

For the Love of Chemistry

Penned by Connie Hayes, CEO



This month we present the High-Purity Standards Guide to Industrial Hygiene and Air Monitoring Certified Reference Materials.

February 2019

High-Purity Standards Guide to Industrial Hygiene and Air Monitoring Certified Reference Materials

Introduction: High-Purity Standards offers a line of Certified Reference Materials (CRMs) for analysis associated with Industrial Hygiene and Air Monitoring needs. This line addresses our customer needs for both inorganic and organic components, dissolved and particulate materials (note, these are not particle sizing reference materials).



PhotoScan by Google Photos

Michael Epstein, Robert Waters and Theodore Rains with Portable Atmosphere Sampler at NBS

Background: High-Purity Standards (HPS) introduced a metals-on-filter (QC-TMFM) product line into our stock offerings in 1995. Mixed cellulose ester (MCE) filters were used. Over the years, this product line has expanded to include metals on other filter media such as PVC, Teflon-coated, acrylic, and quartz. In 2002, HPS was contracted to manufacture spiked PVC filters of alpha quartz and Cristobalite. This contract required the application of particles, not dissolved solids, on the filters. This work was a natural follow-on to work that Dr. Rains had done at NBS/NIST and resulted in the paper "**Development of SRMs 295x and 296x. Respirable Crystalline Silica on Filter**"¹. The success of this project enabled our collaboration in 2005 with the Beryllium Health and Safety Committee (BHSC). The BHSC relationship began with the contribution of beryllium spiked filters to a seminal round robin investigation. The objective of the round robin was to investigate the efficacy of various sample preparation methods. This round robin resulted in the paper "**Preparation,**

certification and inter-laboratory analysis of workplace air filters spiked with high-fired beryllium oxide"². Both of these projects demonstrated our ability to accurately and precisely manufacture filters spiked with particles. In both projects, the filters were spiked with NIST SRM materials.

Products: HPS stocks MCE filters spiked with metals. The metals for the QC-TMFM group are dissolved in an aqueous matrix prior to application to the filter. Beryllium oxide (BeO) for the TMFM-CBEO group is the NIST SRM 1877 Beryllium Oxide Powder.

Current catalog items include:

Part Number	Description
QC-TMFM-A	15 element-spiked MCE filters, low concentration
QC-TMFM-B	15 element-spiked MCE filters, medium concentration
QC-TMFM-C	15 element-spiked MCE filters, high concentration
QC-TMFM-D	15 element + Aluminum-spiked MCE filters, low concentration
QC-TMFM-E	15 element + Aluminum-spiked MCE filters, medium concentration
QC-TMFM-F	15 element + Uranium-spiked MCE filters, low concentration
QC-TMFM-G	15 element + Uranium-spiked MCE filters, medium concentration
TMFM-CBEO-BLANK	Blank 37 mm MCE filters for TMFM-CBEO spiked filters
TMFM-CBEO-0.05	BeO at 0.05 µg/37 mm MCE filter
TMFM-CBEO-0.1	BeO at 0.1 µg/37 mm MCE filter
TMFM-CBEO-0.2	BeO at 0.2 µg/37 mm MCE filter
TMFM-CBEO-0.5	BeO at 0.5 µg/37 mm MCE filter

TMFM-CBEO-1.0	BeO at 1.0 µg/37 mm MCE filter
TMFM-CBEO-2.0	BeO at 2.0 µg/37 mm MCE filter
TMFM-CBEO-5.0	BeO at 5 µg/37 mm MCE filter
TMFM-CBEO-10.0	BeO at 10 µg/37 mm MCE filter
TMFM-CBEO-25.0	BeO at 25 µg/37 mm MCE filter

How to use these products: Laboratories that are engaged in analyzing samples collected for workplace or environmental air particulates or vapors generally follow procedures established by OSHA, NIOSH, EPA, or ASTM. Other methods are available from agencies that recognize specific chemical hazards within their industries, such as crystalline silica hazards by the Mine Safety and Health Administration.

Trace metals on filter media - The QC-TMFM line is the origination of Industrial Hygiene and Air Monitoring products. These products include a variety of dissolved metals in varying concentrations on MCE filters. QC-TMFM-A through QC-TMFM-C were first introduced based upon the concentrations of a combination of NBS/NIST SRM 2675, 2676, 2677, and 3087, products that Dr. Rains worked on during his time at NBS/NIST. The combination of QC-TMFM-A through QC-TMFM-C include low, medium and high concentrations similar to SRM 2675, 2676 and 2677 respectively, but with more metals included on the filters. QC-TMFM-D and -E, and QC-TMFM-F and -G are low and medium concentrations of the same elements but with aluminum or uranium added. The original NBS SRM 267x series was the result of a joint NIOSH/NBS program to develop reference materials related to industrial hygiene analysis and for monitoring the workplace atmosphere. These metal concentrations are designed to simulate metals near detection levels, at the threshold, and well above the threshold level. There are a large variety of methods from NIOSH, OSHA and the EPA associated with these items. For ICP/OES and ICP/MS analysis, OSHA ID-125G and NIOSH 7300 and 7303 are more frequently referenced.

Beryllium oxide on filter - While HPS has always included dissolved beryllium on MCE filters in the QC-TMFM product line, it became necessary to add products that addressed particulate material on filters. Beryllium oxide is a refractory component associated with nuclear facilities, semi-conductor devices, rocket engines, and more, that has been identified as a source leading to beryllium sensitization and chronic beryllium disease (CBD). Analysis of the existence in the workplace air necessitates the need for different methods that are capable of dissolving BeO. Methods that address that need include NIOSH 7102, 9110 and OSHA ID-125G. HPS participated in a round robin study of various methods of sample preparation and analysis of high-fired BeO methods². The use of sulfuric or hydrofluoric acid or ammonium bifluoride resulted in the largest percentage recovery of BeO. HPS introduced the TMFM-CBEO product line following that study. The source of the beryllium oxide applied to the filter is NIST SRM 1877 high-fired BeO powder.

Silica in air methods - There are numerous methods for measuring respirable crystalline silica in workplace air. The most popular ones employ XRD (NIOSH 7500, OSHA ID-142, MSHA P2) and infrared methods (NIOSH 7602, 7603, MSHA P-7, and ASTM D7948)³⁻⁹. In all of these methods, respirable particles (containing crystalline silica) from air are collected on PVC filters. The filters are then either ashed or dissolved in tetrahydrofuran and redeposited on silver filters before being analyzed by XRD or FTIR. Background matrices of Coal Mine Dust, Calcite, or Talc can be added. These materials are first checked for their silica content and forms prior to addition to the filters.

Hexavalent chromium on filter - Popular methods for the analysis of hexavalent chromium analysis in workplace air include OSHA ID-215 and NIOSH 7600.^{10,11} Due to the limited stability of hexavalent chromium on filter media, any product manufactured for use with these procedures needs to be a custom product and shipped at the time of manufacture. The challenges associated with this analysis include: 1) extraction efficiency, 2) analyte stability - including interconversion of Cr(VI) and Cr(III) species, 3) chromium contamination in filters. To overcome many of these challenges, use of an accurate and appropriate standard prepared concurrent with the samples is highly recommended. These products require shipping on ice to maximize stability. When running a reference material as a QC standard against a collected sample, please notify Customer Service of a need for a rush order when samples need to be extracted and tested within a required time frame. HPS has also used EPA method 6800, "**Elemental and Molecular Speciated Isotope Dilution Mass Spectrometry**" for hexavalent chromium analysis.¹² This method employs spiking a sample with isotopic Cr(III)/Cr(VI), separation and analysis via IC-ICP/MS. HPS has measured over 400 ng of chromium on both PVC and acrylic filters. HPS is licensed to use a patented procedure to remove chromium, which may be required when looking at low levels.¹³

Some of the long-term monitoring of hazardous air pollutants regulated under the Clean Air Act were investigated by the National Air Toxics Trends Station (NATTS) Network. Data collected from this network as well as others can be found on the EPA websites. The EPA established a Proficiency Testing program for participating laboratories. Metals samples submitted to the participating labs consist of Teflon filters impregnated with known amounts of the eight metals of interest. Teflon filters are not a common collection media for air samples designed to collect metals, consequently this PT program has had low participation. HPS manufactures

metals on Teflon coated filters as custom products. One of the methods associated with metals analysis is IO-3.5, Determination of Metals in Ambient Particulate matter using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS).¹⁴

Toxic Metals on filter - 2020 will be the 50th anniversary of the signing of the Clean Air Act. This Act began a framework to foster the growth of the US economy while improving human health and the environment. Included in the Clean Air Act are regulations regarding hazardous or toxic air emissions. These are pollutants that are known or suspected to cause cancer or other serious health effects. These Hazardous Air Pollutants (HAP) components are generally located closer to their sources. Thus identifying industrial or human sources along with measuring the levels near those sources became part of the process in establishing rules and promoting mechanisms for air improvement. In the most recent reporting of the National Emission Inventory, 11 HAP metals are identified for monitoring: Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Mercury, Nickel and Selenium. These rules are further expanded at the state level by rules associated with state concerns. Rule 1420, Emission Standards for Lead, promulgated by the California Air Resources Board is such an example.

In 2010, HPS developed a line of spiked filters for use with analysis of Toxic Metals in air, QC-TOXM. This line included 8 of the 11 above-listed elements. Note that mercury is a volatile metal and thus has a low expiration date. For that reason, mercury compounds added to filter media are manufactured upon request as custom products. Methods associated with air monitoring employ a range of filter types, depending upon the environment and analytes of interest. Our QC-TOXM products use Quartz filters, however Teflon-coated filters are also available upon request. EPA Compendium method IO-3.1, "Selection, Preparation and Extraction of Filter Material" provides information on filter selection. Another method associated with metals analysis is IO-3.5, Determination of Metals in Ambient Particulate matter using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS). Other methods include 40 CFR, Appendix G to Part 50 – Reference Method for the Determination of Lead in Total suspended Particulate Matter.

Organic - solvents collected on sampling tubes or in diffusive badges have NIOSH and OSHA methods associated with specific components. The EPA published "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air". Methods TO-1 through TO-17 include a variety of sampling and analysis techniques.

Ordering custom products: For standards associated with inorganic hazards collected on filters, we recommend that the laboratory use filters similar to the method used in sampling. It is for this reason that we offer products on a broad range of filters including, mixed cellulose esters (MCE), PVC, Quartz, Teflon-coated, and Acrylic.

HPS offers custom reference materials for organic solvents on tubes or passive samples analyzed via GC, GC/MS or HPLC. Custom organic solvents will require specific information on the type of tube or passive sampler used. In addition, identification of the method used for sample preparation and analysis will ensure a compatible reference material. Upon receipt of a request for a quotation, our chemists will be in touch to discuss your needs so that we can best manufacture the reference material.

Cleaned filters are also available upon request. HPS offers PVC filters cleaned to remove silicon, chromium or vanadium.

References

- ¹ Yu, L.L., Fassett, J.D., MacDonald, B.S., Butler, T.A., Ramsey, D.M., Key-Schwartz, R.J., and Rains, T.C., Development of SRMs 295x and 296x, Respirable Crystalline Silica on Filter, *Journal of ASTM International*, May 2005, Vol 2., No. 5.
- ² Oatts, T.J., Hicks, C.E., Adams, A.R., Brisson, M.J., Youmans-McDonald, L.D., Hoover, M.D., and Ashley, K., Preparation, certification and interlaboratory analysis of workplace air filters spiked with high-fired beryllium oxide, *J. Environ.Monit.*, 2012, 14, 391.
- ³ <https://www.cdc.gov/niosh/docs/2003-154/pdfs/7500.pdf> (accessed February 11, 2019)
- ⁴ https://www.osha.gov/dts/sltc/methods/inorganic/id142/id142_v4.pdf (accessed February 11, 2019)
- ⁵ <https://arlweb.msha.gov/Techsupp/pshtcweb/MSHA%20P2.pdf> (accessed February 11, 2019)
- ⁶ <https://www.cdc.gov/niosh/docs/2003-154/pdfs/7602.pdf> (accessed February 11, 2019)
- ⁷ <https://www.cdc.gov/niosh/docs/2003-154/pdfs/7603.pdf> (accessed February 11, 2019)
- ⁸ <https://arlweb.msha.gov/Techsupp/pshtcweb/MSHA%20P7.pdf> (accessed February 11, 2019)
- ⁹ ASTM D7948-14e1, Standard Test Method for Measurement of Respirable Crystalline Silica in Workplace Air by Infrared Spectrometry, ASTM International, West Conshohocken, PA, 2014, www.astm.org
- ¹⁰ https://www.osha.gov/dts/sltc/methods/inorganic/id215_v2/id215_v2.pdf (accessed February 11, 2019)
- ¹¹ <https://www.cdc.gov/niosh/docs/2003-154/pdfs/7600.pdf> (accessed February 11, 2019)
- ¹² <https://www.epa.gov/sites/production/files/2015-12/documents/6800.pdf> (accessed February 11, 2019)
- ¹³ Rubenstein, M. Hexavalent chromium and total chromium removal from polyvinylchloride (PVC) polymers. *U.S. Patent 8,415,452*, April 9, 2013.
- ¹⁴ <https://www3.epa.gov/ttn/amtic/files/ambient/inorganic/mthd-3-5.pdf> (accessed February 11, 2019)

