Designation: D8401 – 24

Standard Test Method for Identification of Polymer Type and Quantity of Microplastic Particles and Fibers in Waters with High to Low Suspended Solids Using Pyrolysis-Gas Chromatography/Mass Spectrometry[1]

This standard is issued under the fixed designation D8401; 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 In this pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) test method, an analytical protocol validated specifically for the analysis of water with high to low suspended solids is described. This test method will standardize the identification and simultaneous quantitation of organic polymer particles and fibers in water. It has been designed for and applies to all microplastic particles and fibers, and is intended for use with treated drinking water, surface waters, wastewater influent and effluent (secondary and tertiary), and marine waters. This test method is not limited to these particular water matrices; however, the applicability of this test method to other aqueous matrices shall be demonstrated.

1.2 Microgram quantities of a sample containing microplastics are pyrolyzed (Py) at 600 °C. The pyrolyzates are separated on an analytical column (GC) and detected using a 70-eV electron impact mass spectrometer (MS). Polymers often have similar pyrograms, making it difficult to differentiate the pyrolyzates for a given polymer from those of the composite sample. In this test method, ion ratios at predetermined retention times to facilitate the identification of each polymer present in a sample containing microplastics are compared.

1.3 This test method is to be used in conjunction with Practices D8332, D8333, and D8402. These ASTM International standards enable the collection and preparation of water samples with high, medium, or low suspended solids for the identification and quantification of microplastic particles and fibers without compromising the integrity of the microplastics. This test method is applicable to microplastic fibers and particles, including sizes defined as a nanoparticle; this is a natural extension of this test method because Py-GC/MS technology responds to the total mass of the sample independent of individual particle sizes. The uniformity of particle size influences the reproducibility of the pyrogram and samples with microplastics should be reduced to a fine powder with the final particle size diameter on the order of less than 0.2 mm.

1.4 It is the responsibility of the user to ensure the validity of this test method for untested matrices.

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

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]

D883 Terminology Relating to Plastics
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
D8332 Practice for Collection of Water Samples with High, Medium, or Low Suspended Solids for Identification and Quantification of Microplastic Particles and Fibers
D8333 Practice for Preparation of Water Samples with High, Medium, or Low Suspended Solids for Identification and Quantification of Microplastic Particles and Fibers Using

[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.

Raman Spectroscopy, IR Spectroscopy, or Pyrolysis-GC/MS
D8402 Practice for Development of Microplastic Reference Samples for Calibration and Proficiency Evaluation in All Types of Water Matrices with High to Low Levels of Suspended Solids
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E355 Practice for Gas Chromatography Terms and Relationships
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E2456 Terminology Relating to Nanotechnology

2.2 *EPA Standard:*
SW-846 Hazardous Waste Test Methods[3]

2.3 *TNI Standard:*
GUID-3-110-Rev0 TNI Guidance on Instrument Calibration[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminologies D883 and D1129 and Practice E355.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *backflush, n*—practice of reversing the flow through *(1)* the analytical column at the column connection or *(2)* a pre-column located between the injection port and the column.

3.2.1.1 *Discussion*—This practice prevents high boiling sample constituents from entering and perhaps contaminating the column, which significantly reduces sample analysis cycle time. **(1)**[5]

3.2.2 *calibration factor, CF, n*—area/concentration of the polymer-specific ion in the pyrogram versus the amount of the standard, evaluated from a plot.

3.2.2.1 *Discussion*—CF is often referred to as response factor (RF) when there is an internal standard calibration.

3.2.3 *calibration reference standard, CRS, n*—mixture or solution prepared from the primary polymer standards.

3.2.3.1 *Discussion*—Calibration reference standards are used to calibrate the instrument response with respect to analyte amount.

3.2.4 *continuing calibration check (CCC) sample, n*—25 µg of polystyrene (PS) is commonly used as the representative polymer to monitor system performance.

3.2.4.1 *Discussion*—A CCC shall be run and analyzed after the analysis of every 20 field samples. This sample is often referred to as a CCC.

3.2.5 *cryo-trap, n*—device also known as a "cold-trap" frequently attached to a pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) unit located at the column inlet and uses temperature to narrow the initial bandwidths of the sample vapors.

3.2.5.1 *Discussion*—While cryo-trapping is commonly used with sample introduction devices such as thermal desorption units that slowly introduce volatile compounds to a GC or GC/MS, it is not needed or recommended for this test method because of the high speed in which the polymer sample is introduced into the column.

3.2.6 *effluent, n*—any stage of treated wastewater.

3.2.7 *extracted ion chromatogram, EIC, n*—plot of detector response for a specified ion versus elution time.

3.2.7.1 *Discussion*—The EIC is a graph of signal intensity versus time for a single mass to charge (m/z) or a range of masses. In typical use, this is a subset of the total ion chromatogram (TIC) in which all the mass ions detected are plotted together in a single two-dimensional (2D) graph of signal versus time. Further detail on this definition can be found in Refs **2** and **3**. The most general term for this EIC type of plot was "mass chromatogram" as defined by Ron Hites in 1970 **(4)**. Later, it was recognized that the mass chromatogram may include other ions (for example, multiple charged ions) that contribute toward the actual ion current detected by the MS. The term "extracted ion current" chromatogram or EIC has been in common use for many decades. Sometimes, EIC is also defined as "extracted ion chromatogram." Although other acronyms will be found in the literature such as XIC, in this test method, the more common acronym EIC is used for this 2D plot.

3.2.8 *field replicates, n*—two or more separate samples collected according to the collection protocol for that sample collection, placed under identical circumstances and treated exactly the same throughout field and laboratory procedures.

3.2.8.1 *Discussion*—The analysis of field replicates duplicates provides an indication of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.2.9 *influent, n*—raw sewage entering a wastewater treatment facility.

3.2.10 *laboratory replicates, n*—two or more sample aliquots taken from the same homogenous sample in the analytical laboratory and analyzed separately using identical procedures.

3.2.10.1 *Discussion*—Analysis of laboratory replicates gives an indication of the precision associated with laboratory procedures but not with sample collection as described in Practice D8332, post-collection preparation as described in Practice D8333, preservation, or storage procedures.

3.2.11 *linear dynamic range, n*—concentration range over which an ion signal is linear with analyte concentration.

3.2.12 *microplastic, n*—any solid, synthetic, organic, polymeric material to which chemical additives or other substances may have been added, which are particles <5 mm in their largest dimension and fibers no longer than 15 mm in length with an aspect ratio of at least 30:1 and <500 µm in its smallest dimension. **D8332, D8333**

[3] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

[4] Available from The Nelac Institute, PO Box 2439, Weatherford, TX 76086, https://nelac-institute.org/docs/guidance/21666708.pdf.

[5] The boldface numbers in parentheses refer to a list of references at the end of this standard.