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New Standards for Sample Preparation

Effective Sample Preparation for Metals and Metalloids Using Ammonium Bifluoride

By Kenn White and Mike Brisson

Obtaining the best analytical results from a sampling campaign involves three key elements: a well-designed and executed sampling plan, proper sample preparation, and laboratory analysis. If sample preparation is not done properly, the results are likely to be incorrect no matter how well the analysis is performed and will probably underestimate the actual exposure in the workplace. This is particularly true for surface wipe samples, which can be more challenging to solubilize for analysis.

OVERCOMING LIMITED SOLUBILITY

The preparation of samples to be analyzed for metals and metalloids presents problems due to the limited solubilities of their compounds. Typical preparation methods involve strong acid digestion solutions along with the application of energy through heat, pressure, or both. (Hot plates, hot blocks, or microwave ovens are used for this purpose.) Other methods use concentrated or dilute nitric acid (HNO_3) or mixed acid solutions of HNO_3 and hydrochloric acid (HCl) or HNO_3 and sulfuric acid (H_2SO_4). In some methods, hydrogen peroxide (H_2O_2) is used with HNO_3 for digestion. A mix of perchloric acid ($HClO_4$) and HNO_3 is included in NIOSH 7300, *Elements by ICP (Nitric/Perchloric Acid Ashing)*, but this method is limited by the special equipment and ventilation required for $HClO_4$ use and is not effective for some metals or matrices. Hydrofluoric acid (HF) is also not in general use because concentrated HF presents special health hazards, is highly reactive, will corrode metals to release flammable hydrogen, and will etch glass and ceramics. However, HF solutions are more powerful for digestion compared to many other acids and acid mixtures for most metal and metalloid sample preparations.

The power of using HF for digestion to get metal and metalloid samples into solution for analysis has fostered the use of ammonium bifluoride (NH_4HF_2) solutions for sample preparation. In water, ammonium bifluoride (ABF) dissociates to form a dilute HF solution, a much safer alternative for general laboratory use than concentrated HF. Methods using dilute ABF aqueous solutions in digestions for metal and metalloid analyses have proven to be very effective.

NEW STANDARDS FROM ASTM

ASTM International (ASTM) Committee D22 on Air Quality aims, among other goals, to develop and standardize recognized and widely used test methods, practices, guides, and terminology pertaining to sampling and analysis of atmospheres such as indoor and ambient air. As part of Committee D22, Subcommittee D22.04 on Workplace Air Quality is concerned with the development of methods, practices, and guides for sampling and analysis of chemical agents related to occupational exposures. In addition to airborne sources, contaminants on surfaces and in soil are also of interest. Subcommittee D22.04 disseminates international consensus standards applicable to laboratories interested in the preparation of airborne particulate, settled dust, and soil samples containing metals

and metalloids of interest from anthropogenic sources for analysis. The resulting data can provide information used for the determination of hazardous conditions or to assess possible human exposures.

ASTM recently published two standards: D8344, “Standard Practice for Ammonium Bifluoride and Nitric Acid Digestion of Airborne Dust and Dust-Wipe Samples for the Determination of Metals and Metalloids”; and D8404, “Standard Practice for Preparation of Soil Samples by Ammonium Bifluoride-Nitric Acid Digestion for Subsequent Analysis for Metals and Metalloids.” These standard practices utilize ABF and concentrated HNO_3, along with hot block digestion or heated sonication, as an effective combination to solubilize air, surface, and soil samples.

Since beryllium-containing samples are also difficult to digest, D22.04 has previously published two standards specific to these samples: D7202, “Standard Test Method for Determination of Beryllium in the Workplace by Extraction and Optical Fluorescence Detection”; and D7458, “Standard Test Method for Determination of Beryllium in Soil, Rock, Sediment, and Fly Ash Using Ammonium Bifluoride Extraction and Fluorescence Detection.”

All four of these standards use ABF aqueous solutions (mass fraction less than or equal to 10 percent) for sample digestion. Use of HNO_3 as part of the ABF digestion solution in D8344 and D8404 yields solutions suitable for atomic spectroscopic analysis by flame atomic absorption spectroscopy (FAAS), graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled plasma mass spectroscopy (ICP-MS). Comparisons of the four standards appear in Table 1.

Table 1. ASTM Standards for Preparation of Samples Containing Metals or Metalloids

ASTM Number	**Applications**	**ABF**	**HNO_3**	**Heating/Agitation**
D8344	Air, Surface	1%	Concentrated	Hot block or heated sonication
D8404	Soil	1%	Concentrated	Hot block or heated sonication
D7202	Air, Surface	1%	Not used	Agitation followed by hot block/oven/heating bath
D7458	Soil	3% to 10%	Not used	Oven

Dissolution methods that are effective in fully dissolving the sample and the sampling media, while also being safer and convenient for use in the laboratory, are an important part of obtaining data that can be used to make the best decisions for worker protection and safety.

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Send feedback to **synergist@aiha.org**.

Resources

AIHA: *AIHA Laboratory Quality Assurance Manual*

ASTM International: Method D7202, “Standard Test Method for Determination of Beryllium in the Workplace by Extraction and Optical Fluorescence Detection” (2015).

ASTM International: Method D7458, “Standard Test Method for Determination of Beryllium in Soil, Rock, Sediment, and Fly Ash Using Ammonium Bifluoride Extraction and Fluorescence Detection” (2014).

ASTM International: Method D8344, “Standard Practice for Ammonium Bifluoride and Nitric Acid Digestion of Airborne Dust and Dust-Wipe Samples for the Determination of Metals and Metalloids” (2020).

ASTM International: Method D8404, “Standard Practice for Preparation of Soil Samples by Ammonium Bifluoride-Nitric Acid Digestion for Subsequent Analysis for Metals and Metalloids” (2021).

NIOSH: Method 7300, “Elements by ICP (Nitric/Perchloric Acid Ashing),” **bit.ly/niosh7300** (PDF, March 2003).

Royal Society of Chemistry: “Sample Dissolution Reagents for Beryllium” in *Beryllium: Environmental Analysis and Monitoring* (2009).