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ORIGINAL PAPER

Size-selective poorly soluble particulate reference materials for evaluation of quantitative analytical methods

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Abstract Owing to the absence of readily available certified particulate reference materials (RMs), most analytical methods used to determine particulate contaminant levels in workplace or other environments are validated using solution RMs, which do not assess the robustness of the digestion step for all forms and sizes of particles in a sample. A library of particulate RMs having a range of chemical forms and particle sizes is needed to support a shift in method evaluation strategies to include both solution and particulate RMs. In support of creating this library, we characterized bulk and physically size separated fractions of beryllium oxide (BeO) particles recovered from the machining fluid sludge of an industrial ceramic products grinding operation. Particles were large agglomerates of compact, crystalline BeO primary particles having diameters on the order of several micrometers. As expected, the particle surface area was independent of sieve size, with a range from 3.61 m^2/g (53–63-μm fraction) to 4.82 m^2/g (355–600-μm fraction). The density was near the theoretical value (3.01 g/cm^3). The data support more detailed characterization of the sludge materials for use as size-selective RMs. This work illustrates an approach that can be used to develop RMs that are difficult to digest.

Keywords Reference materials · Particulate · Digestion · Beryllium · Method validation

Introduction

Analytical methods used to determine contaminant levels in workplace and environmental samples must provide accurate results to yield meaningful data for risk assessments. Owing to the absence of readily available certified particulate reference materials (RMs), most analytical methods are validated using solution RMs, which potentially do not assess the robustness of the digestion step for many chemical forms and sizes of particulate analyte in a sample. Because workplace exposure to metals often occurs to material in particulate form rather than in solution, the inability to appropriately validate analytical methods owing to the lack of particulate RMs has quality assurance and efficacy implications for methods to characterize airborne, surface-deposited, and environmental contaminants, especially for particulates that are difficult to digest.

The size distribution of aerosol particles generated in the workplace may vary widely. For example, machining operations such as sawing and milling can generate particles with physical diameters up to 2,000 μm [1], which could become airborne and/or settle on work surfaces. For aerosol materials, airborne particles are collected independently of the chemical form by drawing air at a known flow rate through a sampler to capture the particles on a filter or other

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substrate. Depending upon the design configuration of the aerosol sampler, captured particles may range from just a few nanometers in size to 100 μm and larger in aerodynamic diameter [2]. Contamination on surfaces is usually assessed by wiping a known surface area in a regular pattern with even pressure using a substrate (e.g., a water-moistened filter), whereas contamination in soils and water is usually assessed using bulk sampling techniques. Generally, wipe and bulk sampling techniques are not discriminatory and potentially collect all particles, regardless of chemical form and size. For samples that contain an analyte in the form of a poorly soluble particulate, sample preparation techniques (digestion/extraction) must be capable of completely digesting all chemical forms and sizes of analyte-containing particles to their dissolved form to yield accurate and precise determinations of elemental mass levels. The absence of well-characterized, scientifically certified, and readily available particulate RMs is particularly critical for analytical methods in which the robustness of the digestion step for all forms and sizes of particles in a sample cannot be assessed by use of soluble RMs alone.

Recently, several widely used methods validated with soluble RMs have been shown to provide significant underestimations (25% or more) of exposure for analytes that are difficult to digest [3]. Under our proposed framework for evaluating the efficacy of sample preparation procedures [4], a procedure is considered to be sufficient for monodisperse single-chemical constituent particles if it completely dissolves all analyte primary particles regardless of the number of primary particles in a cluster or the size of a cluster particle. Similarly, a procedure is sufficient for polydisperse single-chemical constituent particles if it completely dissolves the largest analyte particle in the sample. Thus, a library of particulate RMs that are difficult to digest and have a range of chemical forms and biologically relevant particles sizes is needed to augment current analytical method validation strategies that rely solely on solution RMs [3, 4]. The concept of size-selective RMs for quantitative analytical methods has also been recognized by Bello et al. [5] for determination of particle crystalline silica content. Recent work on development of insoluble particulate RMs for beryllium illustrates the challenges and opportunities at hand. For example, as illustrated in Table 1 for beryllium oxide (BeO, an industrial beryllium form of occupational and environmental relevance), several standard and modified methods have been shown to be deficient in their ability to recover known masses of various particle sizes of this material that were deposited onto sampling media. Recovery data for US Environmental Protection Agency Method 3051, US Occupational Safety and Health Administration (OSHA) Method 125G, and US National Institute for Occupational Safety and Health (NIOSH) Method 7300 were generated as part of methods development work for dissolution studies and field exposure assessments [3]. Recovery data for NIOSH Method 7704 were generated as part of an ongoing project to evaluate the efficacy of this method for use in dissolution studies of large BeO particles. Extensive modification of these methods, including use of more concentrated acids, extended thermal treatment, and increased digestion time, were often necessary to achieve acceptable beryllium recovery levels, i.e., 75% or more [6]. Most importantly, these data illustrate that a method validated with a solution RM and/or known to give near-quantitative recovery of beryllium from monodisperse 200 nm BeO particles may not provide sufficient recovery of beryllium from larger polydisperse BeO particles. Thus, a theoretical basis for quantification of total beryllium mass, such as that proposed by Stefaniak et al. [4], coupled with appropriate size-selective RMs would permit performance-based validation of analytical methods. Such a paradigm shift would alleviate continued reliance on (often inadequately described) empirical modifications to methods that were validated using solution RMs alone.

Watters et al. [7] have described the criteria and steps needed to develop particulate and other RMs for beryllium and Stefaniak et al. [8–10] have described the characteristics of commercially available type UOX BeO material (product type UOX-125, Brush Wellman, Elmore, OH, USA) as being suitable for use as one of those RMs. Development of this type UOX BeO RM is currently under way through a joint US National Institute of Standards and Technology (NIST)–NIOSH–Department of Energy–National Nuclear Security Administration effort. This occupationally and environmentally relevant, particulate material with well-characterized [4, 8–10] 200-nm monodisperse single-chemical-constituent BeO particles is scheduled to become NIST Standard Reference Material (SRM®) 1877. As described in this paper, we have been working to develop a candidate companion beryllium RM of even larger particle sizes; sizes that will be suitable for evaluation of the efficacy of methods for digestion of surface samples and for digestion of inhalable airborne particles (e.g., up to 100 μm and larger aerodynamic diameter). The purpose of this study was to evaluate, as a candidate RM, the physicochemical properties of a polydisperse BeO "grinder sludge" material obtained from the machining fluid sump of an industrial grinding operation for the purpose of developing potential large particle size RMs that are difficult to digest. The results of the physicochemical characterization performed to date on the grinder sludge material support its candidacy for large BeO particle size RMs and warrant more detailed characterization of the material.

Table 1 Recoveries of beryllium from a solution reference material and beryllium oxide (BeO) powders digested and analyzed using standard and modified versions of validated analytical methods

Method[a]	Treatment	Material	Particle size (μm)	Recovery mean (CV) (%)
EPA 3051	Microwave	BeO	0.2	94 (10)
OSHA 125G	Hot plate	BeO	0.2	77 (6)
NIOSH 7300	Hot plate	BeO	0.2	96 (1)
NIOSH 7300	Hot plate	BeO	0.2	95 (1)
NIOSH 7704	Ambient	Be solution	NA	98 (1)
NIOSH 7704	Ambient	BeO	0.2	27 (1)
NIOSH 7704	Hot block	BeO	0.2	90 (1)
NIOSH 7704	Hot block	BeO	2.9	40 (1)

NA not available, *CV* coefficient of variation

[a] Standard analytical methods were modified as follows. EPA 3051: A 4:1 concentrated HNO_3 to concentrated HCl solution, rather than 10 mL concentrated HNO_3, was used to digest the sample; the sample solution was microwave-heated for 30 min, rather than for 10 min. Data from Stefaniak et al. [3]. OSHA 125G: A 2.5:1 50% H_2SO_4 to concentrated HNO_3 solution, rather than a 1:2 ratio of these acids, was used to ash the sample; the sample solution was placed on a hotplate straight away rather than left sitting for 1 h at ambient temperature; 1 mL rather than 4 mL concentrated HCl was used to reheat the sample to near boiling. Data from Stefaniak et al. [3]. NIOSH 7300: 25 mL HNO_3, rather than 4:1 HNO_3 to $HClO_4$ solution, was used to ash; the sample solution was placed on a hotplate straight away, rather than left sitting at ambient temperature for 30 min; 2 mL $HClO_4$, rather than 4:1 HNO_3 to $HClO_4$ solution, was added to the ashing solution; this solution was refluxed for 48 h, then taken to dryness; next 5:1 HNO_3 to $HClO_4$ was added to the solution and refluxed to near dryness twice more, rather than adding 4:1 HNO_3 to $HClO_4$ solution and heating repeatedly until the solution turns clear; finally, solid debris from cotton gloves was removed by filtering the digestate through a 0.45-μm pore size polytetrafluoroethylene filter. Data from Stefaniak et al. [3]. NIOSH 7704: Extraction was performed at 80 °C using a hot block rather than at ambient temperature. Data from previously unpublished quality assurance verifications by the authors

Materials and methods

Collection and size separation of BeO material

BeO particles in residual water-based machining fluid (sludge material) were collected from an industrial grinding machine at a ceramics facility with risk of beryllium sensitization and chronic beryllium lung disease among employees [11]. We chose this grinding operation to collect material for potential development of a large particle size RM because the aerosol particles generated are a known occupational exposure material. Only "high-fired" BeO material (calcined at more than 1,000 °C) is used at this machining facility. The feedstock BeO powder received at this facility was in the form of cluster particles of monodisperse 200-nm primary particles [8, 9] and was subsequently wet-milled, spray-dried, pressed, sintered, and machined to final dimensional specifications. The BeO sludge material was obtained from the sump tank of a machine used only for achieving final dimensional specifications of sintered parts; the machine was most often used as a surface grinder but could also be used for sawing; both applications use diamond-tipped tools. At the time of sample collection, the BeO sludge on the bottom of the tank was approximately 50 mm thick and contained material that had accumulated during the preceding 3 weeks. The bulk sample was collected by scraping the BeO sludge from the bottom of the sump tank using a clean 100 mm × 100 mm glass plate. The plate with sludge was placed in a drying oven (Precision Quincy, Woodstock, IL, USA) at 100 °C for 1 h. The resulting cake (188-g semidry weight) was manually broken into chunks and stored in a glass jar.

To prepare the material for size classification, approximately 80 g of the semidry BeO powder was suspended in 18 MΩ deionized water and subjected to ultrasonic agitation for 6 h. The suspension was allowed to stand overnight to settle particles from suspension and the supernatant was then decanted. This washing procedure was conducted a total of three times to remove residual water-based machining fluid on the powder. After the final washing, the bulk BeO material was dried at 95±5 °C overnight in an oven (model 3510FS, Fisher Scientific, Dubuque, IA, USA), then was physically size separated according to diameter using a sonic sifter with 2,000-, 1,700-, 1,400-, 1,180-, 1,000-, and 600-μm US Standard sieves (Advantech Manufacturing, New Berlin, WI, USA). Material that passed through the 600-μm sieve was retained and sized using progressively smaller US Standard sieves (Advantech Manufacturing): 335, 212, 125, 63, and 53 μm. Material that passed through the 53-μm sieve was retained and further sized using electroformed precision sieves (Advantech Manufacturing) having cutoff sizes of 20, 10, and 5 μm. For the purposes of our study, we characterized bulk material and three physical diameter size fractions of material: 355–600, 53–63, and 10–20 μm. The corresponding approximate aerodynamic diameters for these three sieve fractions were 600–1,000, 90–110, and 20–35 μm, respectively (aerodynamic particle diameter ap-

proximately $D_{phys}\sqrt{\rho}$, where D_{phys} is the physical particle diameter and ρ is the density of BeO). The 355–600-μm size fraction represents large particles capable of nasal deposition [12] and particle sizes that could be encountered on surface wipe or bulk samples. The 53–63-μm physical size fraction represents particle sizes that could be encountered if an "inhalable" type air sampler with 50% aerodynamic cutoff diameters of 100 μm [13] is used to collect airborne BeO particles. The 10–20-μm size fraction is the upper size limit of small particles capable of penetrating into the conducting and alveolar regions of the lung [12].

Characterization of BeO study materials

The physicochemical properties of the study materials were characterized using a suite of analytical techniques [3, 8–10]. Bulk and sieved particles were dispersed on separate 3-mm gold 300-mesh electron microscopy grids with lacey carbon substrate (product no. 01810G-F, Ted Pella, Redding, CA, USA) for analysis using transmission electron microscopy (TEM) (model CM30, Philips Electron Optics, Eindhoven, The Netherlands) to assess particle morphology and size and crystalline composition via electron diffraction. TEM–energy dispersive X-ray spectrometry (EDX; germanium detector, Princeton Gamma-Tech, Princeton, NJ, USA) was used to qualitatively identify elemental constituents ($Z \geq 6$) in samples.

Powder samples were degassed for a minimum of 3 h at 200 °C under a light vacuum (0.013 Torr) (Flovac™ degasser, Quantachrome Instruments, Boynton Beach, FL, USA) to remove physisorbed material such as water from the particle surface. Nitrogen gas adsorption and desorption isotherms were collected in triplicate for each material using a NOVA 2000e surface area analyzer (Quantachrome). The Brunauer, Emmett, and Teller (BET) specific surface area (SSA) was calculated for three to five adsorption points in the relative pressure range from 0.05 to 0.30 using ultrahigh-purity nitrogen (cross-sectional area 16.2 $Å^2$) as the adsorbate [14]. The densities of the bulk- and size-fractionated powders were determined using pycnometery with ultrahigh-purity helium gas (model MVP-D160-E multipycnometer, Quantachrome).

X-ray diffraction (XRD; Siemens model D500 powder diffractometer, Bruker AXS, Madison, WI, USA) with Cu Kα radiation and TEM–electron diffraction were used to qualitatively identify crystalline chemical constituents. XRD samples were mounted as a smear on an off-axis-cut quartz plate and run from 2 to 140° 2θ overnight to ensure adequate counting statistics for beryllium. The identities of constituents were determined by comparing diffraction patterns with reference patterns in the Inorganic Crystal Structure Database [15]. Relative abundances of crystalline phases were obtained from Rietveld [16] and full-pattern [17] fitting methods.

Results and discussion

Figure 1 shows the distribution of BeO machining particle mass as a function of sieve diameter. The distribution was approximately lognormal with a particle mass median diameter (MMD) of 500 μm and geometric standard deviation (GSD) of 2.7. These MMD and GSD values were consistent with those of machining aerosols of beryllium metal, nickel–beryllium alloy, and copper–beryllium alloy observed in previously published work [1]. Thus, the BeO material from the sump provided particles representative of an actual industrial operation, of significance for potential exposure of workers, of potential contamination of the workplace and the environment, and therefore may be suitable for use as a BeO RM.

Figure 2 shows an XRD pattern of the bulk powder that illustrates the material is crystalline BeO with traces of silicon carbide nitride and iron hydroxide, possibly contamination from the grinding wheel or sump tank. The TEM–electron diffraction patterns of the physically size separated powders were consistent with BeO, confirming the XRD results. Elemental analyses of individual particles using TEM-EDX identified Al, C, O, and Si (data not shown), which was consistent with the presence of trace impurities identified using XRD and consistent with the known impurities of commercially produced BeO powders [9]. The crystallinity and high purity of this machining sludge material indicated that the material was representative of the industrial material and chemically suitable for use in developing potential BeO RMs.

Figure 3 presents TEM micrographs of the bulk and physically size separated BeO sludge materials illustrating the underlying primary particle size distribution of the BeO

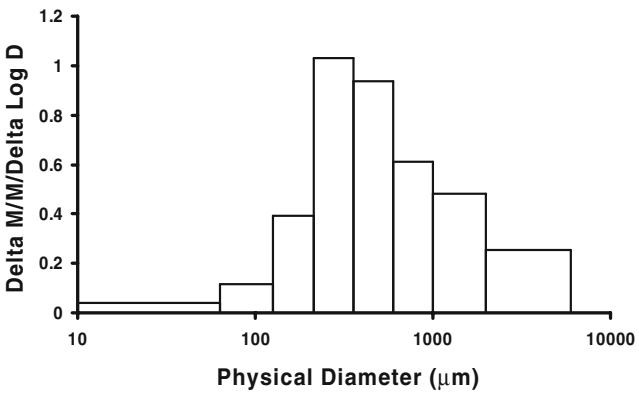

Fig. 1 Size distribution of the physically size separated beryllium oxide (BeO) material, illustrating that material is present in an agglomerated form

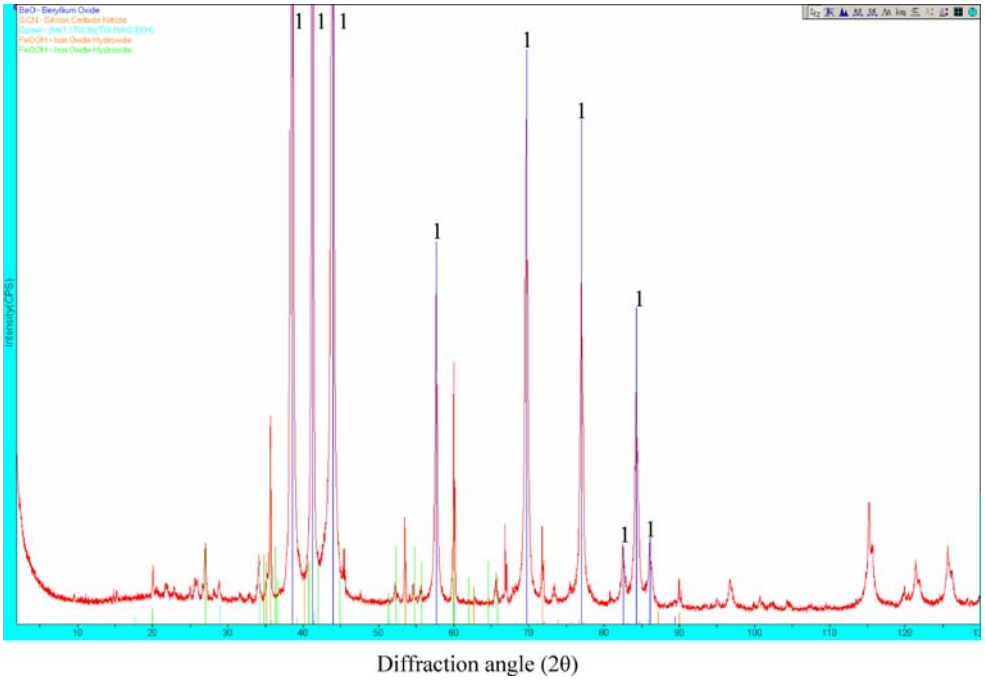

Fig. 2 X-ray diffractogram of bulk BeO powder illustrating that the material is BeO with traces of silica- and iron-containing compounds (most likely from the machine grinding wheel). *1* BeO

material. The centerless grinding operation generated agglomerates of BeO primary particles that had a typical diameter in the range from 0.5 μm to several micrometers (approximately 7 μm), independent of sieved particle size. The primary particle size distribution was approximately lognormal with MMD of 2.9 μm and GSD of 1.6. With regard to providing candidate BeO RMs with a range of particle sizes, the grinder particles have a characteristic diameter that is a factor of 10 larger than commercially available type UOX BeO material that consists of 200-nm monodisperse single-chemical-constituent BeO particles [8]. The centerless grinding particles were block-shaped and compact, which was consistent with growth and densification of the feedstock powder (clusters of monodisperse 200-nm primary particles) during sintering. Thus, this industrial machining material from the centerless grinder appears to meet intermediate particle size RM needs (e.g., 1–5-μm diameter). For even larger particles, this size-separation and material-characterization approach could be used for particles generated by industrial sawing or milling operations, which are known to generate compact discrete particles with physical diameters up to 2,000 μm [1].

Table 2 summarizes the physical characteristics of the bulk and physically size separated materials. (The masses of the 10–20-μm powder size fraction obtained from sieving were insufficient for surface area and density analyses.) The measured densities of the bulk and size-fractionated BeO powders were close to the theoretical density of 3.01 g/cm^3 for BeO, consistent with the high chemical purity of this material. As expected for agglomerates of primary particles, estimates of the size-fractionated BeO powder SSA was independent of agglomerate particle diameter and did not follow the relationship of increasing SSA with decreasing particle sieve size that would apply for smooth, compact (void-free), spherical particles; SSA=6/ρD, where ρ is the particle density and D is the particle diameter. The uniformity of SSA of the size-fractionated BeO powders, independent of particle sieve diameter, was consistent with nearly constant primary particle morphology and size (Fig. 3) among size fractions. Of importance for providing candidate BeO RMs with a range of SSAs, the SSAs of the bulk and size-fractionated BeO powders were at least a factor of 2 lower than those of commercially available type UOX BeO material that consists of 200-nm monodisperse single-chemical-constituent BeO particles [8].

Benefits of size-selective particulate reference materials

For occupationally and environmentally relevant particulate matter samples that contain analytes such as BeO that are difficult to digest, complete digestion of all chemical forms and sizes of analyte-containing particles to their dissolved form during sample preparation is usually necessary to yield accurate and precise determinations of elemental mass levels. The availability of SRM 1877 BeO particles will provide a robust tool for evaluating digestion protocols used for samples containing 200-nm-diameter monodisperse particles, for which the time necessary for complete digestion is hypothesized to be related to the available particle surface area (because there is no variability in particle size distribution) [3, 4]. However, in the workplace, beryllium aerosol size distributions are often polydisperse [1, 9]. While polydisperse size-selective SRMs exist for many applications, such as evaluating and

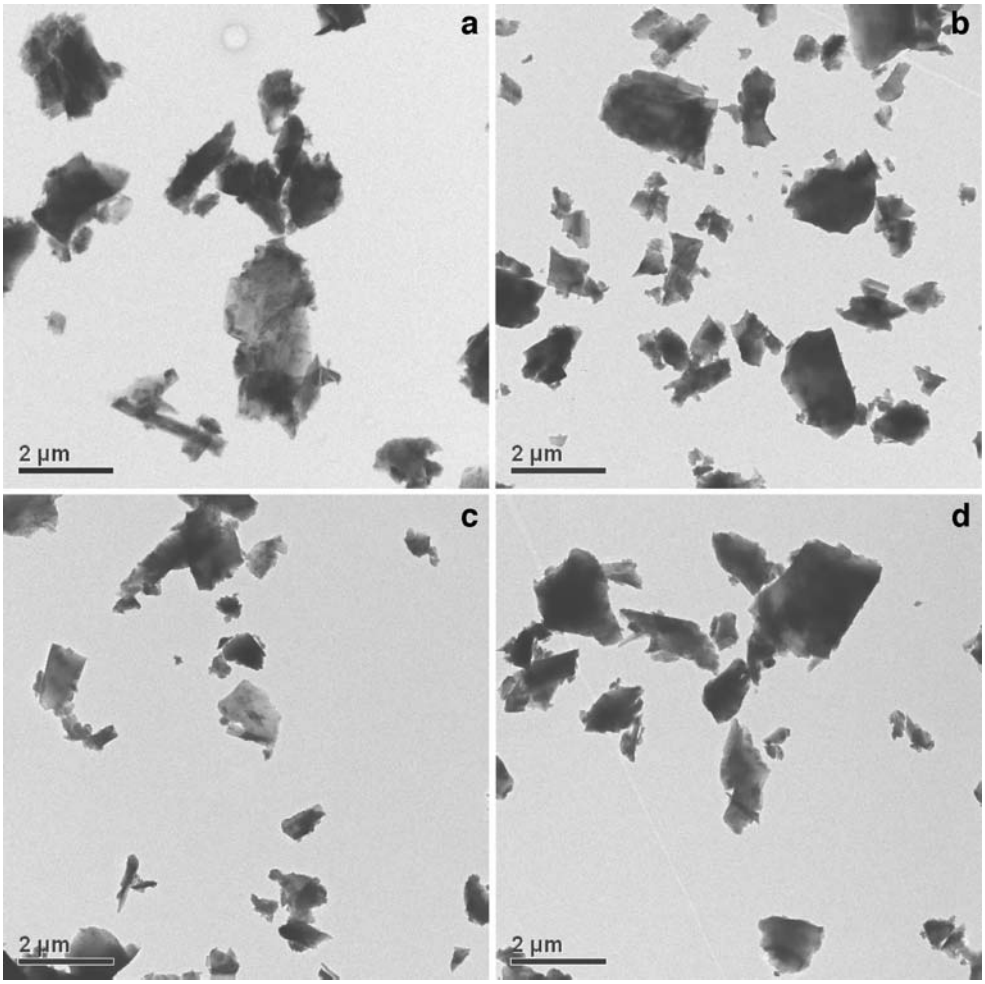

Fig. 3 Transmission electron micrographs of the **a** bulk and **b** 355–600 μm, **c** 53–63 μm, and **d** 10–20 μm physically size separated BeO materials illustrating the underlying primary particle size distribution of the BeO material; primary particles have a typical diameter in the range from 0.5 to 5 μm, independent of sieved particle size

calibrating particle size measuring instruments (see, for example, SRM 1003c, SRM 1004b, SRM 1017b, SRM 1018b, SRM 1019b, and SRM 1021b) and sieving devices (e.g., SRM 8010), the need for size-selective RMs for verifying quantitative analytical methods (e.g., spectroscopy) is just being realized [3–5]. SRMs consisting of well-defined size fractions of polydisperse single-chemical-constituent BeO particles are needed for evaluating digestion protocols used for samples containing polydisperse particles, for which the time necessary for complete digestion is hypothesized to be related to the median particle diameter and the dispersity (GSD) of the size distribution. This dependency on the GSD suggests that a digestion procedure is sufficient for a sample that contains a range of aerosol particle sizes only when the procedure is capable of completely dissolving the largest sized particle in the distribution. Thus, small increases in the GSD are predicted to correspond to long increases in the digestion duration, indicating that a method capable of completely digesting monodisperse BeO particles in an environmental sample may not provide accurate results for a sample that contains polydisperse BeO particles [4] (see also Table 1). The material obtained from the centerless grinder and characterized in this study represents an intermediate primary particle and/or agglomerate particle sizes that may be encountered when analyzing a substrate that was collected using a "respirable" particle sampler. A respirable sampler has a 50% aerodynamic cutoff diameter of 4 μm, which corresponds to an equivalent physical BeO particle diameter of 2.3 μm. In addition to primary particles and agglomerates of this size, much larger particle sizes could be encountered when analyzing a substrate that was collected

Table 2 Physical characteristics of the bulk and physically size separated BeO sludge material

Physical diameter (μm)	Density (g/cm^3)	Specific surface area (m^2/g)
Bulk	2.99±0.00	4.11±0.06
355–600	2.99±0.01	4.82±0.04
53–63	3.02±0.03	3.61±0.04
10–20	–[a]	–[a]

[a] The masses of the powder obtained from sieving were insufficient for surface area and density analyses.

using an inhalable particle sampler with 50% aerodynamic cutoff diameters of 100 μm (equivalent physical BeO particle diameter of 60 μm) or surface wipes and bulk samples (all particle sizes). To ensure that a method is sufficiently robust to digest all BeO particles encountered in air, wipe, and bulk samples, RMs having large particle sizes, such as those generated by industrial milling operations [1], are needed. For completeness in understanding the digestion requirements for occupationally and environmentally relevant particles, it would be useful to know more about both the primary particle size and the degree of agglomeration of particles that may be encountered in the workplace and environment. The digestion chemistry, temperature, and duration requirements will be greater for material encountered as large primary particles than for material encountered as large agglomerates of small primary particles. A challenge in preparing size-fractionated samples of industrial materials is a balance between separating particles according to representative agglomerate sizes and separating particles according to primary particle size alone. The primary particles may be more relevant to evaluating digestion efficacy because, as shown in this study for beryllium and previously by Bello et al. [5] for silica, instrument response can be particle-size-dependent [5]; however, the agglomerates may be more relevant to assessing actual occupational and environmental exposures.

In summary, a library of various chemical forms and ranges of biologically relevant particle sizes of difficult-to-digest particulate RMs is necessary to guide development of digestion procedures to improve the scientific basis for quantification of analytes in environmental samples. To augment existing soluble solution SRMs and the planned 200-nm BeO particulate SRM 1877, we physically size separated and characterized the chemical and physical characteristics of sintered bulk BeO material obtained from a commercial grinding operation. This grinder BeO material appears to meet current needs for larger (1–5 μm) particulate RMs and illustrates a method for creating even larger particulate RMs having primary physical diameters of tens to hundreds of micrometers that may be encountered in occupationally and environmentally relevant commercial operations.

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