This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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Journal of ASTM International, (month) 2005, Vol XX, No. X
Paper ID:
Available online at: www.astm.org
Published XXXX

[1]JOURNAL ARTICLE

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Beryllium Sampling and Analysis Within the DOE Complex and Opportunities for Standardization*

ABSTRACT: Since the U. S. Department of Energy (DOE) published the DOE Beryllium Rule (10 CFR 850) in 1999, DOE sites have been required to measure beryllium in air filter and surface wipe samples for purposes of worker protection and for release of materials from beryllium-controlled areas. Measurements in the nanogram range on a filter or wipe are typically required. Industrial hygiene laboratories have applied methods from various analytical compendia, and a number of issues have emerged concerning sampling and analysis practices. As a result, a committee of analytical chemists, industrial hygienists, and laboratory managers was formed in November 2003 to address the issues. The committee developed a baseline questionnaire and distributed it to DOE sites and other agencies in the U.S. and the U.K. The results of the questionnaire are presented in this paper. These results confirmed that a wide variety of practices were in use in the areas of sampling, sample preparation, and analysis. Additionally, although these laboratories are generally accredited by the American Industrial Hygiene Association (AIHA), there are inconsistencies in execution among accredited labs. As a result, there are significant opportunities for development of standard methods that could improve consistency. The current availabilities and needs for standard methods are further discussed in a companion paper.

KEYWORDS: analysis, beryllium, sampling, standards, workplace

Introduction

Beryllium metal, oxide, and alloys have been used for many years in such diverse applications as aerospace, nuclear weapons, automotive, and sports equipment [1]. Unfortunately, exposure to these forms of beryllium through inhalation [2] or dermal exposure [3] can lead to sensitization and, in a small percentage of those sensitized, to chronic beryllium disease (CBD). For that reason, workplace monitoring is required where beryllium particles can become airborne or deposited on accessible surfaces.

The U.S. Department of Energy (DOE), in response to growing concerns about workplace exposure to beryllium in its nuclear weapons facilities, published its Chronic Beryllium Disease Prevention Program (CBDPP), 10 CFR 850 [4] in December, 1999 (also known as the DOE Beryllium Rule). As part of the CBDPP established under the Rule, monitoring requirements were imposed that included sampling for beryllium in workplace atmospheres and surfaces, both for purposes of worker protection and for release of materials from beryllium-handling areas.

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The resulting air filter and surface wipe samples are analyzed in a laboratory accredited for metals analysis by the American Industrial Hygiene Association (AIHA) or by a laboratory that could demonstrate a quality assurance program equivalent to that required by AIHA accreditation. The intent of this requirement was to assure the quality of the analytical results, and to allow for comparison of results from site to site. Because the action level is 0.2 μg per m^3 of air or per 100 cm^2 of surface, laboratories typically need to be able to measure beryllium in the nanogram range on air filters or surface wipes.

In 2002, issues (as discussed below) began to be identified with the analyses being performed by laboratories supporting DOE sites. It was discovered that, although AIHA-accredited laboratories were being used, there was a wide variety of sample collection, sample preparation, and analysis protocols being employed. As a result, a questionnaire was developed and distributed to a number of sites, including DOE sites and other facilities performing similar work in the U.S. and the U.K., to compile information on the protocols being used. This paper presents the information obtained from that questionnaire. The results demonstrate an opportunity for further method development and standardization, and for development of additional standard reference materials. It is believed that better harmonization of laboratory protocols could improve the consistency of sampling and analytical results from different sites.

Questionnaire Background and Development

Differences among the responding sites focus in three major areas: sampling, sample preparation, and analysis. In air sampling, the principal difference is in the air filter media being employed. In wipe sampling, some sites use wetted wipes while others use dry wipes, with resulting variations in collection efficiency [5]. Additional sampling issues, such as air volumes collected, statistical sampling plans, and bulk sampling, are outside the scope of this paper.

Sample preparation requires digestion of the filter or wipe media, typically in an acid matrix at high temperature and/or pressure. Laboratories typically use a digestion protocol based on a published standard method (e.g., ASTM, U.S. National Institute of Occupational Safety and Health [NIOSH], U.S. Environmental Protection Agency [EPA], U.S. Occupational Health and Safety Administration [OSHA], International Organization for Standardization [ISO], U.K. Health and Safety Executive [HSE]), with modifications in some cases. These standard protocols will typically digest many of the forms of beryllium encountered at worksites, and will also digest beryllium acetate, which is the form of beryllium currently used in AIHA Beryllium Proficiency Analytical Testing Program (BePAT) samples[2]. However, results vary among these methods with respect to digestion of more refractory forms of beryllium, such as beryllium oxide (BeO). Some methods, such as NIOSH Method 7300 [6], provide disclaimers about their ability to digest certain compounds of beryllium. As a result, there may be uncertainty about whether full recovery of all beryllium species is being achieved. Studies are limited due largely to the lack of a BeO standard reference material [7].

Analysis methods are typically based on spectrometric techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES) or graphite furnace atomic absorption spectrometry (GFAAS). Inductively coupled plasma mass spectrometry (ICP-MS) is not widely used, but because it offers a detection limit roughly one order of magnitude lower than ICP-AES or GFAAS [8,9], some sites use ICP-MS when a lower detection limit is required. In ICP-AES, spectral interferences may be encountered which, if not properly corrected, can cause inaccurate

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[2] Personal communication, M. J. Brisson to L. D. Welch (BWXT Y-12), February 2, 2005.

results. In 2002, a number of samples from Savannah River Site (SRS) were sent to two AIHA-accredited laboratories, which reported different results due to disparities in both interference correction protocols and sample preparation (digestion) protocols [10].

The above differences came to light in discussions among industrial hygiene and analytical laboratory personnel at various DOE sites. The principal forum for sharing information has been an ad hoc group known as the Beryllium Health and Safety Committee (BHSC), which includes representatives from DOE sites, NIOSH, OSHA, the U.S. Department of Defense (DOD), and the U.K. Atomic Weapons Establishment (AWE). In November 2003, the BHSC formed an Analytical Subcommittee to improve the consistency and quality of sampling and analysis methodologies and enhance communication between industrial hygiene and analytical laboratory personnel at participating sites [11]. In March 2004, the Subcommittee issued a questionnaire to BHSC member sites to collect information regarding sampling, sample preparation, and analysis protocols being used. A total of 16 responses were received (14 from U.S. locations and one each from the U.K. and Canada).

Questionnaire Results

Table 1 provides background information from the responding sites. This includes information about sample volumes, whether any samples are radiologically contaminated, whether processes involving BeO are used, and accreditation status of analytical laboratories. Sites are identified by country or by U.S. agency, but are not identified by name.

The results indicate a wide variety of sample volumes. Nine of the 16 respondents have radiologically-contaminated beryllium samples. Four have processes involving BeO; in these cases, the firing temperatures used were either not available or not provided for security reasons. All non-radiological laboratories are accredited by AIHA or HSE. Three radiological laboratories are AIHA accredited; one has an equivalent quality assurance program; four are not accredited.

Sampling Protocols

With respect to sampling protocols, the focus of the questionnaire was on surface wipe sampling; for that reason, only six of the responding sites provided information on air sampling. Of the six laboratories reporting on air sampling media, five of them use 0.8 mm mixed cellulose ester (MCE) filters, while one site uses Whatman® 41 ashless cellulose filters.

Information provided for surface wipe samples is provided in Table 2. A wide variety of collection media are employed; several sites use multiple media types. The media type most frequently used are Ghost Wipes® (Environmental Express) [11], which is compliant with ASTM Standard Specification for Wipe Sampling Materials for Lead in Surface Dust (E 1792). ASTM E 1792 is referenced in ASTM Standard Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequent Determination of Metals (D 6966). The questionnaire asked for information about pore size; however, this information is not available for Ghost Wipe® media[3], nor is pore size specified by ASTM E 1792 or ASTM D 6966. Whatman® filters are the next most frequently used media (primarily Whatman® 41).

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[3] Personal communication, M. J. Brisson to Robert Benz (Environmental Express), January 24, 2005.

TABLE 1 – *Background information by site.*

Site ID[a]	# Air Samples per year	% Rad Air Samples	# Wipe Samples per year	% Rad Wipe Samples	Hot Processes (>500°C)	# BeO Proc.	Accreditation[b]
Can-1	650	0	2500	0	0	0	AIHA
DOD-1	44	0	0	0	0	0	AIHA
DOD-2	775	0	3	0	0	0	AIHA
DOD-3	150	0	30	0	0	0	AIHA
DOE-1	200	…	1400	…	0	…	AIHA (both)
DOE-2	37	0	184	11	0	…	AIHA (non-rad)
DOE-3	2522	<1	7746	24	6	0	AIHA (both)
DOE-4	2200	…	13000	14	3	1	AIHA (non-rad)
DOE-5	243	43	329	…	Yes	…	AIHA (non-rad)
DOE-6	269	25	20500	1	0	…	AIHA (non-rad)
DOE-7	50	0	500	0	3	1	AIHA
DOE-8	50	13	600	7	0	0	AIHA (non-rad); equivalent (rad)
DOE-9	6175	13	33250	18	0	0	AIHA (both)
NIOSH-1	…	0	…	0	0	0	AIHA
OSHA-1	...	…	4280[c]	0	3	1	AIHA
UK-1	12000	33	17000	43	3	0	HSE

[a] Sites are identified as to whether they are Canadian (Can), U.S. National Institute for Occupational Safety and Health (NIOSH), Department of Defense (DOD), U.S. Department of Energy (DOE), U.S. Occupational Health & Safety Administration (OSHA), or U.K.

[b] Sites with radiologically-contaminated samples typically analyze them in a different location from the non-rad samples. If "non-rad" is denoted, only that lab is accredited; "both" means that both rad and non-rad labs are accredited.

[c] Only a combined value for air and wipe samples was provided.

The use of wet or dry collection methods has been a major source of discussion among DOE sites performing beryllium analyses. It is noted in Table 2 that, of the 16 respondents, ten use only wetted wipes (water, alcohol, or other organic agent); two use only dry wipes; and four use both types depending on the specific application. Use of dry wipes is typically based on historic practices, which at DOE sites are often based on wipes used for radioactive surface contamination (which are dry). Dry wipes are also required in some cases to avoid damage to the surface being wiped. Advocates of wet wipes typically cite better collection efficiencies; however, as can be seen by Table 2, few collection efficiency studies have been performed.

Collection methods also vary widely, and include NIOSH method 9100 [12], ASTM D 6966, ASTM Standard Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequent Lead Determination (E 1728), guidelines published in 1995 from the U.S. Department of Housing and Urban Development (HUD) [13], OSHA [14], and unpublished in-house methods. As noted in Table 2, a combination of methods and/or modifications to published methods are used at some sites. Even when the same collection method is used, human variability can have an impact on variability of results. The variety of collection methods further increases variability. It is pointed out that a number of these methods were developed for lead sampling and are now being applied to beryllium sampling. In most cases, data have not been collected to demonstrate that these surface sampling methods provide performance for beryllium that is comparable to the performance measured for lead. It should be noted that, subsequent to the questionnaire responses, NIOSH has published Method 9102 [15], which updates NIOSH Method 9100 to include beryllium and other elements.

TABLE 2 – *Surface wipe characteristics by site.*

Site	Media Type	Dry or Wet & Wetting Agent	Collection Efficiency Study?	Collection Method	Reference Materials Used
Can-1	Ghost Wipe®	Water	No	NIOSH 9100/ ASTM D 6966	Spex® standard solutions
DOD-1	Ghost Wipe®	Wet (agent not named)	N/A	…	…
DOD-2	Ghost Wipe®	Alcohol	No	HUD (1995)/ OSHA 125G	AIHA Proficiency Samples
DOD-3	Ghost Wipe®	Alcohol	No	HUD (1995)/ OSHA 125G	AIHA Proficiency Samples
DOE-1	Ghost Wipe®	Organic	No	ASTM D 6966	None routinely
DOE-2	6x6 Gauze	Methanol	No	EPA 6010	None routinely
DOE-3	Whatman® 541 or 41, or linen cloth	Both dry and wet (water)	In progress	NIOSH 9100 (modified)	BeO performance samples
DOE-4	Whatman® 50 smear tab	Dry	No	In-House	…
DOE-5	Smear tab	Water	…	ASTM E 1728	…
DOE-6	Whatman® 41 filter	Both dry and wet (water)	No	NIOSH 9100 (modified)	N/A
DOE-7	Ghost Wipe®, Whatman® 41, or smear tab	Both dry and wet (water)	No	NIOSH 9100	None
DOE-8	Ghost Wipe®	Water	No	…	High Purity Filters
DOE-9	Whatman® 41, Ghost Wipe®	Both dry and wet (water)	Yes	…	AIHA PAT
NIOSH-1	Ghost Wipe®	Water	…	NIOSH 9100	Analytical standards, spiked wipes/filters, BeO suspensions
OSHA-1	Smear Tabs, Whatman® 41 and 42, Ghost Wipe®	Water	Yes	OSHA 125G	None
UK-1	Whatman® 41	Dry	Yes	In-House	…

Similarly, a variety of responses were given to the question, “Which reference sample materials are employed?”, as shown in the last column of Table 2. Respondents were asked what reference materials are lacking and need to be produced. Most sites indicated a need for proficiency test samples containing BeO; however, the lack of a BeO reference material makes it impossible to develop such samples at present.

It should be noted that even when variables such as media type and collection method are eliminated, typical sampling uncertainty is greater than analytical uncertainty. The large variety of media types and collection methods, the lack of collection efficiency data, and differences in reference materials, all make it difficult to compare sampling results. These issues present opportunities for standardization that are discussed in a companion paper [16].

Sample Preparation Protocols

Analytical techniques that meet the requirements of the DOE Beryllium Rule [4], or similar requirements such as the Threshold Limit Value (TLV) published by the American Conference of Governmental Industrial Hygienists (ACGIH) [17], require that the sample be dissolved prior to analysis. To date, no direct-solid measurement technique has been validated to meet these requirements [18]. Therefore, sample preparation is necessary prior to analysis for beryllium.

Table 3 displays information on sample preparation used at the responding sites for air filter samples. Table 4 displays similar information for surface wipe samples. Differences between the two tables are highlighted in Table 4.

As noted in both tables, energy systems include hotplate, hot block, and microwave (open or closed vessel). Some sites use more than one system for air filter samples. Three sites use a different system for surface wipe samples from that used for air filter samples.

Reagent protocols vary widely, and half the respondents use a different protocol for surface wipe samples from that used for air filter samples. Typically, where this is the case, the surface wipe protocol features a more robust acid combination than that used for air filters, since the latter are typically easier to digest. In addition, a range of heating energy systems and dissolution times occurs across the respondents.

Additional variation exists in how much of each acid is used in each site’s sample preparation. This information was captured in the questionnaire responses but, for simplicity, is not reported in Tables 3 and 4.

Final sample volumes also vary widely; four of the respondents use greater sample volumes for surface wipe samples than for air filter samples. This again is a function of the greater difficulty in digesting wipe media. A review of Table 4 indicates that when considering energy system, reagents, and final sample volume, each of the responses is unique. This is close to being true for Table 3 as well (note that Can-1 and CDC-1 are the same for these three parameters, but these two sites vary in their acid concentrations). Although there may not necessarily be a “one-size-fits-all” sample preparation approach that would meet everyone’s needs, this still appears to present a fertile opportunity to improve consistency.

Storage time is simply an indication of the length of time, both typically and in the maximum case, between sample preparation and analysis, based on each lab’s actual experience. There are no official “hold times” such as is typically found for environmental samples, and to our knowledge there has not been any detailed study to support any particular duration. The experience of the respondents suggests that prepared samples can be held up to 30 days before being analyzed, but that two weeks or less is more typical.

TABLE 3 – *Sample preparation techniques for air filter samples, by site.*

Site ID[a]	Energy System	Reagents	Final Sample Volume (mL)	Storage time (typical/maximum)
Can-1	Hotplate	HNO_3, $HClO_4$	10	2-3 days/ …
DOD-1	Hot block	HNO_3, H_2O_2	50	1-2 weeks/ …
DOD-2	Open vessel (OV) microwave	HNO_3, H_2O_2, HCl	25	4 hours/1 week
DOD-3	Hot block or OV microwave	HNO_3, H_2O_2	15-25	4-16 hours/3 days
DOE-1	Hotplate	HNO_3, HCl	10	1-7 days/2 weeks
DOE-2	Closed vessel (CV) microwave	HNO_3	…	<1 day/ …
DOE-3	Hotplate	H_2SO_4, HNO_3, H_2O_2, HCl	10	<1 day/2 weeks
DOE-4	OV microwave	H_2SO_4	25	1-2 days/ …
DOE-6	Hot block	H_2SO_4, HNO_3, H_2O_2, HCl, HF, $HClO_4$	25	1 hour/<1 day
DOE-7	CV microwave	HNO_3	25	24 hours/30 days
DOE-8	Hot block	HNO_3, H_2O_2, HCl, HF	25	24 hours/> 2 weeks
DOE-9	OV microwave	H_2SO_4, HNO_3	10	<1 day/14 days
NIOSH-1	Hotplate	HNO_3, $HClO_4$	10	1 day/ …
OSHA-1	Hotplate	H_2SO_4, HNO_3, H_2O_2, HCl	50	1 day/15 days
UK-1	Hotplate	HNO_3, $HClO_4$	5	<1 week/<2 weeks

[a] Site DOE-5 did not respond to this portion of the questionnaire.

TABLE 4 – *Sample preparation techniques for surface wipe samples, by site.*

Site ID[a]	Energy System	Reagents	Final Sample Volume (mL)	Storage time (typical/maximum)
Can-1	Hotplate	HNO_3, H_2O_2[b]	10	2-3 days/ …
DOD-1	OV microwave[b]	HNO_3[b]	100[b]	1-2 weeks/ …
DOD-2	OV microwave	HNO_3, H_2O_2[b]	100[b]	1 week[b] /1 week
DOD-3	Hot block	HNO_3, H_2O_2	50[b]	1-2 days[b]/1 week[b]
DOE-1	Hotplate	HNO_3, HCl	10	1-14 days[b] /28 days[b]
DOE-2	Hot block[b]	HNO_3, HCl[b]	100	<1 day/ …
DOE-3	Hotplate	H_2SO_4, HNO_3, H_2O_2, HCl	10	<1 day/2 weeks
DOE-4	OV microwave	H_2SO_4, H_2O_2[b]	25	1-2 days/ …
DOE-6	Hot block	HNO_3, H_2SO_4, $HClO_4$[b]	50[b]	1 hour/<1 day
DOE-7	OV microwave[b]	HNO_3, H_2O_2[b]	50[b]	24 hours/30 days
DOE-8	Hot block	HNO_3, H_2O_2, HCl, HF	25	<24 hours/48 hours
DOE-9	OV microwave	H_2SO_4, HNO_3, H_2O_2[b]	10	<3 days[b] /10 days[b]
NIOSH-1	Hotplate	HNO_3, $HClO_4$	10	1 day/ …
OSHA-1	Hotplate	H_2SO_4, HNO_3, H_2O_2, HCl	50	1 day/ …
UK-1	Hotplate	HNO_3, $HClO_4$	5	<1 week/ …

[a] Site DOE-5 did not respond to this portion of the questionnaire.
[b] Response differs from that given in Table 3.

Analysis Protocols

Table 5 displays information on analysis methods used at the responding sites for air filter samples. Table 6 displays similar information for surface wipe samples. Tables 5 and 6 will be discussed together.

TABLE 5 – *Analytical methods for air filter samples, by site.*

Site ID[a]	Instrument	Method	Detection Limit	Reporting Limit	Line(s) Used (nm)	Internal Standard	Known Interferences
Can-1	ICP-MS	In-House	0.0005 µg/sample	0.0005 µg/sample	N/A	Lithium, Scandium	…
DOD-1	ICP-MS	NIOSH 7300 (mod.)	0.0085 µg/filter	0.25 µg/filter	N/A	Lithium	…
DOD-2	ICP-AES	NIOSH 7300	0.05 µg/sample	…	313.107	…	…
DOD-3	ICP-AES	NIOSH 7300	0.01 µg/sample	0.02 µg/sample	…	None	None
DOE-1	ICP-MS	EPA 200.8 (mod.)	0.0007 µg/filter	0.005 µg/filter	N/A	Scandium	None
DOE-2	ICP-AES	NIOSH 7300	…	0.02 µg/filter	…	…	V
DOE-3	ICP-AES	OSHA ID-125G (mod.)	0.003 µg/filter	0.03 µg/filter	313.107	Yttrium	Al, Cu, Fe, V
DOE-4	ICP-AES	In-House	0.02 µg	…	3	Yttrium	…
DOE-6	ICP-AES	NIOSH 7300 (mod.)	0.12 ppb	0.01 µg/filter	234.861	None	Fe
DOE-7	ICP-AES/ ICP-MS	NIOSH 7300/ EPA 6020	0.003 µg/sample (AES); 0.00063 µg/sample (MS)	…	313.042 (AES)	Scandium or Lithium (MS only)	V (AES only)
DOE-8	ICP-AES	NIOSH 7300 mod/ EPA 6010B	0.005 µg/sample	0.05 µg/sample	313.107	…	Fe, Ti
DOE-9	ICP-AES	In-House	0.144 µg/L	1.0 µg/L	313.042 313.107	Scandium	…
NIOSH-1	ICP-AES	NIOSH 7300	0.6 ppb	…	313	None	…
OSHA-1	ICP-AES	OSHA ID-125G	0.017 µg	0.02 µg/mL	313.107	…	Fe, Mn, Mo, Nb, Ni, Ti, V
UK-1	GFAAS	…	2.5 ng/sample	…	234.9	None	…

[a] Site DOE-5 did not respond to this portion of the questionnaire.

TABLE 6 – *Analytical methods for surface wipe samples, by site.*

Site ID[a]	Instrument	Method	Detection Limit	Reporting Criteria	Line(s) Used (nm)	Internal Standard	Interferences Tested
Can-1	…	…	0.005 μg/sample	…	…	Lithium, scandium	…
DOD-1	ICP-MS	EPA 6020	0.19 μg/wipe	CFR	N/A	Lithium	…
DOD-2	ICP-AES	NIOSH 7300	0.1 μg	LOD	313.107	…	None routinely
DOD-3	ICP-AES	NIOSH 7300	0.1 μg	LOD	…	…	None routinely
DOE-1	ICP-AES	NIOSH 7300	0.02 μg/wipe	LOQ	313.042, 234.861	None	Elements not specified
DOE-2	ICP-AES	EPA 6010B	0.1 μg (RL)	LOQ	313.042	None	Al, Fe, Mn, Ca, Mg, Cd, Cu, Cr, Pb, Ti
DOE-3	ICP-AES	NIOSH 7300	0.01 μg/sample	… (0.02 μg/sample)	313.107	Yttrium	Al, Cu, Fe, V
DOE-4	ICP-AES	In-House	0.02 μg	…	…	Scandium	None
DOE-6	ICP-AES	NIOSH 7300 (Mod.)	0.12 ppb	LOQ (0.03 μg/wipe)	234.861	None	Fe, Mg, Ca
DOE-7	ICP-AES/ ICP-MS	NIOSH 7300/EPA 6020	0.0061 μg/sample (AES); 0.0013 μg/sample (MS)	LOQ	313.042 (AES)	Scandium or Lithium (MS only)	V (AES only)
DOE-8	ICP-AES	NIOSH 7300 mod/ EPA 6010B	0.005 μg/sample	PQL (0.05 μg/sample)	313.107	…	Al, As, B, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, Sr, Tl, V, Zn
DOE-9	ICP-AES	In-House	0.144 μg/L	…	313.042 313.107	Scandium	Cr, Fe, Mo, Th, Ti, U, V, Y, Zr
NIOSH-1	ICP-AES	NIOSH 7300	0.6 ppb	LOQ, LOD	313	None	None
OSHA-1	ICP-AES	OSHA ID-125G	0.017 μg	…	313.107 234.861	…	Al, Ce, Cr, Co, Cu, Fe, Mn, Mo, Nb, Ni, Pt, Sb, V, Ti
UK-1	GFAAS	…	0.2 μg/sample	…	234.9	None	…

[a] Site DOE-5 did not respond to this portion of the questionnaire.

[b] Response differs from that given in Table 3.

Both Table 5 and Table 6 indicate that ICP-AES is used by 11 of the 15 responding sites, either exclusively or as the primary instrument. One respondent uses GFAAS, while the remainder use ICP-MS (three as primary, one as backup).

Tables 5 and 6 indicate that a wide variety of methods are in use. While NIOSH method 7300 [6] is widely used (eight respondents), it is modified in some way by four respondents. Other methods used include EPA methods 200.8 [9], 6010B [19], and 6020 [20]; OSHA method ID-125G [14], and in-house methods. It should be noted that all of the standard methods listed are for various suites of elements, not specifically for beryllium, and may not necessarily be optimized for beryllium at trace levels. It is notable that NIOSH Method 7102 [21], which is specific for trace-level beryllium, is not cited. This is probably due to the fact that NIOSH Method 7102 is a GFAAS method, and GFAAS is not used by any of the U.S. respondents.

The questionnaire asked for detection limits for both air filters and surface wipes, and how the detection limits were determined. The responses varied widely both in terms of numerical values and units of measure. Although some of the variation can be attributed to differences in sample preparation (see Tables 3 and 4), sample matrices, and analytical instrumentation, there are also differences in how detection limits are calculated. Various organizations (e.g., NIOSH, EPA, ASTM, ISO, American Chemical Society) have promulgated different methodologies for computing detection limits; a variety of these are used by the respondents. Also, the questionnaire did not distinguish between instrument detection limit (IDL) and method detection limit (MDL), so the values provided are likely a mix of both types.

For air filter samples, the questionnaire also requested reporting limits (RL), which are shown in Table 5. Again, because of differences in how RL's are calculated by each lab, the values vary widely. Terminology is also an issue, since the organizations cited above use different terms. This is further illustrated in Table 6. For surface wipe samples, the questionnaire asked for reporting criteria rather than RL's. A variety of terms are used, including Limit of Quantitation (LOQ), Limit of Detection (LOD), and Practical Quantitation Limit (PQL), definitions of which can be found in a recent EPA comparison of detection and quantitation approaches [22][4].

A significant issue with ICP-AES is spectral interferences. Most spectral lines have one or more spectral interferences that, if present in the sample, may affect the results. Proper correction for such interferences is important. For air filters, we asked for information on known interferences, which is presented in Table 5. In air samples, the list of known interferences appears to be relatively short. For surface wipe samples, we asked for information on the interferences that are tested. Based on the results (shown in Table 6), interference testing is a greater concern for surface wipe samples than for air filters.

Tables 5 and 6 also list the spectral line(s) used by each respondent for ICP-AES or GFAAS, and whether internal standards are applied.

Path Forward

The opportunity for standardization of sampling, sample preparation, and analysis techniques is clearly apparent. This topic is further discussed in a companion paper [16]. The BHSC Analytical Subcommittee is currently working through the ASTM Subcommittee on Workplace Atmospheres (D22.04) to develop some of these standards (www.astm.org). The BHSC

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[4] The authors do not necessarily endorse the conclusions reached in this comparison.

Analytical Subcommittee is also working toward greater consistency in how detection and reporting limits are computed. The Subcommittee and its members function as an ad hoc group and do not perform any advisory functions for DOE or other government agencies.

DOE is currently drafting a Technical Standard that is intended to recommend selected sampling and analytical methods to DOE laboratories as a means of improving consistency within the DOE complex. The DOE Technical Standards Program promotes the use of voluntary consensus standards at DOE [23].

A number of potential research opportunities are also being pursued. Among these are development of a BeO reference material (which should lead to improved proficiency test samples), improved sample preparation techniques, and studies on existing sampling techniques including collection efficiencies. Efforts are also being made toward field-deployable beryllium analyzers [18].

The above efforts will hopefully improve sampling and analytical methodologies, and allow for better comparisons of data among laboratories performing beryllium analyses for worker protection purposes.

Acknowledgements

The authors gratefully acknowledge members of the BHSC analytical subcommittee, and the laboratory directors at the various sites, who provided the questionnaire responses. We also appreciate the valuable assistance of John R. Longo, Savannah River Site, who compiled the responses into a useful electronic format.

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