Analytical
Methods

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Cite this: *Anal. Methods*, 2011, **3**, 1906

www.rsc.org/methods

TECHNICAL NOTE

Trace beryllium determination in polyvinyl alcohol wipes by extraction and fluorescence detection: interlaboratory analysis†

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Received 1st March 2011, Accepted 7th June 2011
DOI: 10.1039/c1ay05115f

In the occupational hygiene field, polyvinyl alcohol (PVA)-based wipe materials are used extensively for beryllium (Be) sample collection and analysis. Hence there is a need for validated methods to determine trace Be in such sampling media. In this work an interlaboratory study was carried out to evaluate the performance of an extraction and fluorescence method for determining trace Be in PVA wipes containing refractory beryllium oxide (BeO). The method entails heated extraction with dilute ammonium bifluoride (NH_4HF_2), followed by fluorescence measurement of extracted Be in extract aliquots after reaction with the high quantum-yield fluorophore, hydroxybenzoquinoline sulfonate (HBQS). Certified BeO-spiked PVA wipe materials were prepared at six different levels ranging from 0.030 to 5.6 μg Be per wipe. Dry wipe materials and wipes wetted with 0.5 mL of deionized water were spiked as above. Duplicates of these materials, plus media blanks, were distributed to eight participating laboratories; spiking levels were unknown to the volunteers. Each participant was requested to carry out extraction and fluorescence measurement in accordance with an ASTM International standard test method, ASTM D7202, and to report their results in units of μg Be per wipe sample. Interlaboratory precision, as estimated by percent relative standard deviations (RSDs), ranged between 4.5% and 16%. Estimated percent Be recoveries were 90–99% for dry wipes and between 87 and 93% for wetted wipe materials after volume correction for water content.

Introduction

Owing to its light weight, high strength and unique electronic and alloying properties, beryllium (Be) is a materials constituent for myriad applications including in aerospace, nuclear energy, defense, automobiles, microcircuitry, and machinery. The ability to measure Be at trace levels on surfaces in workplaces is necessary in view of occupational exposure limits (OELs) as low as 0.2 μg Be per 100 cm^2 surface area that have been established for this element.[1] It has been found that workers can become sensitized to Be through dermal contact with beryllium-containing dust.[2] This exposure pathway, if followed by subsequent exposure to airborne Be *via* inhalation, has been hypothesized to lead to chronic beryllium disease (CBD).[3] To aid in preventing dermal exposures by monitoring of surface Be contamination, sensitive and accurate methods are needed for collection and analysis of this highly toxic element in occupational settings.[4,5]

A standard wipe sampling method for metals (such as Be) on surfaces has been promulgated in an effort to minimize inconsistencies in surface sampling practices.[6] Subsequent determination of trace Be in cellulosic wipe materials by ammonium bifluoride (NH_4HF_2) extraction and fluorescence detection using the high quantum-yield fluorophore, hydroxybenzoquinoline sulfonate (HBQS), has been evaluated and validated.[7] This extraction and fluorescence method for determining Be in occupational hygiene samples has been standardized.[8,9] The methodology enables attainment of detection limits of less than 1 ng Be per sample, and compares favorably with the performance of the highly sensitive atomic spectrometric technique, inductively coupled plasma mass spectrometry (ICP-MS).[10,11] Besides cellulosic wipe sampling media, wipes comprised of polyvinyl alcohol (PVA) have been used extensively for surface dust sampling and subsequent determination of Be by atomic spectrometric methods.[12] However, the use of PVA wipes for surface sampling, in concert with NH_4HF_2 extraction and HBQS fluorescence detection of Be, has not been fully evaluated. Because the use of PVA wipes for sampling of Be in surface dust is

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widespread, there is a need for Be performance data on the NH_4HF_2 extraction and HBQS fluorescence detection method after collection onto PVA media.

Beryllium oxide (BeO) that is prepared at temperatures in excess of 1,200 °C (often referred to as "high-fired" BeO) is employed widely in a variety of materials. High-fired BeO is used extensively in electronics, materials engineering and nuclear technology, thus workers involved in the fabrication of microcircuits, nuclear reactors, and other materials may potentially be exposed to this compound. For analysis purposes, high-fired BeO is difficult to decompose: the complete dissolution of Be in this matrix requires the use of specialized procedures.[13,14] Dilute aqueous (1–3% v/v) NH_4HF_2 heated at 80–90 °C has been shown to quantitatively dissolve high-fired BeO[15] and Be-containing silicate matrices[16] in occupational hygiene and environmental samples. This extraction medium for refractory Be materials thereby offers a safe and less expensive alternative to digestions requiring strong acid mixtures containing hydrofluoric or sulfuric acids heated at high temperatures.[13]

It is noted that commercial PVA wipes are available in larger sizes than those studied here, so as to be able to be applied to large sampling areas (up to ≈1,000 cm^2). For Be surface dust collection the normal sampling area is 100 cm^2, obviating the need for large (15 cm × 15 cm) wipes. With less sampling material to dissolve, lesser amounts of extraction solution are required and smaller extraction tubes can be used. A significant attribute of using smaller wipes for sample collection is the generation of less waste during the sample preparation and analysis process, without loss of analytical sensitivity.

The goal of this work was to carry out an interlaboratory study (ILS) of the NH_4HF_2 extraction/HBQS fluorescence detection method on BeO-spiked PVA wipe materials. Here we report ILS results from eight participating laboratories on certified BeO-spiked PVA wipes fortified with Be at trace levels of occupational hygiene interest. The results presented supplement performance data reported previously for Be measurement in alternative sampling media.

Experimental

The PVA materials evaluated consisted of 5 cm × 5 cm Ghost Wipes (Environmental Express, Mt. Pleasant SC, USA), both dry and wetted with 0.5 (±0.01) mL of deionized water. BeO-spiked materials were prepared and certified by High-Purity Standards (Charleston, SC, USA). The Be spike levels were selected to bracket pertinent OELs for this element (0.2 and 3 μg Be per 100 cm^2 sampling area).[1] High-fired BeO used for spiking was National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1877, Beryllium Oxide Powder (Gaithersburg, MD, USA). BeO spikes onto PVA media were prepared by using a slurry technique[17] wherein an aqueous BeO suspension was prepared, and sonication was used to maintain a uniform suspension from which aliquots of solution were pipetted. Be concentrations and their uncertainties were certified after microwave digestion in HNO_3/HF and confirmatory analysis by ICP-MS.[18] Media blanks consisted of unspiked PVA wipes, either dry or wetted. After spiking, each wipe was placed into a labeled 15-mL plastic centrifuge tube (Becton Dickinson, Franklin Lakes, NJ, USA) and securely capped. The tubes were then packaged for subsequent shipping in individually sealed and labeled plastic bags.

Volunteer laboratories possessing fluorescence instrumentation and having experience in the measurement of Be in occupational hygiene samples were solicited to participate in the ILS. The as-received spiked wipes (housed within packaged centrifuge tubes) were mailed in duplicate to the participants; Be spike levels were unknown to the volunteers. The participating laboratories were requested to carry out sample preparation and analysis in accordance with ASTM D7202.[8] The laboratories were asked to carry out heating in 1% (aqueous) NH_4HF_2 at 85–90 °C for one hour, with subsequent HBQS fluorescence determination of Be in aliquots of sample extracts. For the ILS, solutions of NH_4HF_2 and HBQS were provided by Berylliant, Inc. (Tucson, AZ, USA). Participants were requested to report their results in units of μg Be per wipe sample. Precision and recovery data from the ILS were computed from eight participants who reported results. For purposes of data presentation, laboratories were identified by code in order to maintain confidentiality.

Results and discussion

Summary interlaboratory precision statistics, based on the results reported by the eight laboratories that participated in the ILS, are presented in Tables 1 and 2 for dry and wetted wipe media, respectively. Overall mean values were computed based on the pooled means for the average of the duplicate results reported for each Be spiking level (*i.e.*, for each pair of wetted or dry wipe spikes). It is noted that in only a few cases, low-level Be analysis results were not reported for media blanks or for the lowest-level spikes of wetted wipes. As measures of precision, calculated interlaboratory relative standard deviations (RSDs) ranged from just over 4.5% to slightly below 16%, with no significant differences in precision between dry *vs.* wet wipe materials (Tables 1 and 2). The highest RSDs were observed for the lowest Be spike levels, reflecting the higher uncertainty in the preparation of low-level Be-spiked media. These precision estimates are acceptable in consideration of an overall goal of interlaboratory RSDs less than 20%.[10,11,19] They also compare favorably with interlaboratory RSDs obtained from the Beryllium Proficiency Analytical Testing Program (BePAT) of the American Industrial Hygiene Association (AIHA), which are typically in the realm of 10–20%.[20]

Estimated Be recoveries were between 90% and 100% for dry PVA wipes (Table 1) and spanned from ≈87% to ≈93% for wetted wipes after mathematically correcting for their

Table 1 ILS summary data from dry BeO-spiked PVA wipes; number of laboratories n = 8 unless otherwise indicated

Certified spike level (μg Be)	Mean ± standard deviation (μg Be)	RSD (%)	Mean Recovery (%)
<0.01 (media blank)	0.0025 ± 0.0030 (n = 4)	120	—
0.030 ± 0.005	0.0291 ± 0.00461	15.8	97.0
0.16 ± 0.02	0.144 ± 0.0164	11.4	90.0
0.32 ± 0.02	0.295 ± 0.0169	5.73	92.2
1.8 ± 0.1	1.71 ± 0.0779	4.56	95.0
2.8 ± 0.1	2.76 ± 0.283	10.3	98.6
5.6 ± 0.1	5.29 ± 0.538	10.2	94.5

Table 2 ILS summary data from wetted BeO-spiked PVA wipes; number of laboratories n = 8 unless otherwise indicated

Certified spike level (μg Be)	Reported mean ± std. dev. (μg Be)	Corrected[a] mean ± std. dev. (μg Be)	RSD (%)	Mean Recovery (%)
<0.01 (media blank)	0.0085 ± 0.0123 (n = 6)	0.0090 ± 0.0135	150	—
0.030 ± 0.005	0.0247 ± 0.00353 (n = 7)	0.0270 ± 0.0039	14.4	90.0
0.16 ± 0.02	0.126 ± 0.0105	0.139 ± 0.0116	8.35	86.9
0.32 ± 0.02	0.261 ± 0.0121	0.287 ± 0.0133	4.63	89.7
1.8 ± 0.1	1.49 ± 0.120	1.64 ± 0.132	8.05	91.1
2.8 ± 0.1	2.37 ± 0.335	2.61 ± 0.369	14.1	93.2
5.6 ± 0.1	4.46 ± 0.215	4.91 ± 0.237	4.82	87.7

[a] Computed after correction for 0.50 mL water content.

background water content of 0.50 ± 0.01 mL‡ (Table 2). In comparing Be recoveries from dry *vs.* wet PVA wipes, t-tests of the variances ($p = 0.05$) yielded no statistically significant differences between the overall mean values computed at each spiking level. Also, the presence of background moisture in the wetted wipes did not significantly affect precision (as estimated by RSDs; compare Tables 1 and 2). No significant background Be was reported in media blanks, either for wetted or non-wetted PVA wipes. Overall Be recoveries from all BeO-spiked PVA wipes, whether wetted or dry, ranged from 87% to 99%. Ideally, quantitative recoveries are given by values of 100% ± 10%.[11] However, Be recoveries from challenging matrices such as refractory materials like high-fired BeO are normally expected to be less precise, *e.g.*, 100% ± 15%.[21]

A noteworthy observation of the present study is that acceptable Be recoveries were obtained from BeO-spiked PVA wipes. Preliminary data published previously[15] reported low Be recoveries (<50%) from this matrix (Ghost Wipes) when using the NH_4HF_2 extraction/HBQS fluorescence detection method. However, that work[15] and subsequent research[7,14] reported quantitative recoveries from various cellulosic wipe media that were tested. Those observations led subsequently to an emphasis on the use of cellulosic wipe materials in conjunction with this analytical methodology. It may be that the larger size of the PVA wipes examined in the previous reports contributed to lower reported Be recoveries in those sampling media; lack of deliberate heating may also have been a factor. Nevertheless, given the extensive use of PVA wipes for Be sampling from surfaces,[22] it was considered important to revisit the use of NH_4HF_2 extraction/HBQS fluorescence detection for this matrix.

The information obtained from this investigation can be used to update existing standardized methods for measuring trace Be in surface dust. Also, the ILS performance data generated here will be useful for establishing necessary material specifications for standardized Be wipe sampling media. The content of current and future international voluntary consensus standards will be impacted by these research results.

Conclusion

Beryllium performance data from this interlaboratory study demonstrate that the use of the NH_4HF_2 extraction and HBQS fluorescence detection gives acceptable interlaboratory precision and recoveries from samples of polyvinyl alcohol wipe media containing high-fired beryllium oxide. The results are important in view of the widespread use of this wipe material for Be surface dust sampling,[23] and in consideration of the low exposure limits that have been established for this highly toxic element. The information from this investigation will prove to be valuable in future revisions of standardized Be sampling and analytical methodologies and sampling material specifications.

Disclaimers

Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention. The findings and conclusions in this article are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

Acknowledgements

Sincere gratitude is extended to Brandy Duran (Los Alamos National Laboratory, NM, USA), Davy Rousset (Institut National de Recherche et de Sécurité, France), Rohit Shah (Lawrence Livermore National Laboratory, CA, USA), Tom Yoshida (Los Alamos National Laboratory, NM, USA) and Linda Youmans-McDonald (Savannah River Nuclear Solutions, SC, USA) for their participation in the interlaboratory study. Mike Goldcamp, Bob Streicher and Kenn White kindly reviewed the draft manuscript. Partial funding support for the interlaboratory study was provided by ASTM International.

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