

NMAM 7704

- Title: The title proposed for methods 7704 and 9110 are identical; I suggest for Method 7704: "Beryllium by Field-Portable Fluorescence Measurement (Air)" or some other variation to differentiate the title from Method 9110.
- ACGIH exposure limit: Please delete extra 0; correct value is 0.002 mg/m³
- PROPERTIES: It was unclear if this section pertains to general properties of beryllium (Be) or the properties of forms of Be for which this method is valid. If the latter, including data on the properties of the beryllium salts and beryllium oxides (BeO) used in validation should also be included (Be metal was not used in the validation?). For BeO, density is 3.01 g/ml, melting point is 2578 °C, and vapor pressure is 0 mm Hg.
- MEASUREMENT: a few minor points in this section:
 - Does the term "aqueous" need to be included on the line "Sample Dissolution" to be consistent with Method 9110?
 - Should there be a space between "ESTIMATED LOD" and "0.02"?
 - Under PRECISION, should there be a space between "3" and "ug/filter"?
- APPLICABILITY: The sentence "The analysis is for total beryllium and is not compound specific" should be qualified to better reflect what is known about the physicochemical properties of materials used in the validation tests. In the Backup Data Report, good data on recovery of Be salts were provided as well as data on recovery of BeO with unknown particle size or pedigree (from Acros chemical company, etc.) and recovery of Type UOX BeO (from Brush Wellman) with well characterized particle size, crystallinity, surface area, dissolution, and digestion properties (see Stefaniak et al. J ASTM International, 2005; Kevin Ashley should have a copy of this paper from the symposium he organized in March 2005). No data were provided for recovery of Be metal or Be silicates nor were data provided describing the particle sizes for which digestion is known to be complete. For example, any size particle could be encountered on a surface wipe sample whereas a 37-mm close-faced filter cassette sampler would have an upper particle size cut off of ~40 µm. Dissolution modeling suggests that a method capable of completely recovering a 1 µm BeO particle would not completely recover a 10 µm or 100 µm BeO particle. In sum, limits on the sizes and forms of Be for which this method has been validated should be included, with the understanding that as more data becomes available, the scope of applicability could be expanded.
- INTERFERENCES: On line 3, is there an extra space between "then" and "filtering"? Also, please delete comma at end of sentence and replace with a period.
- SPECIAL PRECAUTIONS: This section was very nice; one minor suggestion: please spell out NH₄HF₂ since this acronym is not defined in the text, rather the phrase ammonium bifluoride is used through out.
- SAMPLE PREPARATION: Step 5 "NOTE: Dissolution of refractory material such as beryllium oxide by heating the solution to 80 °C for 20 minutes without agitation has been shown to be effective." As written, this statement implies that all sizes of BeO can be effectively dissolved, but the exact upper particle size

boundary for this method is unknown. In the Backup Data Report, Appendix 3, it is noted that the BeO material used in the temperature-digestion studies was type UOX BeO from Brush Wellman. Inclusion of a citation to our previous publication, Stefaniak et al. J ASTM Intl. (2005), which establishes that UOX BeO has an average particle size of 0.2 μm , would provide the reader with information regarding the upper BeO particle size boundary for which full digestion is known to occur by this method.

- **CALIBRATION AND QUALITY CONTROL:** Step 10 “Note: If it is suspected that beryllium oxide may be present, then it is recommended to use beryllium oxide for media spikes.” As written, this statement implies that full recovery a media spike containing BeO would provide sound quality control data when analyzing an air sample; however, in the absence of information regarding the aerosol size distribution sampled, this could be an erroneous conclusion. For example, if UOX powder with particle size 0.2 μm were used as the spike material, but the air sample digested contained BeO particles with sizes up to ~40 μm , dissolution modeling suggests complete recovery of beryllium from the media spike could occur while the recovery of beryllium from the air sample could be incomplete (see Figure 3 in Stefaniak et al. J ASTM Intl., 2005).
- **EVALUATION OF METHOD:** As noted in the preface to the Quality Assurance Review, having one Backup Data Report for the two methods made review of the method-specific data difficult; it was not clear what was the source or the characteristics of the BeO used to prepare the spikes at 0, 0.02, ..., and 6.0 μg . If this was Type UOX BeO, citing Stefaniak et al. J ASTM Intl. (2005) would strengthen this statement; however, if the Acros material was used, then it should be made clear that the characteristics of the material, and therefore the range of particles sizes over which this method is valid, are unknown.
- **REFERENCES:** The references for [4] and [5] need to be updated with the full citations given in Method 9110.

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- Under section “Is the user check of the method completed....requirements?” it was not clear what the source was or the characteristics of the BeO used to prepare the spikes at 0.16 μg . If this was Type UOX BeO, citing Stefaniak et al. J ASTM Intl. (2005) in the NMAM document would strengthen the validation; however, if the Acros or Sigma material was used to make these spikes at 0.16 μg , then it should be made clear that the characteristics of the material, and therefore the range of particles sizes over which this method is valid, are unknown.

NMAM 9110

Please note, many of my comments regarding Method 9110 are the similar to comments for Method 7704, but I am treating the method reviews separately and have therefore repeated much of the themes and wording of my earlier comments.

- **Title:** The title proposed for methods 9110 and 7704 are identical; I suggest for Method 9110: "Beryllium by Field-Portable Fluorescence Measurement (wipes)" or some other variation to differentiate the title from Method 7704.
- **OSHA, NIOSH, and ACGIH exposure limits:** Please revise to read "No PEL for surface contamination, No REL for surface contamination, No TLV for surface contamination.
- **PROPERTIES:** It was unclear if this section pertains to general properties of Be or the properties of forms of Be for which this method is valid. If the latter, including data on the properties of the beryllium salts and BeO used in validation should also be included (Be metal was not used in the validation?).
- **SYNONYMS:** If the methods is for all forms of Be, should synonyms for salts, oxides, alloys, mineral forms, hydroxides, matrix materials, etc. be included?
- **MEASUREMENT:** a few minor points in this section:
 - **RANGE:** is given as 0.06 to 6 µg/wipe but under **APPLICABILITY** the lower end of the working range of the method is stated to be 0.02 µg?
 - Should there be a space between "ESTIMATED LOD" and "0.02"?
 - Under **PRECISION**, should there be a space between "3" and "µg/filter"?
- **APPLICABILITY:** Same comment as for Method 7704 regarding the sentence "The analysis is for total beryllium and is not compound specific" should be qualified to better reflect what is known about the physicochemical properties of materials used in the validation tests. In the Backup Data Report, data on recovery of Be salts and BeO with unknown particle size or pedigree (from Acros chemical company) and recovery of Type UOX BeO (from Brush Wellman) with well characterized particle size, crystallinity, surface area, dissolution, and digestion properties (see Stefaniak et al. J ASTM International, 2005). No data were provided for recovery from Be metal or Be silicates nor were data provided describing the particle size limits for which digestion is known to be complete. Any size particle could be encountered on a surface wipe sample. Dissolution modeling suggests that a method capable of completely recovering a 1 µm BeO particle would not completely recover a 10 µm or 100 µm BeO particle. In sum, limits on the sizes and forms of Be for which this method has been validated should be included, with the understanding that as more data becomes available, the scope of applicability could be expanded.
- **INTERFERENCES:** On line 3, is there an extra space between "then" and "filtering"? Please delete comma at end of sentence and replace with a period.
- **SPECIAL PRECAUTIONS:** please spell out NH₄HF₂.
- **SAMPLING:** Because there can be wide inter-surveyor variability in swipe sampling, more detail should be included in this section to better describe the swipe sampling method that should be used for sample collection. The section begins with a detailed description of the method, *i.e.*, don't clove, demarcate the

sampling area, etc. but then refers the reader to another document for the actual wiping method. Could wording not be borrowed from an existing NMAM, e.g., 9102: Elements on Wipes that describes the amount of pressure, technique, etc. or a synopsis of the ASTM method be provided here? As an aside, I understand that recommending a consensus standard is a good thing, but the cited document must be purchased at a cost from ASTM- despite the disclaimer, are we recommending or endorsing a specific product?

- **SAMPLE PREPARATION:** Step 6 “NOTE: Dissolution of refractory material such as beryllium oxide by heating the solution to 80 °C for 20 minutes without agitation has been shown to be effective.” As written, this statement implies that all sizes of BeO can be effectively dissolved, but the exact upper particle size boundary for this method is unknown. This is a critical point because any size particle (including visible particles in the mm size range) could be encountered on a surface wipe sample. In the Backup Data Report, Appendix 3, it is noted that the BeO material used in the temperature-digestion studies was UOX BeO from Brush Wellman. Inclusion of a citation to our previous publication, Stefaniak et al. J ASTM Intl. (2005) which describes the physicochemical properties of UOX BeO would provide the reader with information that full digestion is only known to occur by this method for BeO particle sizes up to 0.2 µm.
- **CALIBRATION AND QUALITY CONTROL:** Step 11 “Note: It is recommended to use beryllium oxide for media spikes.” As written, this statement implies that full recovery a media spike containing BeO would provide sound quality control data when analyzing a wipe sample; however, in the absence of information on the particle size distribution sampled, this could be an erroneous conclusion. For example, if UOX powder with particle size 0.2 µm were used as the spike material, but the wipe sample digested contained BeO particles with sizes up to 100 µm or more, dissolution modeling suggests complete recovery of beryllium from the media spike could occur while the recovery of beryllium from large particles in the wipe sample could be incomplete (see Figure 3 in Stefaniak et al. J ASTM Intl., 2005).
- **EVALUATION OF METHOD:** As noted in the preface to the Quality Assurance Review, having one Backup Data Report for the two methods made review of the method-specific data difficult; it was not clear what was the source or the characteristics of the BeO used to prepare the spikes at 0, 0.02,, and 6.0 µg. If this was Type UOX BeO, citing Stefaniak et al. J ASTM Intl. (2005) would strengthen this statement; however, if the Acros material was used, then it should be made clear that the characteristics of the material, and therefore the range of particles sizes over which this method is valid, are unknown.

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- Under section “Is the user check of the method completed....requirements?” it was not clear what the source was or the characteristics of the BeO used to prepare the spikes at 0.16 µg. If this was Type UOX BeO, citing Stefaniak et al. J ASTM Intl. (2005) in the NMAM document would strengthen the validation;

however, if the Acros material was used to make these spikes at 0.16 µg, then it should be made clear that the characteristics of the material, and therefore the range of particles sizes over which this method is valid, are unknown.

Backup Data – Method Nos. 7704 and 9110 / Beryllium

- Section 1.0 INTRODUCTION
 - Para 1, L8: Please revise the sentence “Further, it has also been shown that skin exposure may result in sensitization towards CBD (3)” to acknowledge that these study used a mouse model and did not follow the animals to see if sensitization progressed to disease. I suggest “Further, it has also been shown in a mouse model that skin exposure to beryllium particles may result in sensitization (3).”
 - Para 1, L12: Please revise the sentence “Thus, one has to monitor and limit which may be ingested via breathing or” to reflect that some fraction of inhaled particles are deposited in the upper airways and cleared via the mucociliary escalator to the gastrointestinal tract and some fraction is retained in the lung. This latter lung-retained fraction may interact with the immune system to cause adverse health effect.
- Section 2.1 Data Set 1: Analytical issues and field data (Appendix 1)
 - For each table, as appropriate, the form and type of beryllium used in the evaluation studies should be provided.
 - Table A1-10
 - Second bullet: please clarify how OSHA 125G was modified.
 - Second bullet: a brief rationale for the choice of method should be included since it is known (Stefaniak et al. J ASTM Intl., 2005) that a modified OSHA 125G [A 2.5:1 50% H₂SO₄ to concentrated HNO₃ 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 let sit for one hour at ambient temperature; and, 1 mL rather than 4 mL concentrated HCl was used to reheat the sample to near boiling] only provided ~75% recovery from UOX BeO powder where as a highly modified NMAM 7300 provided quantitative recovery from the same BeO.
 - Fourth bullet: Should “fom” read “from”? And I suggest using “coating” rather than “skin” to prevent confusion with human dermal skin.
 - Table A1-11
 - Please clarify if the recovery data in the table is the sum of the analytical results from digestate plus the filter residue? If it is just the results from the digestate, please also include the results from the analysis of the filter residue
- Section 2.2 Data Set 2: Evaluation of ammonium bifluoride (Appendix 2)
 - P1, L5: The value for the calcine temperature of Sigma Aldrich BeO, 2000 °C, is suspect; to my knowledge, Brush Wellman is the sole producer of

BeO in the western hemisphere and their material is made at 1300 to 1500 °C. Perhaps the material came from Europe or somewhere else? Because particle size is dependent on calcine temperature (the higher the calcine temperature the larger particle size), accurate knowledge of the preparation temperature is needed to make sound decisions regarding particle size boundaries of the digestion method.

- Section 2.3 Data Set 3: Comparison of dissolution methods.... (Appendix 3)
 - Please provide some rationale for the use of UOX BeO rather than material from Acros or Sigma? Was the choice based on the current initiative within the Beryllium Health and Safety Committee and DOE, NIST, and NIOSH to make UOX a standard reference material? If so, inclusion of citations in the NMAM and copies of the following publications should be included in the Backup Data Report:

Watters RL, Hoover MD, Day GA, **Stefaniak AB**: Opportunities for development of reference materials for beryllium. *J. ASTM International*. 3(1); DOI 10.1520/JAI13171 (2006).

Stefaniak AB, Hoover MD, Day GA, Ekechukwu AA, Whitney G, Brink CA, Scripsick RC: Characteristics of beryllium oxide and beryllium metal powders for use as reference materials. *J. ASTM International*. 2(10); DOI 10.1520/JAI13174 (2005).

- Section 3.0 Source of Reagents and Solutions
 - Item 2, sources of BeO were Acros, Sigma Aldrich, and Brush Wellman
UOX: As in my comment above, was the choice to use UOX based on the current initiative within the Beryllium Health and Safety Committee and DOE, NIST, and NIOSH to make UOX a standard reference material? If so, inclusion of citations in the NMAM and copies of the following publications should be included in the Backup Data
- Appendix 4: Publication: Development of a New Standard Method for Detection of Beryllium on Surfaces
 - Pg 30, P2, L6: Is the statement "Fluorides, usually in the form of HF, is well noted for its ability to penetrate and dissolve metal oxides (18)" well supported by the citation? I have not read the passage in Cotton and Wilkinson (1998), but in the 4th Edition of this text on Pg. 278, Para 3, L1 the authors state "The only halogeno complexes are the tetrafluoroberyllates, which are obtained by dissolving BeO or Be(OH)₂ in concentrated solutions or melts of acid fluorides such as NH₄HF₂." In my interpretation of the sentence, no information supporting the efficacy of this method with regard to particle size range, calcine temp, completeness or reaction, etc. for BeO is provided.
 - Pg 34, P2, L6: Additional information should be included that explains how 7.5 µg BeO was weighed. This mass is an extremely small mass and would require a highly specialized balance and an extremely well-controlled weighing facility.