

SRMs for Contaminants on Air Particulate Matter

In 1997 the Environmental Protection Agency (EPA) issued new standards for air particulate matter (PM) under the national ambient air quality standards, including new regulations for PM less than 2.5 μm ($\text{PM}_{2.5}$), which is the respirable PM fraction, in addition to the existing PM_{10} standards. Research recommendations were made by the National Research Council at the request of Congress and the EPA to focus on evaluating what types of particles cause detrimental health effects. To support compositional analyses and other investigations on the fine PM, quality assurance materials are necessary; however, few appropriate fine particulate materials are currently available to support this research. NIST has been collaborating with the EPA to develop SRMs to support measurements of organic species in fine PM. In addition, research continues on the composition of bulk urban dust with the benchmark SRM 1648 being renewed.

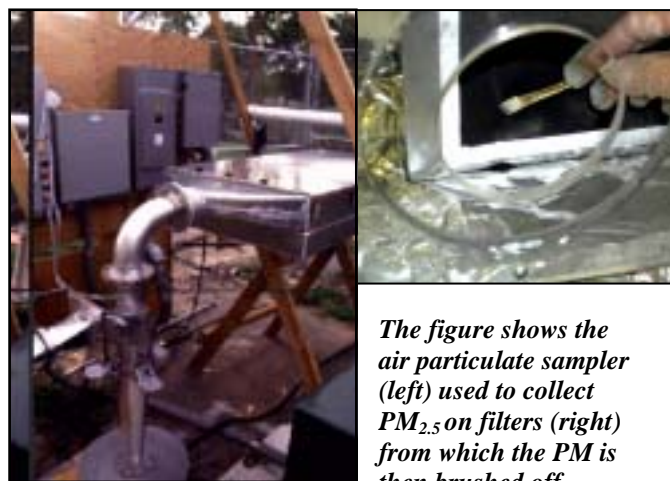
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NIST and the EPA collaborated in the late 1970s to develop two SRMs for ambient air particulate matter. SRM 1648 Urban Particulate Matter, which was collected in St. Louis, MO, was issued in 1978 with certified concentrations for trace element content. SRM 1649 Urban Dust/Organics, which was collected in Washington, DC, was issued in 1982 with certified values for five polycyclic aromatic hydrocarbons (PAHs) and was reissued in 1998 with values assigned for over 100 organic contaminants. Both of these air particulate SRMs have been widely used in the environmental/atmospheric particulate measurement community for nearly three decades. Supplies of both SRM 1648 and 1649 are nearly exhausted; bulk PM (< 60 μm) from the original late 1970s collections is available and measurements are in progress to reissue these SRMs. The reissuing of these materials, however, does not address the need for a more contemporary PM reference material, particularly for $\text{PM}_{2.5}$. Recently the EPA and NIST initiated a new collaboration to address reference materials for fine PM.

The recent NIST/EPA collaboration focused on three projects: (1) establishment of an interlaboratory comparison program to assess measurement comparability, (2) development of solution SRMs for organic compounds of interest for PM measurements, and (3) collection of bulk contemporary $\text{PM}_{2.5}$ for use as a future SRM. Three interlaboratory comparison exercises have been conducted for the determination of organic contaminants and source markers in PM samples. A series of calibration solution SRMs

have been ampouled for aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), nitro-substituted PAHs (nitro-PAHs), hopanes/steranes, ^{13}C -labeled and deuterium-labeled levoglucosan, and acids (alkanoic and resin; deuterium-labeled and non-labeled).

As part of this collaboration, the Organic Speciation Working Group was formed in 2000 to assist in this effort by participating in interlaboratory comparison studies and by providing input for the development of SRMs to support these measurements. This group has participated in three interlaboratory comparison studies for the determination of PAHs, nitro-PAHs, alkanes (including hopanes and cholestanes), sterols, carbonyl compounds (ketones and aldehydes), acids (alkanoic and resin), phenols, and sugars in PM-related samples. Based in part on the results of these studies and input from the Organic Speciation Working Group, priorities for the development of a number of calibration solution SRMs were identified including: aliphatic hydrocarbons, PAHs, nitro-PAHs, hopanes/steranes, ^{13}C -labeled and deuterium-labeled levoglucosan (for use as internal standards), and acids (deuterium-labeled for use internal standards and non-labeled). SRM 1494 Aliphatic Hydrocarbons in *Iso*-Octane was issued in early 2004. SRMs 2260a PAHs in Toluene and 1491a Methyl-Substituted PAHs in Toluene, which are redesigned solutions with values assigned for an expanded list of 53 PAHs and alkyl-substituted PAHs, were issued in 2005. Five additional solutions will be issued in early 2007: SRM 2264 and SRM 2265 Nitro-PAHs I and II, respectively, in Methylene Chloride, SRM 2266 Hopanes and Steranes in 2,2,4-Trimethylpentane, SRM 2267 Deuterated Levoglucosan in Ethyl Acetate, and SRM 2268 Carbon-13 Labeled Levoglucosan in Ethyl Acetate. Three organic acid solutions have been prepared and are being monitored for stability prior to issuing SRMs.



The figure shows the air particulate sampler (left) used to collect $\text{PM}_{2.5}$ on filters (right) from which the PM is then brushed off.

Two recent collections of 20 g each of ultra fine particulate matter at a site in Baltimore, MD (see figure) have been used to prepare an interim reference material for distribution in the NIST/EPA interlaboratory comparison exercises for the determination of organic compounds. The results from the second interlaboratory study using the interim reference material have been used in conjunction with NIST measurements to assign concentration values for the compounds of interest. This interim reference material is now available to laboratories involved in EPA PM_{2.5} research programs for use as a control or reference material. The second PM_{2.5} material collected in Baltimore was used in the third NIST/EPA intercomparison study along with SRM 1648 Urban Particulate Matter and RM 8785 Air Particulate Matter on Filter Media (A Fine Fraction of SRM 1649a Urban Dust on Quartz-Fiber Filters). The sampler has been adapted to isolate the PM_{2.5} portion from a subsample of SRM 1649a Urban Dust. This PM_{2.5} portion of SRM 1649a has been homogenized and bottled for use in a future intercomparison study.

SRM 1648 is being replaced with SRM 1648a using PM from the original collection. Instrumental neutron activation analysis, X-ray fluorescence spectrometry, and solid-sample graphite furnace atomic absorption spectrometry have established homogeneity of SRM 1648a for a typical sample size of several milligrams and have confirmed the identical composition of SRM 1648 and SRM 1648a. Analyses for value assignment by NIST and collaborating expert laboratories were completed in late 2006, and SRM 1648a will be issued in early 2007. For the replacement of SRM 1649a, measurements for PAHs, nitro-PAHs, polychlorinated biphenyls (PCBs), chlorinated pesticides, and brominated flame retardants are in progress with completion targeted for late 2007.

Impact: The development of SRMs to support measurements for organic species in fine PM will expand quality assurance capabilities to important source markers and species critical to human health. Replenishment of the supply of bulk urban dust will extend NIST's support for inorganic characterization of aerosols for many years. Users can continue to rely on their experience with SRM 1648 and 1649a and can refer to extensive literature resource on both materials.

Publications:

- Pancras, J. P., Ondov, J. M., Zeisler, R., "*Multielement Electrothermal AAS Determination of Eleven Marker Elements in Fine Ambient Aerosol Slurry Samples Collected with SEAS-II*," Analytica Chimica Acta 2005, 538, 303-312.
- Schantz, M.M., Wise, S.A., and Lewtas, J., "*Intercomparison Program for Organic Speciation in PM_{2.5} Air Particulate Matter: Description and Results for Trials I and II*," NISTIR 7229 (2005).
- Schantz, M., Poster, D., Kucklick, J., Wise, S., McDow, S., and Lewtas, J., "*Intercomparison Program for Organic Speciation in PM_{2.5} Air Particulate Matter: Description and Results for Trial III*," NISTIR 7303 (2005).

Future plans: The high-volume sampler will be used to prepare a PM_{2.5} fraction from a collection of contemporary total suspended particulate matter as a means of providing sufficient fine PM for future SRM development.