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A theoretical framework for evaluating analytical digestion methods for poorly soluble particulate beryllium

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Abstract Complete digestion of all chemical forms and sizes of particulate analytes in environmental samples is usually necessary to obtain accurate results with atomic spectroscopy. In the current study, we investigate the physicochemical properties of beryllium particles likely to be encountered in samples collected from different occupational environments and present a hypothesis that a dissolution theory can be used as a conceptual framework to guide development of strategies for digestion procedures. For monodisperse single-chemical constituent primary particles, such as those encountered when handling some types of beryllium oxide (BeO) powder, theory predicts that a digestion procedure is sufficient when it completely dissolves all primary particles, independent of cluster size. For polydisperse single-chemical constituent particles, such as those encountered during the handling of some types of beryllium metal powder, theory predicts that a digestion procedure is sufficient only when it completely dissolves the largest particle in the sample. For samples with unknown or multi-chemical constituent particles and with particles having undefined sizes, e.g., fume emissions from a copper–beryllium alloy furnace operation or dust from a beryl ore crushing operation, a surface area-limited and single-constituent-dependent dissolution theory may not predict complete dissolution, thereby requiring non-routine robust treatment procedures with post-digestion filtration, followed by examination of residual particulate material. Additionally, for beryllium, and likely other poorly soluble materials, particulate reference materials of various chemical forms and size distributions are needed to better evaluate and harmonize analytical digestion procedures.

Keywords Analytical methods · Beryllium compounds · Quantitative analysis

The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

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Introduction

Beryllium is a lightweight metal that is commercially extracted from the minerals beryl and bertrandite [1]. The three primary forms of industrially-produced beryllium are the oxide (BeO), metal, and alloys (most notably copper-beryllium) [2]; other industrial forms include E-materials (beryllium

metal/BeO matrix) and AlBeMet (aluminum–beryllium). In occupational and environmental settings, beryllium may be encountered, e.g., in dusts generated during the cutting and grinding of aquamarine and emerald gemstones [3], fumes and settled dusts in aluminum smelters [4], and fly ash from coal-fired power plants [5]. Exposure to airborne beryllium particles is associated with development of chronic beryllium disease (CBD), a slowly progressive respiratory disease, characterized by the formation of inflammatory structures known as granulomas (i.e., compactly grouped cells that replace normally functioning tissue) [6, 7]. National Institute for Occupational Safety and Health (NIOSH) investigators have estimated that more than 130,000 workers in the USA are potentially exposed to beryllium under a wide variety of circumstances [8]. Thus, accurate determination of beryllium levels in air and on surfaces in the workplace environment is of particular importance to occupational and environmental health professionals.

A number of standard sampling methods have been developed for assessing total airborne and surface elemental beryllium contamination. Airborne beryllium is collected by drawing air at a known flow rate through a filter that is placed in a fixed location (i.e., an area sample) or positioned in the breathing zone of a worker (i.e., a personal sample). Beryllium contamination on surfaces is usually collected by wiping a known surface area in a regular pattern with even pressure using a substrate (e.g., a water-moistened filter). There are numerous standard digestion procedures available [9], each typically involving digesting the sample and its associated matrix to completely dissolve the analyte, followed by analysis of the digestate to determine the mass of analyte in the sample (e.g., by atomic or mass spectroscopy). For environmental samples that contain poorly soluble metals such as beryllium, complete digestion of all chemical forms and sizes of beryllium-containing particles to their dissolved form during sample preparation is usually necessary to yield accurate and precise determinations of elemental mass levels. There is limited information on digestion-effectiveness for standard digestion procedures that rely only on beryllium solution standard reference materials to validate method recovery efficiency for particulate beryllium. As such, many laboratories have found it necessary to modify "standard" methods to improve mass recovery [9]. Our research group was first to report complete recovery of beryllium from an aqueous standard reference material (using a modified US Environmental Protection Agency Method 3015), but incomplete recovery of beryllium from well-characterized BeO powder, which ranged from 77% (using a modified—2:1 sulfuric to nitric acid digestion—US Occupational Safety and Health Administration [OSHA] Method 125G) to 95% (using a modified—concentrated nitric rather than perchloric acid digestion—US National Institute for Occupational Safety and Health [NIOSH] Method 7300) [10].

The purposes of this paper are to describe the physicochemical properties of beryllium aerosol materials likely to be encountered in environmental samples, present a hypothesis that a dissolution theory can be used as a conceptual framework to guide development of digestion procedures to improve the scientific basis for quantification of beryllium in environmental samples, and articulate the need for development and use of particulate beryllium certified reference materials having a range of environmentally relevant chemical forms and particle sizes.

Theoretical framework for digestion procedures

Mercer [11] originally developed a dissolution theory to understand lung burdens due to slightly soluble particles depositing in the respiratory tract. Because deposition of airborne particles onto the lung surface, with subsequent dissolution in lung fluids, is conceptually the same as deposition of airborne particles onto filter media, with subsequent dissolution in solvent for analytical purposes, we hypothesize that Mercer dissolution theory can be used as a conceptual framework to guide development of digestion procedures. The unique applicability of the Mercer equations to particle digestion is that this theory accounts for changes in particle physicochemical properties, including surface area and size, during dissolution. According to Mercer's theory, the mass fraction remaining from a single-chemical constituent particle or monodisperse population of single-chemical constituent particles at a time, t, is:

$$\frac{\mathrm{m}}{\mathrm{m_0}} = \left[1 - \frac{\alpha_\mathrm{s} \cdot \mathrm{k} \cdot \mathrm{t}}{3 \cdot \alpha_\mathrm{v} \cdot \rho \cdot \mathrm{D_0}}\right]^3$$

m is the mass of particle remaining

$\mathrm{m_0}$ is the initial particle mass

α_s is the surface shape factor (proportionality constant)

α_v is the volume shape factor (proportionality constant)

k is the chemical dissolution rate constant, $\frac{\text{mass}}{\text{unit area} \cdot \text{time}}$

ρ is the particle density

$\mathrm{D_0}$ is the initial particle diameter

(1)

Mercer also describes an equation for the mass fraction remaining, $\frac{M}{M_0}$, from a log-normally distributed polydisperse population of single-chemical constituent particles characterized by a mass median diameter (D_m) and geometric standard deviation (σ_g):

$$\frac{M}{M_0} = \sum_{i=0}^{3} K_i \int_{y_i}^{\infty} f(y)dy$$

$$\text{where, } f(y) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{y^2}{2}\right)$$

$$K_0 = 1$$

$$K_1 = -\beta \exp\left(0.5\sigma^2\right)$$

$$K_2 = \left(\frac{\beta^2}{3}\right)\exp\left(2\sigma^2\right) \quad (2)$$

$$K_3 = -\left(\frac{\beta^3}{27}\right)\exp\left(4.5\sigma^2\right)$$

$$\sigma = \ln\sigma_g$$

$$\beta = \frac{\alpha_s k t}{\alpha_v \rho D_m} = SSA \exp\left(\frac{-\sigma^2}{2}\right) kt$$

SSA is the particle specific surface area (surface area/unit mass)

$$y_i = \left(\frac{1}{\sigma}\right)\ln\left(\frac{\beta}{3}\right) + i\sigma$$

Using Eq. (2), Mercer calculated $\frac{M}{M_0}$ as a function of β for σ ranging from 0.5 to 1.0 (i.e., σ_g ranging from 1 to 2.7). Mercer demonstrated that for values of β up to 6 and values of σ in the range 0.5 to 1.0, the integrals for $\frac{M}{M_0}$ in Eq. (2) are well-approximated by the sum of two exponentials:

$$\frac{M}{M_0} = f_1 \cdot \exp(-\lambda_1 \cdot \beta) + f_2 \cdot \exp(-\lambda_2 \cdot \beta), \quad (3)$$

where the constants f and λ are determined from Mercer's curve fitting for the value of σ_g under consideration.

In relating Mercer dissolution theory to particle digestion, the physical form of the analyte, its chemical dissolution rate constant (k), and time are important parameters. The physical form of the particulate is strictly related to the material being digested, i.e., for monodisperse particles (Eq. 1), digestion is related to available particle surface area, whereas for polydisperse particle populations (Eq. 3), digestion is related to the median particle diameter and dispersity (σ_g) of the size distribution. Mercer theory assumes that the shape factors of all particle sizes are geometrically similar and uses a characteristic specific surface area that is based on the entire particle population. The chemical dissolution rate constant is related to the chemical properties of the particles and a given digestion environment. The time required for complete digestion is strongly dependent upon the dispersity of the size distribution; small increases in σ_g are related to long increases in the digestion duration when the fractional mass remaining is less than about 0.2 (i.e., 80% complete digestion) [11]. The analytical chemist has primary control over the digestion environment, which includes the medium (typically acid), thermal source (e.g., microwave, plasma), and temperature and pressure. These factors determine, in part, the aggressiveness of the digestion procedure; however, there are practical considerations, such as special handling requirements for chemicals (e.g., hydrofluoric acid). Because the time required for complete digestion is dependent on the dispersity of particle sizes in the sample, the analytical chemist has less control over the needed duration, but can expedite the procedure by using a hot plate or a microwave and varying temperature and pressure.

Applicability of the theoretical framework for commonly encountered environmental sample scenarios

Table 1 summarizes our hypothesized applicability of Mercer dissolution theory to evaluation of three different sample digestion scenarios with common real-world exposure implications: 1) monodisperse single-chemical constituent particles, 2) polydisperse single-chemical constituent particles, and 3) multi-chemical-constituent particles and particles having undefined sizes or unknown samples. A suite of analytical techniques was used to characterize the physicochemical properties of occupationally-encountered beryllium materials fitting these scenarios [12–15]. Transmission electron microscopy (TEM) (Model CM30, Philips Electron Optics, Eindhoven, The Netherlands) was used to assess particle morphology and size. Nitrogen gas adsorption (Monosorb Model MS-16 Automated Direct-Reading Surface Area Analyzer, Quantachrome Corp., Syossett, NY) was used to determine powder specific surface area (SSA). X-ray diffraction (Model XDS2000 powder diffractometer, Scintag, Inc., Sunnyvale, CA) and electron diffraction were used to qualitatively identify crystalline chemical constituents. TEM-energy dispersive x-ray spectrometry (germanium detector, Princeton Gamma-Tech, Princeton, NJ), TEM electron energy loss spectrometry (Model 766 DigiPEELS, Gatan, Pleasanton, CA), and x-ray photoelectron spectroscopy (Model PHI 5600, Perkin-Elmer Corp., Eden Prairie, MN) were used to qualitatively identify elemental constituents of samples.

Monodisperse single-chemical constituent particles

Aerodynamically size-separated, finished-product BeO powder (Product Type UOX, Brush Wellman Inc., Elmore, OH) was selected as a real-world example of monodisperse single-chemical constituent particles. The finished-product BeO powder, used to make ceramics, consisted of aggregate clusters of primary particles having physical diameter

Table 1 Application of Mercer [11] dissolution theory to digestion of three different environmental sample scenarios

Sample scenario	Mercer dissolution regime	Equation	Examples
Single-chemical constituent	Monodisperse	1	Powder from preparing and handling UOX BeO
Single-chemical constituent	Polydisperse	3	Powder from preparing and handling I-400 metal
Unknown composition/sizes	Limited application?	–[a]	Fumes from a copper–beryllium alloy furnace

[a] If dissolution of the individual chemical constituents is independent, specialized equations based on Mercer dissolution theory may be applicable, otherwise other mathematical formulations must be developed

of 0.19±0.04 μm, independent of cluster size (see Fig. 1a). The SSA of the BeO (11 to 13 m^2/g) was largely independent of aerodynamic particle cluster size, but dependent upon average BeO primary particle size [13]. The only crystalline constituent identified in UOX powder was BeO. Analysis of elemental composition identified primarily beryllium and oxygen, with traces of silicon [14]; only BeO was identified on the surface of the BeO powder [15]. Mercer dissolution theory is applicable for predicting the completeness of a digestion procedure for a sample that contains monodisperse, single-chemical constituent particles such as UOX BeO powder. In this sample scenario, Mercer dissolution theory predicts that a digestion procedure is sufficient when it completely dissolves all primary particles independent of cluster size (Eq. 1).

Polydisperse single-chemical constituent particles

Aerodynamically size-separated finished-product metal powder (Product Type I-400, Brush Wellman Inc.) was selected as a real-world example of polydisperse single-chemical constituent particles. The finished-product metal powder consisted of compact particles of varying sizes (see Fig. 1b). The SSA of metal powder (4 to 21 m^2/g) was dependent on particle size [13]. Analysis of crystalline constituents identified only beryllium metal in I-400 metal powder. Elemental constituents identified in the powder included beryllium and oxygen with traces of silicon; in addition to beryllium, a thin layer of incidentally, formed (i.e., under ambient conditions of atmosphere, temperature, and pressure) BeO, approximately 40- to 50-Å thick, was present on the surface of the metal powder [12, 14, 15]. Mercer dissolution theory is applicable for predicting the completeness of a digestion procedure for a sample that contains polydisperse, single-chemical constituent particles such as I-400 powder. In this sample scenario, Mercer dissolution theory predicts that a digestion procedure is sufficient for a sample that contains a range of aerosol particle sizes when the procedure is capable of completely dissolving the largest size particle in the distribution (Eq. 3).

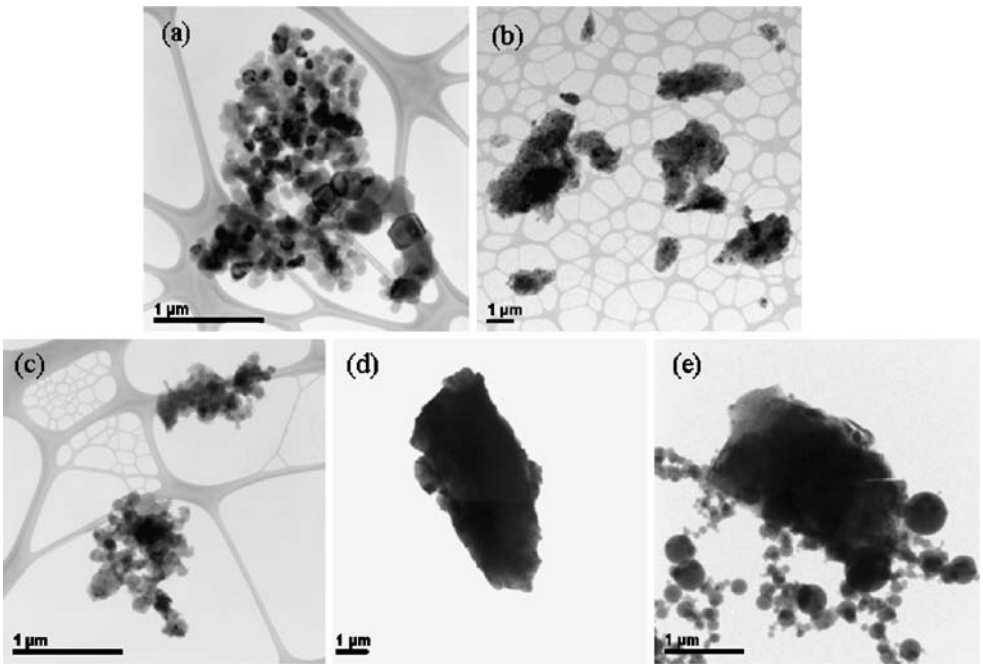

Fig. 1 Transmission electron micrographs of beryllium-containing materials commonly encountered in different workplace environments which illustrate unique combinations of particle morphology and size: **a** product type UOX beryllium oxide, **b** product type I-400 metal powder, **c** copper–beryllium fumes from a furnace operation, **d** post-sintered UOX BeO from a wet grinding operation, and **e** beryl ore dust from a mechanical crusher operation

Multi-constituent particles having undefined sizes/unknown samples

Fume aerosol sampled from the local exhaust ductwork of a copper–beryllium alloy production process was selected as a real-world example of multi-constituent particles having undefined sizes. The fume aerosol (see Fig. 1c) was aggregate clusters of mixed-oxide (copper and beryllium) primary particles; however, the size distribution of the BeO-containing particles was unknown. Determination of SSA using gas-adsorption analysis provided an estimate of the total surface area rather than SSAs of separate chemical constituents. The SSA of these fume particles (3.7 to 5.3 m^2/g) was nearly independent of aerodynamic particle size [13]. Several crystalline constituents were identified in this fume aerosol, including BeO, cuprous oxide [copper(I) oxide (Cu_2O)], cupric oxide [copper(II)oxide (CuO)], and calcium fluoride. Elemental constituents identified in these particles were consistent with the constituents identified by diffraction analyses [14]; the particle surface layer (top 50 to 75 Å) contained BeO and CuO, but Cu_2O was not detected [15].

If the BeO and copper oxide constituents in this fume aerosol were separate single-chemical constituent primary particles that dissolved independently of each other, Mercer dissolution theory [11] may correctly predict complete dissolution, depending on the size distribution of the BeO primary particles (monodisperse or polydisperse). On the other hand, if this fume aerosol were multi-constituent BeO/copper oxide particles, Mercer theory may not be directly applicable for predicting conditions for complete digestion because dissolution of one constituent (dissolving faster or slower relative to another) would limit the available surface area for making contact with the acid reagent, thereby potentially influencing digestion. In the case of environmental samples containing multi-chemical constituent materials and multi-constituent particles having undefined sizes or unknown samples, if a theoretical basis for quantification of total beryllium content is lacking, more robust treatment procedures than are used in many routine digestions would be required. The effectiveness of such empirical "over kill" digestion protocols should be verified by post-digestion filtration and analysis of filter residue. Alternatively, for materials with σ_g that varies and is unbounded, sequential digestion could be a component of the development or periodic validation phase of the sample preparation procedure to ensure that all forms of beryllium were sufficiently digested. Note that unless sample masses are high, sequential digestion may not be feasible for routine analytical use because of detection issues associated with quantification of low masses of analyte in divided samples and losses of analyte and residual sample during handling.

Discussion

Our three examples of commonly encountered environmental sample scenarios illustrate that as the physicochemical complexity of beryllium-containing particles increases from ideal monodisperse single-chemical constituent particles to multi-chemical constituent particles with unknown sizes, the complexity of the digestion strategy necessary to prepare the sample for accurate analysis also increases.

Monodisperse single-chemical constituent particles

The UOX BeO powder is an example of an ideal digestion scenario where the beryllium mostly consists of monodisperse single-chemical constituent primary particles. If a single primary particle size aggregate or agglomerate analyte is the only aerosol source term for a work operation (as is encountered during the manufacture of this oxide powder), then a simple digestion study can be used to define the digestion conditions (solvent, thermal source, temperature, pressure, and duration) that assure complete digestion of all air and surface wipe filter samples collected in the vicinity of the operation. We observed that a modified OSHA Method 125G (2:1 sulfuric acid:nitric acid digestion) provided incomplete recovery of beryllium form UOX BeO powder, whereas modified NIOSH Method 7300 (concentrated nitric acid digestion) provided quantitative recovery [10]. Agrawal et al. also observed complete recovery of beryllium from UOX BeO powder, but using 1% ammonium bifluoride digestion solvent with heat and agitation [16]. Processing UOX BeO powder (pressing, sintering, then machining) increased the primary particle size several-fold (see Fig. 1d). Mercer dissolution theory predicts that a digestion procedure that is capable of completely dissolving 0.2 μm primary particles may not be completely efficacious when the analyte primary particle size becomes larger or the particle size distribution changes as the result of processing, suggesting that the digestion efficiency of modified NIOSH Method 7300 [10] or the 1% ammonium bifluoride protocol [16] may need to be evaluated prior to analyzing work place samples that contain this processed BeO.

Polydisperse single-chemical constituent particles

The incrementally more complex sample scenario is where the analyte largely consists of polydisperse single-chemical constituent particles from a single aerosol source. According to Mercer theory [11], dissolution of polydisperse aerosol material, such as encountered during the handling of I-400 metal powder, is dependent upon the dispersity of the particle size distribution, and the duration required for a given level of digestion increases with σ_g [11]. Thus,

depending on the σ_g of the particle sizes in an environmental sample, complete digestion may require very long digestion durations. If the dispersity of the analyte particle sizes in an environmental sample is quite large, as could be encountered if using an "inhalable"-type air sampler (aerodynamic particle diameter cutoff of 100 μm) to collect airborne particles [17], then the ideal of complete digestion may not be practical due to prohibitively long digestion durations. In this situation, complete digestion may be replaced by a concept of "sufficient digestion," recognizing that digestion duration can be limited to achieve recovery above a defined upper bound (e.g., 99%). A prospective sequential digestion investigation, e.g., digestion of a representative sample or high masses of an appropriate reference material with filtration and analysis of the digestate, followed by digestion of residual particulate material on the filter and analysis of the digestate (repeating this protocol until beryllium is no longer detected in the filtered digestate) may be needed to adequately characterize the population of samples presented for analysis. Once the digestion investigation is completed, only limited routine sequential digestion may be required to assure recovery meets the pre-defined level of sufficiency.

Multi-constituent particles having undefined sizes/unknown samples

The most complex digestion scenario is samples containing multi-constituent analyte particles with undefined size ranges or particles comprised of unknown constituents. In these scenarios, when dissolution of the individual chemical constituents is independent, specialized equations based on Mercer dissolution theory may be applicable, otherwise other mathematical formulations must be developed. For these latter situations, careful consideration must be given to the appropriateness of the digestion protocol (e.g., choice of acid, thermal treatment). If data quality requirements warrant, confirmation of complete digestion (or sufficient digestion) could be accomplished by filtration of the initial digestate, followed by examination of the post-digestion residue collected on the filter using a variety of analytical approaches, including laser ablation inductively coupled plasma mass spectrometry [see, for example, 18] or x-ray fluorescence.

If samples contain particulate beryllium in more than one chemical form or if there are multiple particulate analytes of interest on the same filter, as could be encountered with samples collected that contain beryl dust (see, for example, particles collected from an ore crusher in Fig. 1e) or anthropogenic coal fly ash, then hydrofluoric acid [19, 20] or lithium metaborate fusion [21, 22] may be efficacious digestion protocols (assuming that all beryllium is in silicate form). If beryllium in fly ash is not in silicate form or if special handling requirements preclude the use of hydrofluoric acid, then increasingly aggressive chemically specific digestion environments might be applied in a sequential manner to apportion the beryllium into the different chemical forms [21]. If necessary, this beryllium speciation approach could be utilized in combination with sequential digestions of post-initial digestion residue to develop digestion methods for these highly complex sample scenarios.

Further applicability of Mercer dissolution theory to environmental sample scenarios

Mercer dissolution theory may also be applicable to sample scenarios encountered in less commonly encountered work environments. For example, in a work environment that contains multiple emission sources, each generating a different chemical form of monodisperse single-chemical constituent beryllium particles, complete digestion of all primary particles independent of aggregate cluster size can be predicted by adding Mercer's [11] equation for single particle dissolution for each form of beryllium, provided that the mass ratio of the two beryllium components is known (e.g., by using x-ray diffraction) and that dissolution of the individual chemical constituents in the sample were independent of each other:

$$\frac{m}{m_0} = \left[\frac{m_{0,1}}{m_0}\left(1 - \frac{\alpha_s \cdot k \cdot t}{3 \cdot \alpha_v \cdot \rho \cdot D_{0,1}}\right)^3\right] + \left[\frac{m_{0,2}}{m_0}\left(1 - \frac{\alpha_s \cdot k \cdot t}{3 \cdot \alpha_v \cdot \rho \cdot D_{0,2}}\right)^3\right] \quad (4)$$

A more complex sample scenario would involve samples containing a mixture of monodisperse and polydisperse single-chemical constituent beryllium particles. Such an exposure situation might be encountered during the production of E-materials, if the feed stock BeO powder for this matrix had physicochemical properties similar to UOX BeO powder and the feed stock beryllium metal powder had physicochemical properties similar to I-400 metal powder. If the mass ratio of the two components is known, for the monodisperse analyte material in the sample, the overall mass fraction remaining is the fractional-weighted sum of the individual components using Mercer's single particle dissolution equation. Similarly for the polydisperse analyte material in the sample, the overall mass fraction remaining is the fractional-weighted sum of the individual components using Mercer's polydisperse particle population equation.

A third sample scenario would be environmental samples containing mixtures of different polydisperse single-chemical constituent beryllium particles. Such samples could be encountered in workshops that simultaneously cut and grind different beryllium-containing gemstones [3] or in machine shops that simultaneously machine sintered metal and sintered BeO parts. Assuming that the different chemical forms of analyte particles dissolve independently of one another, complete dissolution of these aerosol materials can be predicted by the superposition of multiple Mercer polydisperse dissolution curves. For these samples, development of digestion protocols may be similar to that described above for a sample containing a single polydisperse analyte aerosol; however, longer prospective digestion investigations may be required. Additionally, final digestion protocols may require more extensive routine digestion because of variation in the aerosol source output and the contribution of the individual sources collected on specific samples.

Implications for analysis of environmental samples

The physicochemical properties of beryllium particles likely to be encountered in environmental samples, each associated with different work processes and scenarios, were highly variable (see Fig. 1 and Table 1). To account for differences in beryllium particle physicochemical properties and dissolution behavior, we presented a conceptual framework based upon an established dissolution theory that could help to evaluate existing digestion procedures and guide development of new procedures, thereby improving the scientific basis for quantification of beryllium in environmental samples. Existing and newly developed digestion protocols must account for beryllium particle physicochemical properties. Thus, particulate beryllium reference materials having various chemical forms and particles sizes that match real-world samples are needed to augment current analytical method validation strategies that rely solely on soluble beryllium acetate [10]. Additionally, given the numerous modifications to standard digestion procedures [9], such reference materials with certified beryllium quantity value(s) [23] would allow for development of performance-based analytical methods and/or help to harmonize current national and international beryllium digestion analysis protocols.

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References

1. Stonehouse AJ (1986) J Vac Sci Technol 4:1163–1170
2. Kolanz ME (2001) Appl Occup Environ Hyg 16:559–567
3. Wegner R, Heinrich-Ramm R, Nowak D, Olma K, Poschadel B, Szadkowski D (2000) Occup Environ Med 57:133–139
4. Rouleau M, Dion C, Plamondon P, L'Espérance G, Zayed J (2005) J Toxicol Env Health, Part A 68:1907–1916
5. Hansen LD, Fisher GL (1980) Environ Sci Technol 14:1111–1117
6. Kreiss K, Mroz M, Newman LS, Martyny J, Zhen B (1996) Am J Ind Med 30:16–25
7. Kreiss K, Mroz M, Zhen B, Wiedemann H, Barna B (1997) Occup Environ Med 54:605–612
8. Henneberger PK, Goe SK, Miller WE, Doney B, Groce DW (2004) J Occup Environ Hyg 1:648–659
9. Brisson MJ, Ekechukwu AE, Ashley K, Jahn SD (2006) J ASTM Int 3(1). DOI 10.1520/JAI13157
10. Stefaniak AB, Hoover MD, Day GA, Ekechukwu AA, Whitney G, Brink CA, Scripsick RC (2005) J ASTM Int 2(10). DOI 10.1520/JAI13174
11. Mercer TT (1967) Health Phys 13:1211–1221
12. Hoover MD, Castorina BT, Finch GL, Rothenberg SJ (1989) Am Ind Hyg Assoc J 50:550–553
13. Stefaniak AB, Hoover MD, Dickerson RM, Peterson EJ, Day GA, Breysse PN, Kent MS, Scripsick RC (2003) Am Ind Hyg Assoc J 64:297–305
14. Stefaniak AB, Hoover MD, Day GA, Dickerson RM, Peterson EJ, Kent MS, Schuler CR, Breysse PN, Scripsick RC (2004) J Environ Mon 6:523–532
15. Stefaniak AB, Day GA, Hoover MD, Breysse PN, Scripsick RC (2006) Toxicol In Vitro 20:82–95
16. Agrawal A, Cronin J, Tonazzi J, McCleskey TM, Ehler DS, Minogue EM, Whitney G, Brink C, Burrell AK, Warner B, Goldcamp MJ, Schlect PC, Sonthalia P, Ashley K (2006) J Environ Mon 8:619–624
17. Harper M (2006) J Environ Mon 8:598–604
18. Abduriyim A, Kitawaki H (2006) Gems & Gemology 42:98–118
19. United States Environmental Protection Agency (1996) SW-846: Method 3052. Test methods for evaluating solid waste, physical/chemical methods. US EPA Office of Solid Waste. Update III. NTIS, Springfield, VA
20. Profumo A, Spini G, Cucca L, Pesavento M (2002) Talanta 57:929–934
21. Brenner IB, Watson AE, Russell GM, Goncalves M (1980) Chem Geol 28:321–330
22. Panteeva SV, Gladkochoub DP, Donskaya TV, Markova VV, Sandimirova GP (2003) Spectrochim Acta B 58:341–350
23. Watters RL, Hoover MD, Day GA, Stefaniak AB (2006) J ASTM Int 3(1). DOI 10.1520/JAI13171