

Standard reference materials for the determination of trace organic constituents in environmental samples

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1. Introduction

The National Institute of Standards and Technology (NIST) provides calibration solutions, natural matrix Reference Materials (RMs), and Standard Reference Materials (SRMs) to aid in analytical method development and help validate measurements of organic compounds. The first natural matrix material issued by NIST for organic compounds was on 10 March 1980, SRM 1580 Organics in Shale Oil (<https://tsapps.nist.gov/srmext/certificates/archives/1580.pdf>). This material was certified for trace-level organic compounds like polycyclic aromatic hydrocarbons (PAHs) and cresols. While SRM 1580 was discontinued, it was available and used by scientists for over 35 years.

Since the first natural matrix SRM became available from NIST, many other SRMs have become available, including sediment, air particulate matter, mussel tissue, fish tissue and oil, house dust, agricultural

products, and human materials. The previous editions of this book detailed the development of many natural matrix SRMs. This chapter's intent is to update the readers on the activities at NIST on the development of reference materials for organic constituents in environmental samples. This chapter will also discuss newer matrix SRMs in the categories of agricultural products and human materials as they apply to environmental organic chemical measurements.

2. Reference materials provided by the National Institute of Standards and Technology

NIST RMs and SRMs are commercially available materials that have been characterised for chemical composition (chemical identity and concentration within reported uncertainty) and whose composition is homogenous and stable for a defined period [1]. NIST RMs and SRMs have many uses, including calibration of measurement methods and qualification of measurement method performance [1].

Historically there were three types of assigned values for chemical composition certification at NIST [2]: certified, reference, and information values. However, in 2020, a new classification system to define modes of value certification was published. Beauchamp et al. [1] outlined a shift in the type of values reported to only two types, certified and non-certified values. The difference between the two types of values is related to confidence associated with the reported measurands. For certified values, the specified measurand must be thoroughly characterised, homogenous throughout the material, stable for a defined period when following specified storage conditions, accurate based on several types of independent measurement techniques, metrologically traceable (e.g., to the SI unit), and documented to be fit for purpose. Non-certified values report measurands with the same requirements for characterisation, homogeneity, and stability, but do not comply with one or more of the following: accuracy, traceability and/or documentation. Accuracy may not be met if generated values were not evaluated exclusively by NIST, were generated from one unit or a grand mean from multiple units of material or were generated as part of an interlaboratory study. Measurands may not be classified as a certified value if the measurand is not traceable to an SI unit.

NIST currently produces six types of reference materials, SRMs, RMs, Research-Grade Test Materials (RGTM), primary standards, Research Gas Mixtures, and NIST Traceable Reference Materials. NIST materials used for the analysis of organic constituents in environmental samples fall within the categories of SRMs, RMs, and RGTM. SRMs are NIST-certified reference materials or CRMs under the definition set by the International Bureau of Weights and Measures' BIPM International

Vocabulary of Metrology. An SRM will deliver a minimum of one certified value but can also convey non-certified information. NIST RMs provide non-certified values and are fit for the material's intended uses. Typically, NIST RGTMs are exploratory materials prepared to be stable and homogeneous, but have not been fully characterised for all intended applications [1].

3. Types of environmental standard reference materials

Environmental SRMs can be broken down into two categories, calibration solutions and fortified or non-fortified natural matrix materials (Fig. 12.1). Calibration solutions are useful for the validation of chromatographic separation and analyte detection and quantification, while the natural matrix materials can be used to validate the analytical method, from extraction to quantification. While the scope of this chapter is reference materials for organic compound analysis, it is important to emphasise that many National Metrology Institutes (NMIs), including NIST, also produce CRMs for inorganic analysis of environmental samples, such as the detection of inorganic lead in soil.

4. Calibration solutions

Calibration solution SRMs and RMs are useful for determining response factors for quantification, determining chromatographic retention times, spiking/fortifying samples, and performing analyte recovery studies. Several calibration SRMs are available from NIST (<https://shop.nist.gov>), with some materials originally being produced in the 1980s (e.g., SRM 1543 GC/MS System Performance Standard). Typically, calibration solution reference materials are provided for organic chemicals



FIGURE 12.1 NIST standard reference materials and reference materials for environmental measurements.

that are not available commercially or have unique characteristics that provide measurement challenges. New calibration SRMs and RMs have been released over the past years that focus on chemicals of emerging concern like per- and polyfluoroalkyl substances (PFAS; e.g., RMs 8446 and 8447 PFAS in Methanol), phthalates (e.g., SRM 3060 monoester phthalates in acetonitrile), and polybrominated diphenyl ethers (PBDEs; e.g., SRM 2257 PBDE Congeners in 2,2,4-trimethylpentane). Table 12.1 lists the current calibration solutions available at NIST for environmental, and organic measurements.

5. Fortified and non-fortified natural matrices

Natural matrix SRMs and RMs aid in the validation of analytical procedures. Typically, an SRM or RM is selected because it is similar to the matrix normally being analysed, and both the selected SRM or RM and samples are run through the same analytical procedure, including solvent extraction, cleanup of extracts, and chemical analysis. Occasionally, measurands of interest may be applicable or desired, but not originally endogenous to the SRM or RM. These measurands will therefore be added to an existing natural material resulting in a

TABLE 12.1 NIST calibration solution RMs and SRMs for the determination of organic contaminants.

SRM number	SRM title	Year issued	Certified values	Noncertified values
869b	Column Selectivity Test Mixture for liquid chromatography (PAHs)	2008	PAH (1)	PAHs (2)
1491a	Methyl-Substituted polycyclic aromatic hydrocarbons in toluene	2005	PAHs (18)	
1493	Polychlorinated Biphenyl congeners in 2,2,4-Trimethylpentane	1993	PCBs (18)	PCBs (2)
1494	Aliphatic hydrocarbons in 2,2,4-Trimethylpentane	1993	Hydrocarbons (20)	
1647f	Priority pollutant polycyclic aromatic hydrocarbons in acetonitrile	2014	PAHs (16)	

TABLE 12.1 NIST calibration solution RMs and SRMs for the determination of organic contaminants.—cont'd

SRM number	SRM title	Year issued	Certified values	Noncertified values
2257	PBDE congeners in 2,2,4-Trimethylpentane	2008	PBDEs (38)	
2258	BDE 209 in 2,2,4-Trimethylpentane	2008	PBDE (1)	
2259	Polychlorinated Biphenyl congeners in 2,2,4-Trimethylpentane	2009	PCBs (80)	
2260a	Aromatic hydrocarbons in toluene	2004	PAHs (35)	
2261	Chlorinated pesticides in Hexane (Nominal Mass concentration 2 µg/mL)	1992	Pesticides (15)	
2262	Chlorinated Biphenyl congeners in 2,2,4-Trimethylpentane	1995	PCBs (25)	PCBs (3)
2266	Hopanes and steranes in 2,2,4-Trimethylpentane	2007	Hopanes (3) steranes (4)	Hopanes (2) steranes (1)
2269	Perdeuterated PAH-I solution in Hexane/Toluene	2001	Perdeuterated PAHs (5)	
2270	Perdeuterated PAH-II solution in Hexane/Toluene	2001	Perdeuterated PAHs (6)	
2274	Polychlorinated Biphenyl congeners in 2,2,4-Trimethylpentane	2001	PCBs (11)	
2275	Chlorinated pesticide Solution-II in 2,2,4-Trimethylpentane	2001	Pesticides (8)	
3060	Monoester phthalates in acetonitrile	2016	Monester phthalates (9)	Monoester phthalates (5)
3074	Phthalates in Methanol	2013	Phthalates (6)	
8446	Perfluorinated Carboxylic acids and Perfluorooctane Sulfonamide in Methanol	2014		PFAS (12)
8447	Perfluorinated Sulfonic acids in Methanol	2014		PFAS (3)

fortified material. The addition of a measurand will provide additional reported value(s) and support for these new measurands.

When discussing natural matrices for environmental measurements, these materials fall into three categories: environmental matrices, agricultural and food materials, and human biomonitoring matrices (Table 12.2). NIST has many natural matrix SRMs and RMs that can be used for measurement validation in environmental matrices, including soil, sediment, sludge, dust, biological tissues, and fish oil. There are also natural matrix SRMs and RMs for agricultural products (e.g., fish, oat flour) which can be used to underpin measurements related to the exposure to organic contaminants in foods. In addition to these two classes of natural matrix materials that can be analysed for organic compounds, there are human biomonitoring matrices (e.g., serum, urine) quantified for organic chemicals that are used to validate measurements related to human exposure to environmental chemicals.

TABLE 12.2 NIST natural matrix RMs and SRMs for the determination of organic contaminants in environmental samples.

SRM number	SRM title	Year issued	Category
1936	Great Lakes sediment	2021	Environmental
1941b	Organics in marine sediment	2002	Environmental
1944	New York/New Jersey Waterway sediment	1999	Environmental
1945	Organics in Whale Blubber	1994	Environmental
1975	Diesel particulate extract	2000	Environmental
1991	Mixed Coal Tar/Petroleum extract in Methylene chloride	2013	Environmental
2585	Organic contaminants in house dust	2005	Environmental
2586	Trace elements in soil Containing lead from Paint (Nominal 500 mg/kg lead)	1999	Environmental
2706	New Jersey soil, organics and trace elements	2018	Environmental
2777	Weathered Gulf of Mexico crude oil in toluene	2018	Environmental
2779	Gulf of Mexico crude oil	2012	Environmental
2781	Domestic sludge	1995	Environmental
2786	Fine Atmospheric particulate matter (mean particle Diameter <4 µm)	2011	Environmental

TABLE 12.2 NIST natural matrix RMs and SRMs for the determination of organic contaminants in environmental samples.—cont'd

SRM number	SRM title	Year issued	Category
2787	Fine Atmospheric particulate matter (mean particle Diameter <10 µm)	2011	Environmental
2860	Phthalates in polyvinyl chloride	2018	Environmental
2975	Diesel particulate matter (Industrial Forklift)	2000	Environmental
3077	Aroclor 1242 in Transformer oil	2003	Environmental
3079	Aroclor 1254 in Transformer oil	2003	Environmental
3080	Aroclor 1260 in Transformer oil	2003	Environmental
1649b	Urban dust	2009	Environmental
1946	Lake Superior fish tissue	2003	Environmental/ Agricultural
1974c	Organics in mussel tissue (<i>Mytilus edulis</i>)	2015	Environmental/ Agricultural
2974a	Organics in freeze-dried mussel tissue (<i>Mytilus edulis</i>)	2010	Environmental/ Agricultural
3253	Yerba Mate Leaves	2018	Agricultural
8238	Glyphosate in oat flour (high level)	2022	Agricultural
8239	Glyphosate in oat flour (low level)	2022	Agricultural
8256	Wild-caught Coho Salmon	2021	Agricultural
8257	Aquacultured Coho Salmon	2021	Agricultural
8258	Wild-caught Shrimp	2022	Agricultural
8259	Aquacultured Shrimp	2021	Agricultural
1953	Organic contaminants in non-fortified human milk	2009	Human material
1954	Organic contaminants in fortified human milk	2009	Human material
1957	Organic contaminants in non-fortified human serum (freeze-dried)	2009	Human material
1958	Organic contaminants in fortified human serum (freeze-dried)	2009	Human material
3672	Organic contaminants in Smokers' urine (frozen)	2014	Human material
3673	Organic contaminants in Non-Smokers' urine (frozen)	2014	Human material

6. Environmental matrices

NIST has several environmental materials quantified for organic constituents (e.g., soils, dust, biological tissues, etc.). NIST produced environmental SRMs useful for chemical analysis of a small scope of organic chemical classes (PAHs, PCBs, and organochlorine pesticides) and the matrices limited to crude oil/fossil fuels, freeze-dried mussel tissues, particulate matter, sediments, and solvent-extracted materials [3]. As measurement techniques improved and technologies advanced, an expanded list of organic chemicals is now being measured in NIST SRMs and RMs. Some of these new classes of compounds are discussed later in this chapter. Enhancements in the late 1980s to material production (creating frozen tissues instead of freeze-dried) have expanded the types of environmental matrices NIST provides [4]. In the Biospecimen Science Group at NIST there is the Cryogenic Reference Material Production Facility (<https://www.nist.gov/programs-projects/reference-material-production-and-support>). This is a unique facility which uses specialised equipment for the cryogenic homogenisation of biological matrices [5]. Table 12.2 lists the environmental SRMs/RMs available.

6.1 Response to environmental incidences

Environmental incidents and disasters resulting in organic contamination require new or more frequent environmental measurements which may also require the need of new reference materials to support those measurements. For example, NIST has a long history of measuring PAHs in environmental matrices, so when the Deepwater Horizon oil spill occurred off the coast of Louisiana (April 2010), two SRMs were quickly developed: SRM 2779 Gulf of Mexico Crude Oil (<https://tsapps.nist.gov/srmext/certificates/2779.pdf>) and SRM 2777 Weathered Gulf of Mexico Crude Oil in Toluene (<https://tsapps.nist.gov/srmext/certificates/2777.pdf>). These materials were and are used as quality control materials for the ongoing environmental impact assessments.

Just days after the explosion of the Deepwater Horizon oil rig in the Gulf of Mexico on 20 April 2010, it was determined that the resulting crude oil spill had the potential to cause significant environmental impacts. This accident resulted in the loss of lives and the worst marine oil spill in the country's history. On 21 May 2010, at the direction of the National Oceanic and Atmospheric Administration (NOAA), 45 L of crude oil were collected directly from the Macondo well during spill remediation efforts to provide materials for natural resource damage assessments. A portion of the crude oil was separated from the entrained sea water and ampouled [6]. Most of the material was designated as SRM

2779 Gulf of Mexico Crude Oil, then characterised for PAHs, alkylated PAHs, hopanes, and steranes using a gas chromatograph coupled to mass spectrometry (GC–MS). The Certificate of Analysis for SRM 2779 (<https://tsapps.nist.gov/srmext/certificates/2779.pdf>) lists certified values for 20 PAHs and non-certified (reference) values for an additional 22 PAHs, 31 groups of alkylated PAHs, 7 hopanes, and 6steranes. In addition to its main purpose as a control material for validating methods for measuring PAHs, alkylated PAHs and biomarkers in crude oils, SRM 2779 has been used for interlaboratory studies including those described by Schantz and Kucklick [6], Reddy et al. [7], and Murray et al. [8]. These studies using SRM 2779 have helped analysts refine their methods for measuring the species described above, as well as provide data for additional analytes including normal hydrocarbons. Obtaining relatively large samples of crude oil and producing a control material (SRM 2779) for future use in measuring the environmental impact of that specific crude were unique efforts that supported future studies of the fate of the millions of gallons of oil spilt in the Gulf of Mexico during this tragic event.

As crude oil weathers, the chemical composition changes. This can include the loss of some normal alkanes, branched alkanes, and other saturates, but also the formation of oxygenated residues [9,10]. As a result, the analysis of weathered crude oil can pose different analytical challenges compared to the analysis of crude oil. To support studies on the long-term environmental impact of oil spills, NIST developed SRM 2777 Weathered Gulf of Mexico Crude Oil in Toluene. The source material to prepare SRM 2777 was donated by Woods Hole Oceanographic Research Institute. The weathered oil was extracted from sand collected from beaches in Alabama that were impacted by the 2010 Deep Water Horizon oil spill. Geochemical analysis by Aeppli et al. [11] determined that the weathered residue used to prepare SRM 2777 was weathered Macondo Well oil. The extracted weathered oil was delivered to NIST, diluted with toluene, and ampouled, resulting in SRM 2777. Currently, SRM 2777 has six certified values and seven non-certified (or reference) values for parent and alkylated PAHs and one non-certified value for $17\alpha(\text{H}),21\beta(\text{H})$ -hopane (<https://tsapps.nist.gov/srmext/certificates/2777.pdf>).

These materials have been useful for the community and SRM 2777 was used in the interlaboratory study initiated by the Gulf of Mexico Research Initiative. Interlaboratory data is available for several alkanes, PAHs, alkylated PAHs, hopanes and steranes [7,8] and also measurements by ultrahigh resolution mass spectrometry and non-chemical analyses for both SRM 2777 and SRM 2779 including toxicity, shear viscosity, and interfacial tension [7].

7. Agricultural and food materials

The intersection of the environment and food systems can be vitally important to understanding the routes of exposure to environmental contaminants. Historically, NIST has provided and supported SRMs for agricultural and food materials starting with SRM 1571 Orchard Leaves, which was issued in 1971 with certified concentrations of toxic elements and organic chemical measurands [3]. Since then, NIST has expanded its efforts to provide SRMs and RMs for the measurements of organic contaminants in a wide variety of agricultural and food matrices, including plant materials (RMs 8238, 8239) and seafood (SRMs 1946, 1974, 2974a). Organic contaminant values, both certified and non-certified, may include pesticides, PAHs, and halogenated organic compounds (e.g., PCBs, PBDEs, and PFAS) for numerous agricultural and food materials. [Table 12.2](#) lists the related agricultural and food SRMs/RMs available.

8. Human biomonitoring materials

Although not commonly thought of as an environmental matrix, human biomonitoring samples are used to understand human exposure of environmentally relevant organic chemicals. NIST, in collaboration with the Centers for Disease Control and Prevention, developed SRMs for measurements of organic chemicals related to human exposure [12]. These matrices include human urine, human milk, and human serum. Organic contaminant values, both certified and non-certified, may include PCBs, PBDEs, chlorinated pesticides, polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), PFAS, hydroxylated PAHs, phthalate metabolites, phenol metabolites, and volatile organic compound metabolites. The inclusion of SRMs into biomonitoring studies supports the accuracy of biomonitoring data, while also providing a material that can be used for comparability across biomonitoring studies [12]. [Table 12.2](#) lists the related human NIST SRMs/RMs available.

9. Recent activities

Activities related to organic contaminant measurements for environmental samples at NIST are ongoing. Most recent efforts are focused on natural matrix RMs and SRMs. The majority of the activities fall into three categories: (1) Certification updates on existing materials (recertification), (2) Replacement of materials that have become out of stock (renewals), and (3) Development of new materials.

10. Recertification

During the production and development of natural matrix materials, a set quantity of material is produced. During the initial development phase of an RM or SRM, ideal quantities of material are obtained to support and stock the material from NIST for approximately five to eight years. While most RMs and SRMs are depleted and sold over this time, there are quite a few RMs and SRMs that have enough material to continue sales beyond this time (eight years). If there is sufficient material available after the initial selling phase of the material (for example an additional ten years of material left) and as analytical methods have changed/developed during the time the materials have been offered, a recertification process can allow new methods to be used on the existing material. These new methods can result in new analytes being measured in the RMs and SRMs. One example is the addition of PFAS, polycyclic musks, and α -hexabromocyclododecane to SRM 2585 Organic Contaminants in House Dust in 2018. New methods for existing analytes can also provide values complementary to those obtained using older methods and help reduce the uncertainties associated with the concentrations.

11. Renewals

As mentioned in the recertification section, when RMs and SRMs are prepared at NIST, the intent is to have approximately a five to eight-year supply of the material created. Once the material is depleted, a new batch of material can be prepared, analysed for the compounds of interest, value assigned for organic constituents, and issued as a renewed material in the SRM series. Typically NIST creates renewal materials using the same RM/SRM number but adds a letter (a, b, c, d, ...) distinguishing it as part of the series of materials, but as a newly produced material in that series. In [Table 12.2](#) you can see that NIST sells a material SRM 1974c Organics in Mussel Tissue (*Mytilus edulis*). This is the fourth iteration of organics in mussel tissue issued by NIST [13]. The SRM 1974 series of materials (SRMs 1974, 1974a, 1974b, and 1974c) is quite unique. Mussel tissue was collected from the same location during the production of these materials (Dorchester Bay, MA) and because of this, NIST researchers were able to evaluate new contaminants of interest using additional, complementary chemical analysis methods and were able to assess trends of organic constituents in Dorchester Bay [13].

12. New materials

New matrices and analytes for environmental analysis are continually being assessed to determine if there is a community need for the creation of new RMs and SRMs to help solve new measurement questions. There are several new materials currently in development. These include the creation of PFAS in aqueous film forming foams (AFFFs), PFAS in contaminated soil, PFAS in agricultural products such as livestock muscle tissues and plants, PFAS in drinking water material, single polymer microplastics generated from consumer products, and a phthalate diester solution in acetonitrile. Each of these new materials is filling a much-needed measurement question and will help support accurate and reproducible data.

13. Analytical approaches

Historically NIST's activities with organic constituents in environmental RMs and SRMs focused on measurements of PAHs, PCBs, and chlorinated pesticides [2]. However, the need for RMs and SRMs with certified and noncertified values for other emerging organic contaminants is increasing. Therefore, NIST is currently focused on measurements of three groups of emerging organic contaminants known to be found in environmental samples: PFAS, phthalates and plastic additives, and PBDEs. One way to develop analytical methods for chemical analysis of emerging compounds is to examine existing RMs and SRMs for these emerging analytes. Since NIST knows that the materials are homogeneous for the persistent organic pollutants already measured in them, they can be useful materials for developing chemical methods.

14. PFAS

To date there are numerous analytical methods at NIST, commercially, and in research institutions for the measurement of PFAS in a variety of matrices, including food, drinking water, non-potable water, AFFFs, and other solid matrices. With rapidly evolving regulations regarding PFAS in food, drinking water, and environmental matrices, many methods have varying lists of targeted PFAS analytes and required limits of detection and quantitation. All current reference methods utilise reversed-phase liquid chromatography with negative polarity electrospray ionisation tandem mass spectrometry. To reduce or remove the impact of non-targeted/interfering matrix components on the detection of PFAS, most reference methods employ a "clean-up" step that includes a weak anion

exchange solid-phase extraction step that preferentially retains the anionic PFAS from non-ionic, neutral, zwitterionic, and cationic matrix components.

For analytical methods, there is a limited availability of calibration reference materials that can be used to quantify individual PFAS. Certified values for concentrations of PFAS require a high level of traceability, which requires purity and identity to be verified by quantitative $^1\text{H-NMR}$ or other higher-order techniques [1]. $^1\text{H-NMR}$ has limited utility on the fully fluorinated perfluoroalkyl acids. Therefore, all concentration values for PFAS in reference materials are presented as non-certified values. Most reference methods are focused on the measurement of those PFAS detectable by negative electrospray ionisation (ESI-) mass spectrometry, yet previous studies have demonstrated the presence of compounds detectable by positive electrospray ionisation (ESI+) only [14]. Analytical standards and reference methods will be needed to better understand the presence and concentration of these other PFAS in environmental, food, and water materials. In addition, neutral, non-ionic PFAS are also thought to be excluded from quantitation by ESI methods, and other mass spectrometry techniques (e.g., GC-MS) should be explored for use.

15. Phthalates

Phthalates can occur in multiple forms in the environment, as diesters or monoesters, and can have varying alkyl ester structures; common phthalates include bis(2-ethylhexyl) phthalate and di-*n*-octyl phthalate. Different measurement techniques are also needed to measure phthalates. When measuring phthalates in water, air, and food the analyst measures the diester compounds that represent their main use as plasticisers, but in human and biological samples phthalates are easily and rapidly metabolised and must be measured as their corresponding monoester [15,16]. There are two primary methods of analysis for phthalates: GC-MS for diester phthalates and liquid chromatography-tandem mass spectrometry for monoester phthalates. NIST has developed calibration solutions (SRM 3060 and SRM 3074) and phthalates in matrix materials, such as shredded polyvinyl chloride (SRM 2860) and human urine (SRM 3672 and SRM 3673). The calibration solutions and the shredded polyvinyl chloride provide certified measurements of the phthalates, while the human urine materials provide noncertified values for phthalate metabolites (i.e., monoester phthalates).

Measurements of phthalates can be challenging because phthalates are used in a wide variety of consumer products and concentrations in “blank” and background measurements show the presence of phthalates [17]. For some matrices, phthalates are found at very low levels (ng/g

concentration range), which can be similar to the background measurements made in a laboratory. Guo and Kannan [17] provide suggestions/recommendations to help minimise phthalate contamination in the laboratory to help improve the chemical analysis.

16. PBDEs

The first detection of PBDEs in environmental samples was in 1979; however, it was not until 2003 that existing NIST SRMs were examined for these compounds [18]. At the time of the Zhu and Hites paper [18], no RMs or SRMs existed for the measurements of PBDEs, and these researchers examined existing NIST materials to look for PBDEs [18]. This was an innovative use of existing materials NIST already had available. This assessment of existing NIST materials led NIST to develop analytical methods for the quantification of PBDEs and their measurements in SRMs [19,20]. Currently, NIST has PBDE congeners in calibration solutions (SRM 2257 and SRM 2258) and an assortment of matrix SRMs that are characterised for PBDEs including particulate matter (SRM 2786 and SRM 2788), marine tissues (SRM 1945, SRM 1946, and SRM 2974a), house dust (SRM 2585), human milk (SRM 1953 and SRM 1954), and human serum (SRM 1957 and SRM 1958).

In the early 2000s measurements of PBDEs were challenging because of the lack of commercial standards, degradation/debromination of highly brominated PBDE congeners, and chromatographic interferences or coelution with other halogenated compounds [21]. Many measurement methods have been optimised and there are quite a number of accurate and precise methodologies to measure PBDEs in environmental samples [21]. Measurements of PBDEs are still challenging because of the presence of PBDEs in “blank” measurements. PBDEs tend to be omnipresent in the laboratory [22].

17. Future NIST measurements: Plastic additives and microplastics

In addition to phthalates and PBDEs, there has been considerable work on measuring other plastic additives in RMs and SRMs. Plastic additives, as a class of chemicals, are quite large and include many compounds which have different functionalities when used in plastic formulations [23]. Both phthalates and PBDEs are functional additives used in plastics and have been measured in NIST SRMs. (e.g., NIST SRM 2860 is certified for phthalates in PVC, and NIST SRMs 2859 and 2861 are certified for

restricted elements in PVC). In addition to these two groups, there is a wide range of additional chemicals that can be classified as plastic additives. For example, NIST SRM 2855 is certified for elemental performance additives and catalysts in polyethylene (PE) plastic, including Na, P, S, Ca, Zn, Si, Ti and Cr. NIST is currently developing measurement methods for a wide variety of plastic additives. Once measurement methods are developed, NIST will look into providing RMs and SRMs with values assigned for these new compounds.

Beyond plastic additives, reference materials for plastic particles are in increasing demand. NIST already produces a variety of NIST SRMs that are in plastic pellet or powder form. These include NIST SRMs 1961, 1690, 1691, 1963a and 1964 which are polystyrene (PS) spheres certified for size; NIST SRMs 1478, 1479, 705a and 706a which are PS spheres or rodlets certified for molecular weight distribution; NIST SRMs 1484a, 1473c, 1476a, 1474b, and 1496 which are certified PE resin pellets; NIST SRM 1488 which is poly(methyl methacrylate) certified for molecular weight distribution; and NIST RM 8634 which consists of 1–30 μm ethylene tetrafluoroethylene particles of irregular shape for ground for size and morphology measurements. As clear by their certifications, these materials were not generated to mimic plastic particles in the environment and represent only five polymer types. However, there is increasing demand for reference materials to validate measurements of plastic particles in many environmental matrices (for contaminant monitoring as well as human health studies), including nanoplastics $<1\ \mu\text{m}$, microplastics $1\ \mu\text{m}$ – $5\ \text{mm}$, and larger. This includes a need for both plastic particles (used for building reference libraries and method validation), as well as environmental NIST SRMs with consistent plastic concentrations. This is a major challenge as plastics in the environment are primarily weathered fragments of plastic products, creating a wide variety of sizes, shapes and surface chemistries, and consisting of a diversity of polymer/additive combinations. Nonetheless, NIST is currently working to develop reference materials for plastics in the environment to meet the ever-growing demand.

18. Concluding remarks and future prospects

NIST has developed a multitude of environmental RMs and SRMs. These materials are homogeneous and well-characterised for a wide variety of organic constituents. RMs and SRMs can be used to validate chemical measurements and improve the quality of the analytical data when used in the development of chemical analysis and/or when run as part of a quality assurance programme.

In the future NIST hopes to sell new RMs and SRMs for plastic additives and microplastics. In addition to this future work, our current RMs and SRMs can be used to discover and quantify chemicals of emerging concern. With regulatory and health agencies across the world continuously identifying compounds of suspected toxicological risk, accurate analytical methods will need to be developed and verified for these emerging chemicals. Historic RMs and SRMs are useful for this type of research already (PBDEs, PFAS) and will be useful for these future measurement challenges.

19. Disclaimer

Certain commercial equipment or instruments are identified in the paper to specify adequately the experimental procedures. Such identification does not imply recommendations or endorsement by the NIST, nor does it imply that the equipment or instruments are the best available for the purpose.

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