



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 Spectrometry¹

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 Methods³

2.3 *TNI Standard:*

GUID-3-110-Rev0 TNI Guidance on Instrument Calibration⁴

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.

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.

3.2.13 *MQ water, n*—water that has been purified using resin filters and deionized to a high degree by a water purification system and typically characterized as a 18.0 Mohm.cm at 25 °C water (Specification D1193, Type 1 laboratory water).

3.2.14 *nanoparticle, n*—in nanotechnology, a subclassification of ultrafine particle with lengths in two or three dimensions greater than 0.001 µm (1 nm) and smaller than about 0.1 µm (100 nm), and that may or may not exhibit a size-related intensive property.

3.2.14.1 *Discussion*—This term is a subject of controversy regarding the size range and presence of a size-related property. Current usage emphasizes size and not properties in the definition. The length scale may be a hydrodynamic diameter or a geometric length appropriate to the intended use of the nanoparticle. **E2456**

3.2.15 *pyrogram, n*—plot of detector (MS) response signal to elution time, often referred to as a TIC.

3.2.16 *pyrolyzer, n*—device that heats a sample for the purpose of performing pyrolysis.

3.2.16.1 *Discussion*—The term pyrolyzer can be used synonymously with furnace or another heater type to describe this device; this includes filament-based, curie point-based, and furnace-based pyrolyzer technologies.

3.2.17 *pyrolysis, Py, n*—sudden thermal degradation of organic compounds.

3.2.17.1 *Discussion*—The sample shall be “heated” (to a temperature high enough to break covalent bonds) instantaneously in an inert atmosphere. The sample path shall be inert and at a uniform elevated temperature. The sample shall be at ambient temperature in an inert atmosphere before pyrolysis.

3.2.18 *reactive pyrolysis, RxPy*—thermal hydrolysis followed by methylation of acidic functionality on reactive molecules.

3.2.18.1 *Discussion*—Reactive pyrolysis is the breakdown of a sample under thermolysis in the presence of a chemical reactant added to that sample. This can be, but is not limited to, methanolysis by for example, tetramethylammonium hydroxide (TMAH). The compound, CaCO₃, is a solid, and when present in the sample cup, reactive pyrolysis can be induced in specific pyrolyzates.

3.2.19 *relative standard deviation, RSD, n*—is expressed in percent and is obtained by multiplying the standard deviation by 100 and dividing this product by the average.

3.2.19.1 *Discussion*—RSD compares the standard deviation with the mean of the given data set and tells you whether the “regular” standard deviation is small or large when compared to the mean of the given data set.

3.2.20 *response factor, RF, n*—the area/weight of the polymer-specific ion in the pyrogram versus the amount of standard analyzed, evaluated with a plot.

3.2.21 *retention indices, RI, n*—relative retention times normalized to closely eluting *n*-alkanes.

3.2.21.1 *Discussion*—Retention indices are system-independent and exhibit long-term reproducibility. Identifying

peaks by combining retention indices and spectral library search results is common in many laboratories.

3.2.22 *retention time, RT, n*—measure of the time required for a solute to pass through a chromatographic column and defined as the time from injection to the apex of the chromatographic “peak.”

3.2.23 *sample cup, n*—vessel made from deactivated stainless steel, quartz, or quartz-coated glass in which the sample is placed before pyrolysis.

3.2.24 *surface waters, n*—water body with its surface in contact with the ambient atmosphere and examples include lakes, rivers, and streams.

3.2.25 *suspended solids, n*—all matter that remain in suspension in water media and are removed by a 0.45 µm filter.

4. Summary of Test Method

4.1 This analytical test method has been developed specifically for water samples with high to very low suspended solids. It has been designed for and applies to all microplastic particles and fibers regardless of polymer type and has been validated for use with treated drinking water, surface waters, wastewater influent and effluent (secondary and tertiary), and marine waters for those polymer types identified in Table 1.

4.2 This test method is used in conjunction with the collection and preparation practices of Practices D8332, D8333, and D8402.

4.3 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 MS (SW-846) (5-8). Polymers often have similar pyrograms making it difficult to differentiate the pyrolyzates for a given polymer from those of the composite sample; comparing ion ratios at predetermined retention times will often facilitate the identification of each polymer present in the sample containing microplastics. Various software algorithms are used to simplify the complex chromatogram commonly associated with a multi-polymer pyrogram.

4.4 Methyl Eicosanoate (Me-Eic) is added to all samples as an analytical check standard. Me-Eic is used not as a surrogate nor an internal standard (ISTD) but as an indicator of the analytical quality of each injection. It monitors the quality of the analysis of the GC/MS instrument because the Me-Eic molecule is a thermally and chemically stable compound. It is not degraded at typical pyrolysis temperatures, and it does not react with pyrolyzates from polymers.

4.5 In Table 1, the polymers and reference ions used to validate this test method are listed. This test method is not limited to the polymers listed in the table; however, the applicability of this test method to polymers not listed shall be demonstrated (see 4.9 – 4.11 and Section 6). If desired, particle size, shape, or surface features, or combinations thereof, may be noted before analysis using appropriate instrumentation, such as scanning electron microscopy or infrared (IR) and Raman spectroscopy.

4.6 For the proper pyrolysis of a sample and to enable an accurate determination of the mass of microplastics in the

TABLE 1 Polymers Validated for This Test Method

Compound (Abbr.)	Primary Quantitation Ion (Name, Abbr.)	Polymer Identification (Ion) Representatives
Polyethylene (PE)	82 (1,20-Heneicosadiene, C21 ⁺)	C10 ⁺ , C14 ⁺ , C21 ⁺
Polypropylene (PP)	126 (2,4-Dimethyl-1-heptene, C9 ⁺)	C9 ⁺ , C12 ⁺ , C15 ⁺
Polyvinylchloride (PVC)	128 (Naphthalene, Naph)	Naphthalene, Indene, 3-methyl Indene
Polycarbonate (PC)	134 (4-Isopropenylphenol, IPP)	4-tert-Butylphenol, Bisphenol A ^A
Polyethylene terephthalate (PET)	182 (Benzophenone, BP)	4-Isopropenylphenol
Poly (methyl methacrylate) (PMMA)	100 (Methyl methacrylate, MMA)	Benzophenone
Nylon-6 (N-6)	113 (ϵ -Caprolactam, Capro)	Methyl methacrylate
Polystyrene (PS)	91 (Styrene trimer, SSS)	ϵ -Caprolactam,
Acrylonitrile-butadiene-styrene copolymer (ABS)	170 (2-Phenethyl-4-phenylpent-4-enenitrile, SAS)	N-(5-cyanopentyl)hex-5-anamide
Styrene-butadiene rubber (SBR)	54 (4-Vinylcyclohexene, VCH)	Styrene monomer, Styrene dimer, Styrene trimer
Nylon-6,6 (N-66)	84 (Cyclopentanone, CP)	Styrene monomer,
MDI-Polyurethane (PU)	198 (4,4'-Methylenedianiline, MDA)	2-Phenethyl-4-phenylpent-4-enenitrile
Reference (Ref)	326 (Methyl Eicosanoate, Me-Eic)	4-Vinylcyclohexene, SB (C12H14, hybrid dimer), SBB (C16H12 hybrid trimer) ^B
		Cyclopentanone, hexane-1,6-diamine ^C
		4,4-Methylenedianiline
		Methyl Eicosanoate

^A BPA (bisphenol A) is a polar compound and it would be more susceptible to analytical deviations due to a less-than-optimally-performing system, from gradual column degradation or possible system contamination. IPP (4-Isopropenylphenol) is a less polar compound and more robust in this analytical method.

^B Terminology for SB (C12H14) and SBB (C16H12) includes "S" for styrene and "B" for butadiene for this hybrid dimer and trimer.

^C DA (hexane-1,6-diamine) could be used for identification. However, DA is a very polar compound and susceptible to analytical deviations due to a less-than-optimally-performing system from gradual column degradation or possible system contamination.

sample cup, some samples may require additional pretreatment beyond that described in Practice D8333 and Section 11. Samples may include large pieces that need to be reduced in size or may be excessively wet and need to be dried. In these instances, the additional pretreatment might be as simple as crushing, filtration, drying, or solvation of the sample. Prepared sample homogeneity is essential.

4.7 A known amount of prepared sample is placed in a clean pyrolysis vessel such as a deactivated cup or quartz capillary tube and automatically purged with helium to remove oxygen before pyrolysis. Any pyrolysis GC/MS system combination may be used that meets the performance specifications and system settings in this test method. The vessel (sample cup) is inserted into the 600 °C environment of the pyrolyzer so that the polymers are instantaneously thermally degraded ("pyrolyzed"). In practice, the larger the surface area to mass ratio the more instantaneous the degradation and the more reproducible the pyrogram. The smaller the diameter of microplastic particles and fibers, the higher the surface-area/mass ratios; thus, analytical precision is high. Note that the uniformity of particle diameter influences the reproducibility of the pyrogram; the sample should be reduced to a fine powder using a cryogenic mill with the final particle diameter on the order of less than 0.2 mm.

4.8 The pyrolyzates are flushed from the pyrolysis tube into a GC column via a deactivated needle fixed in a split injection port. The column is interfaced to a MS. The pyrolysis and sample introduction process is fast and there is no need to cryo-trap at the head of the column (see Appendix X7). The GC column is temperature-programmed to separate the analytes (that is, pyrolyzates) formed by the thermal degradation of the polymer and detected by the MS. A plot of signal versus retention time is called a pyrogram, and a plot of the total MS signal versus time is often referred to as a TIC. A plot of the detector response from a single ion (m/z) versus time is generated, and this plot is referred to as an EIC.

4.9 The concentration of each identified polymer is determined using either internal or external standard calibration procedures (1). Data presented in support of this test method (Fig. 1) was determined using external standard calibration procedures (15.1) and collected using a 13 min backflush of the pre-column (1). Back-flushing of the pre-column is strongly recommended because it is an integral function of the separation process that reduces contamination of the analytical column, which reduces sample-to-sample cycle time.

4.10 Each polymer is identified based on the presence of a preselected pyrolyzate (that is, target compound) at a known retention time in the sample pyrogram and confirmation of the specific reference compounds. In Table 2, the target compounds and other ions used to identify each of the twelve target polymers are identified. For example, in the case of Nylon-6 (N-6), it is identified and quantified based on the presence or absence of ϵ -Caprolactam, m/z = 113 amu, at a retention time of 10.76 min. If N-6 is not present in the polymeric sample, ϵ -Caprolactam will not be present in the sample pyrogram.

4.11 The choice of target compound for each polymer is based upon its uniqueness in the pool of pyrolyzates created by all polymers (and non-polymeric contaminants) in the sample, and discretion is necessary in its selection. For example, benzene is present in the pyrogram of the twelve polymer mixture in Fig. 1, but it is not used as a target compound. Benzene is a pyrolyzate found in the pyrograms of many types of polymers, and because the benzene peak in the pyrogram is the sum of all the benzene formed when the twelve polymer mixture is pyrolyzed, it cannot be definitively assigned as a target compound to a specific polymer.

4.12 This is a test method for identifying and quantifying polymers on the list of twelve with the provision for qualifying additional polymers specific to one's interest (Section 6). The process of polymer identification begins with confirmation of the target compound followed by confirmation of the specific

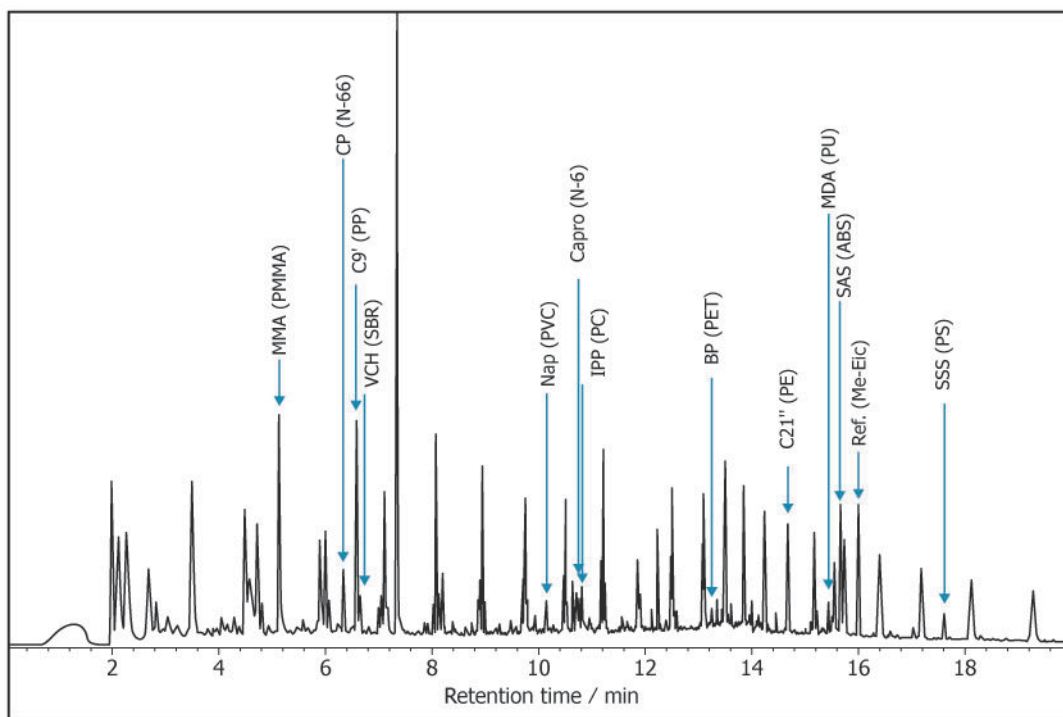


FIG. 1 Typical Pyrogram (TIC) of the Twelve Target Polymers

TABLE 2 Polymers and Their Associated Target Ion Information (9)

Polymers		Target Compound		m/z			R.T.
Name	Abbr.	Name	Abbr.	Measure	Other Ions	M.W.	(min.)
Polyethylene	PE	1,20-Heneicosadiene	C21''	82	41, 55, 97	208	14.67
Polypropylene	PP	2,4-Dimethyl-1-heptene	C9'	126	43, 55, 70	126	6.62
Polyvinylchloride	PVC	Naphthalene	Naph	128	102	128	10.17
Polycarbonate	PC	4-Isopropenyl-phenol	IPP	134	91, 119	134	10.83
Polyethylene terephthalate	PET	Benzophenone	BP	182	51, 77, 105	182	13.26
Polymethyl methacrylate	PMMA	Methyl methacrylate	MMA	100	69, 41, 99	100	5.17
Nylon-6	N-6	ϵ -Caprolactam	Capro	113	30, 55, 85	113	10.76
Polystyrene	PS	Styrene trimer	SSS	91	117, 207, 312	312	17.63
Acrylonitrile butadiene styrene copolymer	ABS	2-Phenethyl-4-phenylpent-4-enenitrile	SAS	170	91, 115, 118	261	15.68
Styrene-butadiene rubber	SBR	4-Vinylcyclohexene	VCH	54	79, 66, 108	108	6.68
Nylon-6,6	N-66	Cyclopentanone	CP	84	39, 55, 56	84	6.38
Polyurethane	PU	4-4'-Methylenedianiline	MDA	198	106, 182, 197	198	15.58
Reference	Ref	Methyl Eicosanoate	Me-Eic	326	74, 143	326	16.01

reference compounds. In this second step, the reference compounds shall be present in the correct ratios of peak intensities to each other and the target compound. These ratios are established through the analysis of a known calibration standard for each of the polymers on the list of twelve. See Ref 5 for many pyrogram examples and the pyrolyzate ratios for a specific set of experimental conditions. Be advised that the pyrolyzate ratios depend on the specific conditions and the type of pyrolyzer. Each individual laboratory shall separately estab-

lish the pyrolyzate ratios using the calibration standards for the instrumentation in their laboratory.

5. Significance and Use

5.1 Preliminary studies have identified polymeric organic compounds as contaminants in treated drinking water, wastewater, surface water, ground water, and marine waters. These polymers may be harmful to the environment and adversely affect human health, and in some circumstances,

mass estimation is commonly required. A universal, analytical method will help to normalize data from around the world and better understand which polymers are most frequently found in various climatic and geological locations (5-7). Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) has many advantages in that both polymer identification and mass quantification can be easily accomplished by chromatographic separation in combination with mass spectral analysis.

6. Adding and Validating Non-Target Polymers

6.1 In this test method, the procedures and analytical conditions used to determine accurately and precisely twelve specific polymers is described, and the target compound list can be any combination of these twelve polymers as listed in Table 1. The procedures can be easily modified if a subset of the twelve validated polymers is of interest (“polymers of interest”), which will then simplify the preparation of the calibration samples, the analytical samples, and the processing of the MS data. Additional polymers can be added to this analytical protocol only after it is confirmed that the “additional polymer” is (1) completely soluble in the solvent(s) being used, (2) that the resulting solution is stable (in its lowest energy state), and (3) there is no interference from either the analytical system or catalyzed interactions involving the pyrolysis products from other components in the analytical sample. A completely insoluble polymer can also be added by following the method technique as described for PE and polypropylene (PP) polymers.

6.2 The spectra of each peak in the pyrogram of the unknown polymer is compared to the spectra of the corresponding peak in the library database. Ideally, all peaks in the pyrogram of the unknown polymer are identified. The library database is available in Ref 5.

6.3 In instances in which the pyrograms of both the unknown polymer and the library have similar peak profiles at the same retention times, a “tentative identification” is made and the next step in the process (6.4) is taken.

6.4 The last step is to analyze the “polymers of interest” with and without the “tentatively identified” polymer. Examine the pyrograms (TIC) and plot the intensity of the potential target ion versus retention time. The original mixture without the “tentatively identified” polymer should not have a response at the expected retention time of the compound being considered as a new target compound; the pyrogram of the mixture spiked with the “tentatively identified” polymer will have a signal for the ion being considered as a target compound for the new polymer of interest.

6.5 When adding non-validated polymers to the protocol, it is essential to select target compounds that do not interfere with the pyrolyzates created from the pyrolysis of other components in the analytical sample. See 4.5 – 4.7. For example, in Table 2, naphthalene as the target compound for polyvinyl chloride (PVC) identification and quantitation is listed even though benzene has a higher response than naphthalene (2:1 at 600 °C). Although the naphthalene response compared to the benzene response is lower, the naphthalene response is unique and only PVC on the list of twelve target polymers forms naphthalene when pyrolyzed at 600 °C.

6.6 If a unique target compound cannot be identified, it may be necessary to alter the original blend (leaving out the polymer that is the source of the interference), or it may be easier to analyze the “additional” polymer separately or with a different group of polymers.

6.7 The analyst needs to be aware that the new polymer cannot be added to the twelve polymer database used to identify and quantitate the twelve compounds specified in Table 1. Each laboratory shall evaluate their need to automate the entire process. The laboratory may deem it essential (that is, higher numbers of samples, request for fast turnaround time, and so forth) to develop in-house software compatible with their existing protocols or purchase software compatible with in-house protocols. On the other hand, small projects can often be effectively processed using existing in-house software or third-party software.

7. Interferences

7.1 This test method uses external standard calibration to quantitate each polymer to accommodate a broad range of target compound concentrations. However, if the concentration range is such that all target compounds fall within a range consistent with the linear dynamic range of the analytical system, internal standards are recommended. Care should be taken when preparing, using, and storing the calibration standards: in preparing the solutions, avoid plastic containers and tools throughout the process. Artifacts introduced when using the standards may degrade data quality. The frequent analysis of the continuing calibration check sample (CCC) and the commitment to maintaining a current quality control (QC) chart will enable the changes in the standards or the analytical system to be noted in a timely manner.

7.2 Contamination of the system will be apparent by monitoring the baseline and peak symmetry during the routine analysis of the CCC. While extended periods of heat may temporarily “clean” the system, it may be necessary to clean (or replace) the pyrolysis tube, the needle interface, and the injection port liner to rid the system of contamination.

7.3 Leaks in the system are detected by monitoring the area of Me-Eic.

7.4 In a typical GC chromatogram with a non-MS detector, column resolution may be critical to resolve two closely eluting compounds. EICs assist in peak separation.

7.5 Column resolution is a measurement to quantify column performance in this regard; however, with GC/MS, EICs are used and the method does not include critical peak pairs that shall be carefully resolved under optimum conditions.

7.6 If the laboratory is using the recommended column, then this test method does not need nor require a specific determination of column resolution. If the column is not performing and providing the expected separation, then installation of a new column is advised.

7.7 Sample cups should not be reused because pyrolysis of samples containing polymers will often leave an inorganic residue or char on the sample cup surface.

surface inertness. This residue is very difficult to remove without damaging the inertness of the surface.

8. Apparatus

8.1 Pyrolysis System—Conceptually, pyrolysis is a simple process. Apply sufficient heat to a complex chemical species until organic bonds begin to break, forming smaller, stable molecules commonly referred to as pyrolyzates. The GC separation of the pyrolyzates is called a pyrogram. The pyrolyzates formed and their relative intensities provide insight into the nature of the original material. While data quality is a function of the entire GC system, the design of the pyrolyzer has the greatest impact on data quality. Three factors are of paramount importance:

8.1.1 The sample shall be “heated” instantaneously to minimize secondary reactions that will adversely affect reproducibility. Pyrolyzer temperature stability is directly related to pyrolysis data quality. The pyrolyzer temperature shall be constant within ± 0.1 °C. Thermal instability has an adverse effect on data quality.

8.1.2 The sample path shall be inert and at a uniform temperature. Ideally, there is no transfer line, that is, the pyrolyzates flow directly from the furnace to the GC column, thus eliminating the contamination and thermal gradients associated with conventional transfer lines.

8.1.3 The sample shall be in an inert atmosphere and shall be kept at ambient temperature to prevent unexpected reactions, to ensure that all peaks and peak ratios form properly during pyrolysis. This maintains sample integrity and contributes to the accuracy, precision, and reproducibility of the dataset.

8.2 GC/MS/DS:

8.2.1 The GC shall be capable of temperature programming and should be based on the use of pressure regulation so that

the column flow rate will remain constant as the column temperature increases.

8.2.2 Capillary GC Columns—Any GC separation and pre-column combination that meets the performance specifications of this test method may be used. Separations of the calibration mixture shall be equivalent to, or better than, those described in this test method. The prescribed method is based on the column and conditions described in Fig. 2. This enables the analyst to compare the chromatogram of the “standard” obtained at the beginning of an analytical sequence easily with that existing during the course of multiple “real-world” analyses. Differences can be notated and their effect on analytical data can often be reconciled. The pre-column prevents or, at a minimum, reduces the accumulation of chemical residue in the separation column. For best system performance, the pre-column should be evaluated or replaced when needed if experiencing peak shape distortion for many polar compounds or degradation in peak area reproducibility, or both, compared to the previous MP calibration standard analysis. A common GC column stationary phase for polymer analysis is 5 % phenyl 95 % methylpolysiloxane (PMPS-5); however, cyclopentanone (N6,6) can overlap with other matrix peaks from other polymers. The 50 % phenyl 50 % methylpolysiloxane (PMPS-50) GC column has a semi-polar phase that helps in the separation of several peak combinations in close elution time zones when using a short length of PMPS-50 as a pre-column. This improves the robustness of this test method.

8.2.3 The MS shall be capable of electron ionization at a nominal electron energy of 70 eV. The MS shall be capable of scanning from a minimum of 20 amu to 700 amu with a complete scan cycle time (including scan overhead) of 0.2 s to 0.5 s (scan cycle time = total MS data acquisition time in seconds divided by number of scans in the chromatogram) and consistent with the manufacturer’s suggested or recommended

Pyrolyzer (Micro furnace type) Automatic solid Sampler Backflush System - Furnace: 600 °C - ITF: 300 °C - Backflush time: 13 min
GC /MS - Injector: split/splitless injector - Insert tube: filled with deactivated packing - Injection port temperature: 300 °C - Oven: 40 (2 min) - 20 °C/min → 280 °C (11 min hold) - Pre-column: (50% phenyl 50% methylpolysiloxane, 2 m, 0.25 mm i.d., 1.0 µm) - Column: (5% phenyl) methylpolysiloxane (30 m, 0.25 mm i.d., 0.5 µm) - Carrier gas (He): Column flow: 1.0 mL/min, - Total flow: 50 mL/min, - Split ratio: 1/50 - Vent-free GC/MS adaptor - MS interface: 300 °C - Scan range: m/z 29 - 400 - Scan speed: 4 scans/s - Threshold: 150 counts
Analytical semi-micro balance

FIG. 2 Specific Set Points for the Analytical Method

scan cycle time, which is a function of the machine's settings, not its tuning. The spectrometer shall produce mass spectra that meet all the performance criteria published in the manufacturers' product support documents.

8.2.4 An interfaced data system is required to ensure that the MS meets expected performance criteria and to acquire, store, reduce, and output mass spectral data. The computer software should have the capability to process stored GC/MS data by recognizing a GC peak within any given retention time/retention index (RI) window comparing the mass spectra from the GC peak with spectral data in a user-created or commercial database or library and generating a list of tentatively identified compounds within their retention times/RI and scan numbers. The software shall allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software should also allow calculation of the final polymer concentrations based on the results of an external standard calculation.

8.2.5 *Analytical Balance Capable of Weighing to ± 0.00001 g (0.01 mg)*—Standard preparation of micro-polymers shall be scaled accordingly to ensure that the data are accurate to three significant figures. The analysis of submicron and nano-sized particles may require the use of a more sensitive balance (0.0001 mg) to ensure that the data are accurate to three significant figures. Sample preparation often uses various optical techniques to identify particles of interest. Special tools are available that facilitate the selection of a specific particle(s).

8.2.6 *Cryo-Mill*—Cryo-milling or cryo-crushing is the process of cooling or chilling a material and then reducing it into a smaller particle size. Polymers such as polyethylene (LDPE, HDPE) and PP with a glass transition temperature (T_g) below room temperature may require liquid nitrogen to embrittle them for milling into a smaller particle size. For field samples, in particular, in the absence of knowing which polymers are in the sample, embrittlement with liquid nitrogen followed by milling/crushing is the recommended default preparation for analysis in the pyrolysis sample cup.

8.2.7 *Pyrolysis Sample Cup*—The pyrolysis sample cup should be clean and free of organic material. Sample cups can be used in which the surface is deactivated stainless steel, quartz, or quartz-coated glass.

9. Reagents

9.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁶ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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.

9.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type 1 of Specification **D1193**.

9.2.1 References to water shall be understood to mean MQ water.

9.3 *Laboratory Reagent Blank*—Fill a 10 mL volumetric flask with an organic solvent and adjust to the mark with no air bubbles. Inject 10 μ L of the reagent blank into a sample cup and let it evaporate at room temperature until there is a light coating on the inside of the cup. A clean quartz fiber filter disc or a small amount of organic-free quartz wool can be placed in the top of the sample cup if there is reason to suspect tumultuous air flow around the cup. Analyze using the conditions listed in **Fig. 2**.

10. Hazards

10.1 The toxicity or carcinogenicity of chemicals used in this test method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of Occupational Safety and Health Administration (OSHA) regulations regarding safe handling of chemicals used in this test method.

11. Sample Collection and Storage

11.1 See Practice **D8332**.

11.1.1 Sample contents should be stored at $4^\circ\text{C} \pm 2^\circ\text{C}$ for the sample preparation phase.

12. Calibration Reference Standard: Pyrolysis-Specific Preparation

12.1 The calibration reference standard is a multi-component standard that includes all twelve of the target polymers and a calibration standard (**Appendix X2**). Some of the polymers are soluble, a few are not. Some polymers include a variety of chemical functionalities. No single solvent has been identified that will dissolve all twelve target polymers; consequently, polymers are grouped according to their solubility. Aliquots of the dissolved polymers are combined, in a predetermined order, in one sample cup that becomes the "calibration" sample of record. The procedure is illustrated in **Fig. 3**.

12.2 Care shall be taken to ensure the purity of each polymer standard and the purity of the solvents used. The individual polymers are stable and can be used for up to six months if properly sealed and stored at room temperature. It is recommended that polymer/solvent solutions can be retained for the course of an analysis not to exceed two weeks when stored tightly-capped in a refrigerator at 4°C to 6°C .

12.3 The polymers of interest are listed in **Table 1**. The present protocol is not limited to the twelve polymers listed in **Table 1**, but its applicability to other polymers shall be demonstrated using tests similar to those discussed in this test method.

12.4 The composition of each solution is described in **Fig. 3**. The amount of each polymer reflects the variability in the MS response for the various pyrolyzates, which is shown in **Fig. 3**.