BHSC Sampling and Analysis Subcommittee
Round Robin Project Summary Data Report
Beryllium Oxide Spiked Filter Project – November 2009

INTRODUCTION

The Beryllium Health & Safety Committee (BHSC) Sampling and Analysis Subcommittee (SAS) Working Group for Beryllium Oxide and Sample Digestion Issues undertook a special project to conduct a volunteer round robin laboratory analysis project of beryllium oxide spiked on air filters. The project was designed to gather data on the effectiveness of methods currently in use for sample preparation and analysis of high-fired beryllium oxide. The study utilized NIST SRM® 1877 "Beryllium Oxide Powder" as the solid-standard material deposited onto 37 mm nitrocellulose air filters. The round robin project consisted of five spiked filters (in duplicate) and two blank filters, for a total of twelve unique air filters. The beryllium levels of the spiked filters were chosen to mimic the American Industrial Hygiene Association (AIHA) Beryllium Proficiency Analytical Testing (BePAT) program, and were between 0.5 µg and 25 µg of beryllium as BeO. The true spiked levels of the round robin samples were blind to all participants during the study.

The project was designed to gather data on the effectiveness of methods currently in use for sample preparation and analysis of high-fired beryllium oxide. High-fired beryllium oxide was chosen as the spiking material was made to represent a known, difficult-to-digest beryllium material that may exist in typical work sites where beryllium is found, and to collect data on the efficiency, accuracy, precision and robustness of in-use sample preparation and analytical methods used for air samples of beryllium-containing aerosol particulates. All volunteer labs were requested to follow their normal sample preparation and analytical methods currently in use for samples of this type. Data was collected on the preparation and analysis method details to allow for data comparison and categorization. A total of 27 different laboratories from the U.S., U.K., France and Canada participated in the round robin, see table 1. Several labs requested more than one sample set to check unique lab methods employed for these sample types, and a total of 36 sets of samples were distributed to the 27 participants. Data was submitted for 34 of the 36 sets of samples.

A data acceptance criterion of 75% to 125% was chosen to represent the "pass/fail" condition for acceptance. A similar data acceptance criterion is currently used in the BePAT program. All submitted data were compared directly to the as-spiked levels, and recovery was determined for each sample in the study. In order to maintain the individual labs identities, only the unique lab identifier code for each data set is used.

A summary data table is shown as Figure 1 and consists of information on the various methods used by each lab. Information on sample preparation, instrumentation and specific reagents used in the sample preparation is shown in this table. The analysis data suggested groupings to exist in four areas: the Sulfuric group, the Ammonium Bifluoride (ABF) group, the Hydrofluoric (HF) group, and the Nitric group. These groupings come from the reagents used in the sample preparation portion of the various methods used in the study. The analysis data are therefore grouped based upon the use of common reagents. Results from the use of sulfuric acid, or combinations of reagents that included sulfuric acid, are grouped in the Sulfuric group. Results from use of ammonium bifluoride, or combinations using ABF, are grouped in the ABF group. Results from the use of hydrofluoric acid, or combinations using HF, are grouped in the HF group. The Nitric group combines all the labs that had used either nitric acid alone, or had used some combination of nitric acid and other components not already grouped above. The most notable combinations in the Nitric group were combinations of nitric and hydrochloric acids, which are common to EPA and similar environmental-type sample preparation methods. Figure 1 also shows the number of samples that passed or failed the acceptance criterion used in this study and the individual lab mean recovery for all samples in the study, along with other statistical data for standard deviation, relative standard deviation, and range of recovery (low to high).

A graphical presentation of the individual lab recoveries is shown in Figure 2. The high, low, and mean recoveries for each lab against the accepted 100% standard (green line), and the low (75%) and high (125%) acceptance limits (red lines). The data are presented by reagent grouping shown as colored boxes around the appropriate lab ID. This chart shows the data grouping and the significance of the reagent effectiveness for recovery. There were no (zero) labs found outside the acceptance limits that used either sulfuric or hydrofluoric acid in their preparation method. There was only one lab that used ammonium bifluoride in their preparation method that did not recover within the 75% - 125% limits. A further review of the method used by that lab showed they did not heat their samples, which is a condition known to affect ABF recoveries. Only a single lab out of nine was able to employ nitric acid and recover beryllium within the acceptance limits.

Figure 3 is a histogram showing the four data groupings and prep reagent effectiveness. The Sulfuric and HF groups lead the way with 170 total passes and 0 failures, while the ABF group had 68 passes and 12 failures (10 by a single lab). Two of the failures in the ABF group were determined to be statistical outliers from a specific lab and were not included in the statistical evaluation tables, but are shown in the data report. The lab recognized the outliers but was unable to ascertain what the problem may have been for those two samples. The histogram dramatically shows the lack of effectiveness that nitric acid, alone or in combination with acidxs other than sulfuric or hydrofluoric, have on BeO spiked filters as 54 failed the acceptance limits and only 36 samples passed.

This round robin project has demonstrated that procedures utilizing either sulfuric or hydrofluoric acid are effective in recovering beryllium from beryllium oxide particulate on air filters. Methods utilizing ammonium bifluoride also seem to be highly effective in recovery of this difficult to digest material. The use of nitric acid alone, or combinations of nitric and hydrochloric acid, is not complete in solubilizing beryllium from beryllium oxide. It also appears that the use of procedures designed to produce multi-element data may not be effective for beryllium, in the form of high-fired beryllium oxide. Many of the procedures used by the lab participants are designed for multi-element reporting; however the lack of efficiency towards beryllium, as BeO, may lead to underestimating the total beryllium level in particulate air samples. It is recognized that not all real world samples contain beryllium oxide; however it may be difficult to determine the chemical form of the element in air particulate matter. The round robin data clearly show which analytical conditions will solubilize beryllium, as the high-fired oxide form, and those that lack the chemical conditions necessary to solubilize the oxide form.

ACKNOWLEDGEMENTS

This round robin project could not have been accomplished without the participation of the volunteer laboratories shown in Table 1. Additional assistance was received from Theodore C. Rains, Ph. D, Amy Adams, Racheal Shelmire, Cheryl Reed, Eldon Delong (all from High Purity Standards, Charleston, SC), Michael Brisson (Savannah River Nuclear Solutions, LLC), Amy Ekechukwu, Ph.D (Savannah River National Laboratory), Kenn White (Consultive Services), David Weitzman (DOE), and members of the BHSC Sampling and Analysis Subcommittee.

Table 1. Volunteer laboratories that participated in the BeO spiked filter round robin study.

Name of Laboratory	Location
ALS Datachem	Salt Lake City, Utah
B&W Pantex	Amarillo, Texas
Berylliant, Inc.	Tucson, Arizona
Bureau Veritas North America	Novi, Michigan
Center for Disease Control / National Institute for Occupational Safety and Health (CDC/NIOSH)	Cincinnati, Ohio
Comprehensive Industrial Hygiene Laboratory Navy and Marine Corps Public Health Center	San Diego, California
Fluor Hanford	Richland, Washington
Forensic Analytical Laboratories	Hayward, California
Galson Laboratories	East Syracuse, New York
Health and Safety Laboratory	Buxton, Derbyshire, England
Health Physics Analytical Laboratory	Abingdon, Oxon, England
Institut National de Recherche et de Sécurité (INRS)	Vandoeuvre-les-Nancy, France
Institut de Recherche Robert Sauvé et de Sécurité en Travail (IRSST)	Montréal, Quebec, Canada
Los Alamos National Laboratory	Los Alamos, New Mexico
Lawrence Livermore National Laboratory	Livermore, California
Lawrence Livermore National Laboratory / Environmental Monitoring Radiochemistry Laboratory (EMRL)	Livermore, California
Navy & Marine Corps Public Health Center Laboratory	Norfolk, Virginia
National Security Technologies, LLC	Mercury, Nevada
Oak Ridge National Laboratory	Oak Ridge, Tennessee
Occupational Safety and Health Administration (OSHA)	Salt Lake City, Utah
Savannah River Nuclear Solutions, LLC (non-rad IH lab)	Aiken, South Carolina
Savannah River Nuclear Solutions, LLC (rad IH lab)	Aiken, South Carolina
Savannah River National Laboratory	Aiken, South Carolina
U.S. Air Force School of Aerospace Medicine (USAFSAM/OEHTA)	Brooks City-Base, Texas
United States Enrichment Corporation, Inc	Piketon, Ohio
Wisconsin Occupational Health Laboratory	Madison, Wisconsin
Y-12 National Security Complex	Oak Ridge, Tennessee

Figure 1. Analytical Method Information

Beryllium Oxide Spiked Filter Round Robin Project - 2009

Analytical Method Information

				Prep Reagent Components						BePAT acceptance limit criteria (75%-125%)					Recovery range (%)			
Lab ID #	Analytical_method	Instrument	Prep reagents	H2SO4 (1)	ABF (2)	HF (3)	HNO3 (4)	HCl (5)	HClO4 (6)	# Passed	# Failed	Mean recovery (%)	Std Dev	RSD	Low	High	Lab ID #	Prep reagents
1007	Microwave digestion	ICP	1	H2SO4						10	0	96.0%	5.12%	5.3%	90.8%	109.8%	1007	1
1011	NIOSH 7300 Modified	ICP	1	H2SO4						10	0	98.6%	2.64%	2.7%	94.2%	103.8%	1011	1
1005	H2SO4 + HNO3	ICP	1,4	H2SO4			HNO3			10	0	92.5%	1.86%	2.0%	89.3%	95.6%	1005	1,4
1009	Microwave digestion	ICP	1,4	H2SO4			HNO3			10	0	100.4%	1.39%	1.4%	98.1%	102.8%	1009	1,4
1013	Acid Digestion	FAAS	1,4	H2SO4			HNO3			10	0	98.0%	3.58%	3.6%	91.7%	103.3%	1013	1,4
1020	Not specified	ICP-MS	1,4	H2SO4			HNO3			10	0	88.2%	5.93%	6.7%	82.1%	97.2%	1020	1,4
1004	OSHA ID 125G	ICP	1,4,5	H2SO4			HNO3	HCl		10	0	99.9%	1.65%	1.6%	97.9%	102.3%	1004	1,4,5
1036	Not specified	ICP	1,4,5	H2SO4			HNO3	HCl		10	0	88.6%	2.30%	2.6%	85.8%	92.5%	1036	1,4,5
1012	WP-0014, 3.6	ICP	1,4,6	H2SO4			HNO3		HClO4	10	0	97.1%	1.34%	1.4%	94.4%	98.5%	1012	1,4,6
1023	NIOSH 7102	ICP	1,5	H2SO4				HCl		10	0	95.2%	4.24%	4.5%	89.1%	103.1%	1023	1,5
1029	NIOSH 7300, OSHA ID-125G	ICP	1,5	H2SO4				HCl		10	0	97.7%	2.34%	2.4%	94.4%	101.7%	1029	1,5
1001	NIOSH 7704 ASTM D7202	Fluorescence	2		ABF					10	0	97.1%	3.02%	3.1%	90.4%	101.2%	1001	2
1003	NIOSH 7704	Fluorescence	2		ABF					8	2	100.1%	3.76%	3.8%	96.7%	107.4%	1003	2
1010	ASTM D7202-06 Modified	Fluorescence	2		ABF					10	0	105.1%	1.68%	1.6%	103.3%	107.5%	1010	2
1017	NIOSH 7704	Fluorescence	2		ABF					10	0	101.1%	5.62%	5.6%	87.2%	106.6%	1017	2
1022	NIOSH 7704	ICP	2		ABF					0	10	61.3%	8.48%	13.8%	44.4%	70.2%	1022	2
1025	ASTM D7202	Fluorescence	2		ABF					10	0	98.9%	4.23%	4.3%	93.3%	105.0%	1025	2
1028	NIOSH 9110	Fluorescence	2		ABF					10	0	98.5%	2.41%	2.4%	94.7%	102.7%	1028	2
1016	NIOSH 7300 Modified	ICP-MS	2,4		ABF		HNO3			10	0	104.6%	3.49%	3.3%	99.6%	111.2%	1016	2,4
1008	NIOSH 7300 Ports DTR	ICP-MS	3			HF				10	0	101.9%	4.13%	4.1%	95.6%	108.1%	1008	3
1033	EPA 3052	ICP-MS	3,4			HF	HNO3			10	0	88.6%	3.28%	3.7%	84.7%	96.5%	1033	3,4
1006	HCl + HNO3 + HF	ICP	3,4,5			HF	HNO3	HCl		10	0	104.4%	3.43%	3.3%	99.1%	109.7%	1006	3,4,5
1024	Not specified	ICP-MS	3,4,5,6			HF	HNO3	HCl	HClO4	10	0	94.3%	4.13%	4.4%	88.9%	99.4%	1024	3,4,5,6
1026	NIOSH 7303 Modified	ICP	3,4,5,6			HF	HNO3	HCl	HClO4	10	0	102.0%	3.90%	3.8%	95.6%	107.7%	1026	3,4,5,6
1027	NIOSH 7303 Modified	ICP	3,4,5,6			HF	HNO3	HCl	HClO4	10	0	95.0%	3.49%	3.7%	89.6%	101.0%	1027	3,4,5,6
1015	NIOSH 7300 Modified	ICP-MS	4				HNO3			10	0	86.7%	5.70%	6.6%	76.5%	93.8%	1015	4
1018	NIOSH 7300 Modified	ICP-MS	4				HNO3			0	10	38.6%	8.40%	21.8%	28.3%	49.9%	1018	4
1035	NIOSH 7300 Modified	ICP	4				HNO3			0	10	63.1%	3.36%	5.3%	57.3%	69.0%	1035	4
1002	NIOSH 7300 Modified / OSHA 125G Modified	ICP	4,5				HNO3	HCl		0	10	63.7%	3.89%	6.1%	58.3%	69.3%	1002	4,5
1014	EPA Method 3051	ICP	4,5				HNO3	HCl		5	5	70.1%	10.42%	14.9%	47.2%	78.9%	1014	4,5
1019	OSHA 206	ICP	4,5				HNO3	HCl		7	3	78.4%	9.96%	12.7%	60.3%	88.3%	1019	4,5
1021	NIOSH 7303	ICP	4,5				HNO3	HCl		0	10	66.5%	5.27%	7.9%	54.6%	73.2%	1021	4,5
1030	NIOSH 7301 Modified	ICP-MS	4,5				HNO3	HCl		8	2	81.7%	5.62%	6.9%	72.0%	89.5%	1030	4,5
1032	NIOSH 7303	ICP	4,5				HNO3	HCl		6	4	75.3%	6.26%	8.3%	66.4%	82.2%	1032	4,5
										274	66							
										340								

Lab 1003 datapoints of 245.7% and 275.2% were statistical outliers and not included in mean and std deviation calculations

Figure 2. Lab Recovery Groupings

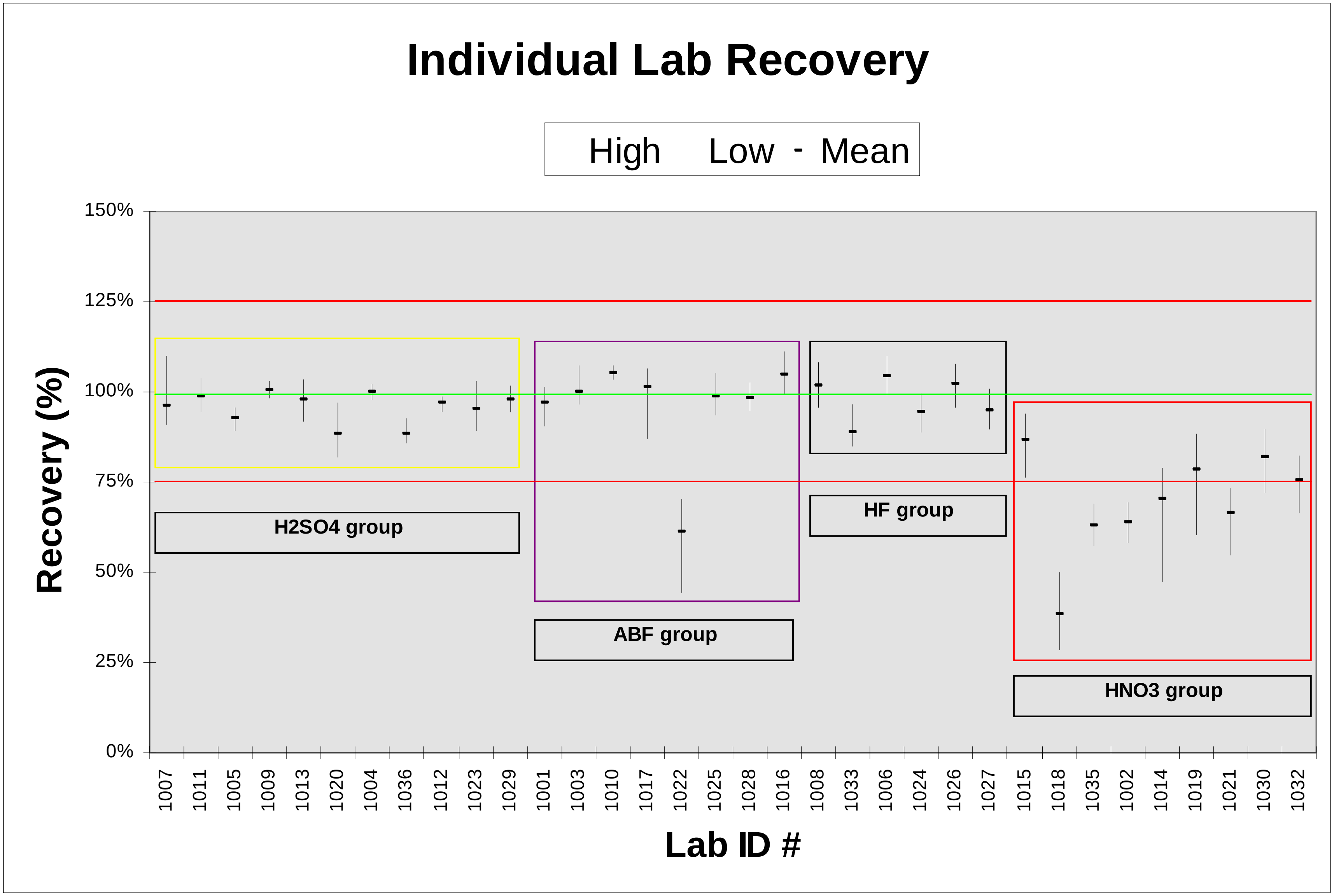

Figure 3. Prep Reagent Effectiveness