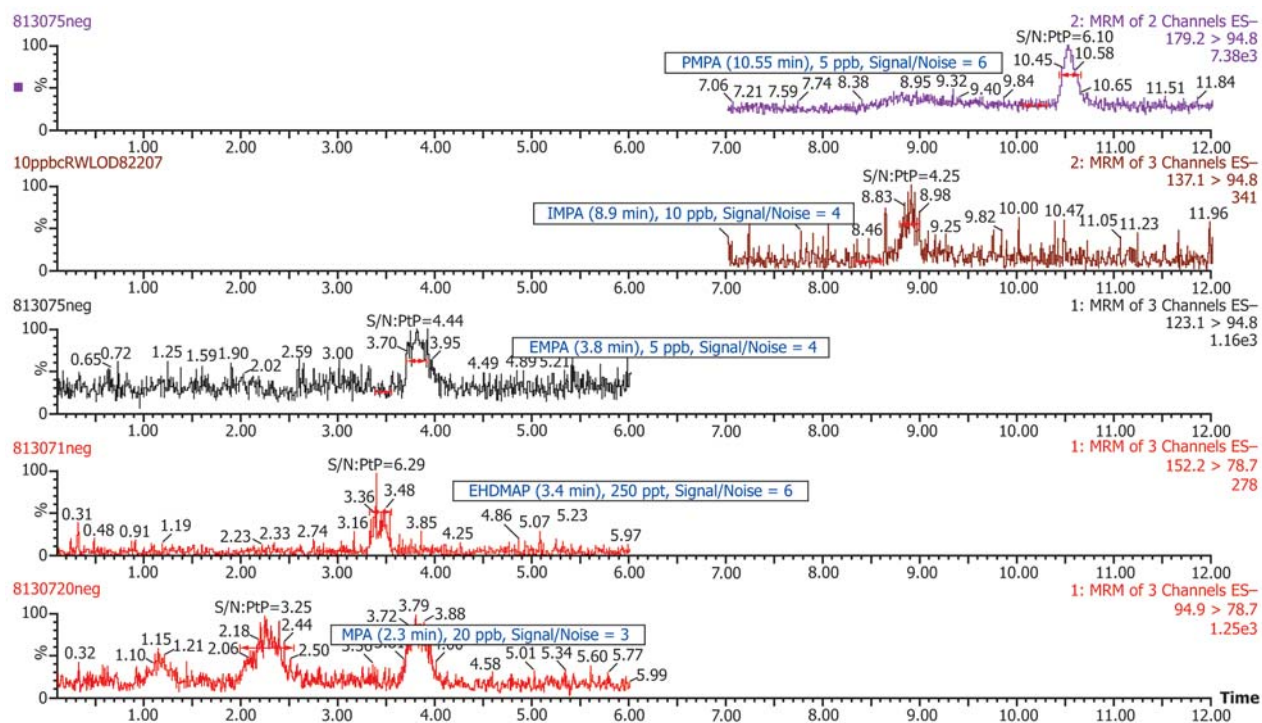


FIG. 2 Example ESI Negative Mode SRM Chromatograms Signal/Noise Ratios

TABLE 2 Concentrations of Calibration Standards (PPB)

Analyte/Surrogate	LV 1	LV 2	LV 3	LV 4	LV 5	LV 6	LV 7
Diisopropyl methylphosphonate	5	10	20	35	50	100	150
Ethyl hydrogen dimethylamidophosphate	5	10	20	35	50	100	150
Ethyl methylphosphonic acid	50	100	200	350	500	1000	1500
Isopropyl methylphosphonic acid	50	100	200	350	500	1000	1500
Methylphosphonic acid	50	100	200	350	500	1000	1500
Pinacolyl methylphosphonic acid	50	100	200	350	500	1000	1500
DIMP-D14 (Surrogate)	5	10	20	35	50	100	150
PMPA-13C4 (Surrogate)	25	50	100	175	250	500	750
MPA-D3 (Surrogate)	25	50	100	175	250	500	750

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 μ M, *n*—micromolar, 1×10^{-6} moles/L
- 3.3.25 VOA, *n*—Volatile Organic Analysis

4. Summary of Test Method

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

4.2 For organophosphonate analysis, samples are shipped to the lab between 0°C and 6°C and analyzed within 1 day of