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

November 1, 2004

Keywords: Industrial Hygiene
Wipe Samples
Air Samples

Evaluation of High-Fired Beryllium Oxide Digestion Methods to Measure Beryllium in Industrial Hygiene Samples by Inductively Coupled Plasma-Atomic Emission Spectroscopy

AUTHORS:

C. J. Coleman, Analytical Development Section

A.R. Jurgensen, Analytical Development Section

D. R. Click, Analytical Development Section

J.C. Hart, Analytical Development Section

R.L. Rutherford, Analytical Development Section

W.M. Smith, Analytical Development Section

T.L. White, Analytical Development Section

B.H. Burch, Analytical Development Section

D.M. Missimer, Analytical Development Section

Table of Contents (page 1 of 2)

Table of Contents (continued-page 2 of 2)

November 1, 2004

Keywords: Industrial Hygiene
Wipe Samples
Air Samples

TO: L.M. Chandler, 773-A and S.D. Jahn, 730-4B

FROM: C.J. Coleman, 773-A, A.R. Jurgensen, 773-A, D.R. Click, 773-A,
J.C. Hart, 773-A, R. L. Rutherford, 773-A, W.M. Smith, 773-A,
T.L. White, 773-A, B.H. Burch, 773-A, D.M. Missimer, 773-A

Evaluation of High-Fired Beryllium Oxide Digestion Methods to Measure Beryllium in Industrial Hygiene Samples by Inductively Coupled Plasma-Atomic Emission Spectroscopy

1.0 Introduction and Summary

Several digestion methods were tested to determine their effectiveness on high-fired BeO (ceramic BeO that has been heated to a temperature of approximately 1450 °C). High-fired BeO is an extremely insoluble, refractory compound that may be present at some DOE sites. Because of the toxicity of air-borne BeO particulates, detection and measurement of high-fired BeO is required. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is a sensitive technique for measuring Be. However, the Be must be dissolved prior to analysis. Accurate detection of the presence of Be depends on digestion methods that are effective for all forms of Be, including high-fired BeO, that may be in Industrial Hygiene (IH) wipes or air filter samples.

The experimental program had three principal objectives:

1. **Determine the effectiveness of the digestion procedure developed by Industrial Hygiene Department for high-fired BeO.**

   Result: The average recovery of high-fired BeO using the Industrial Hygiene (IH) procedure [1] was 90 % with a 6 % relative standard deviation (RSD). Considering the fact that the tests were performed with working standards that contained approximately 1485 times the DOE free release limit of 0.2 • g Be, the IH procedure produced acceptable recoveries of high-fired BeO and with high precision.

2. **Develop a more rapid and convenient digestion method than the IH procedure that also would be effective on high-fired BeO.**

   Result: Some sulfuric acid digestions produced quantitative or near quantitative recoveries of BeO. However, there is no clear speed/convenience advantage for switching from the IH digestion procedure to a sulfuric acid-based digestion at this time. A complicating factor for using sulfuric acid to dissolve BeO is that fuming sulfuric acid can char the organic residue from the GHOSTWIPE ™ used by SRS IH to take wipe samples. The charring of the GHOSTWIPE ™ produces solid residue that must be separated from the solution prior to ICP-AES analyses. Prolonged digestion of the GHOSTWIPE ™ residue with concentrated HNO_3 solves this problem, but this step lengthens digestion time and reduces the time advantage of the H_2SO_4 digestion over the IH method. However, the optimized H_2SO_4 digestion is very rigorous and could have applications at SRS. For this reason, we recommend that ADS work instructions be developed that contain full details of this digestion method.

   Two methods for dissolving Be, a combination of hot H_2SO_4 with ammonium sulfate [3] and contacting the sample with a 1 % ammonium bifluoride solution [4] provided, in our laboratory, less % recoveries than either the IH Procedure or the optimized sulfuric acid digestion.

3. **Develop a safe, practical, and rapid digestion method applicable to a Be analytical field method that would be effective on high-fired BeO.**

   Result: Because of the large amount of NO_x gas produced from digestion of GHOSTWIPE ™, and because of the requirement to use hazardous acids to dissolve the BeO in the samples, in our opinion, none of the methods tested would be amenable to field applications. The digestions should be performed in a fume hood for worker safety.

   The 1 % ammonium bifluoride solution used in a field method [4] is probably the most innocuous solution, but this solution does not dissolve GHOSTWIPES ™ and, as stated above, did not yield acceptable recoveries on the high-fired BeO samples used in these tests.

2.0 Recommendations

- The IH digestion procedure should continue to be the reference digestion methods for GHOSTWIPES ™ and air filter samples.

- ADS work instructions should be developed for the sulfuric acid digestion of Be samples taken with GHOSTWIPES ™ should this digestion be required in the future.

3.0 Note on Experimental Limitations

Three experimental limitations to the tests in this report should be discussed at the outset:

1. **There are no suitable standards of high-fired BeO at concentrations near the DOE free release limit of 0.2 • g/wipe sample available from either government or commercial sources. This fact required the report authors to prepare working standards that are neither certified nor independently validated by another laboratory to test digestion methods.**

2. **The working BeO standards prepared by the report authors contain much higher concentrations of BeO than the DOE free release limit for Be of 0.2 • g/wipe sample. The higher concentration of BeO in the standards was due to uncertainties about being able to accurately dilute and sub-sample slurries that have extremely low concentrations of solid particles. The major technical issue with the relatively high concentration of BeO in the working standards involves the assessment of the practical effectiveness of digestions. For example, a digestion method that recovers 40 % of the Be in a wipe that has been spiked with 297 µg Be has dissolved 119 ug Be or nearly 600 times the free release limit of 0.2 • g Be/wipe. However, this does not mean that 119 • g of Be would be quantitatively dissolved by the technique, but neither can one assume that much lower quantities of Be (2 µg Be/wipe, for example) would be recovered at only 40 %.**

3. **Funds were insufficient to perform multiple trials of each method tested. Single experiments were performed for most of the H_2SO_4 digestion method optimization tests since the amount of BeO used for these tests allowed visual indication that the BeO sample dissolved. Only one trial was also used for methods that we felt were not likely to achieve high recoveries, but that we wanted to include for completeness of these scoping tests.**

4.0 Summary Table of Results

Results of the high-fired BeO digestion tests are summarized in Table 1. Additional method details are discussed in the Experimental Section.

Table 1

Methods Tested , % Be Recovery, and % RSD

Method No.	Method Description	% Be Recovery	% RSD n=
1	IH Digestion Procedure-HNO_3, H_2O_2, HCl, HF ~ 5 hours elapsed time Ghostwipe™ present	90 %	6 % n= 4
2	ADS shortened version of IH Procedure ~ 0.5 hour elapsed time Ghostwipe™ present	45 %	26 % n=2
3	HNO_3/H_2O_2 only ~ 0.25 hour elapsed time Ghostwipe™ present	0.3 %	N/A n= 1
4	HNO_3/H_2O_2 + H_2SO_4; no external heating ~ 0.5 hour elapsed time Ghostwipe™ present	16 %	N/A n=1
5	HNO_3/H_2O_2 + H_2SO_4; 5 minute hot plate heating ~ 0.5 hour elapsed time Ghostwipe™ present	32 %	26 % n=3
6	HNO_3/H_2O_2 + H_2SO_4; 1.5 hour hot plate heating ~ 1.75 hour elapsed time Ghostwipe™ present	34 %	14 % n=3
7	Destruction of the GHOSTWIPE™ by fuming with 120 mL concentrated HNO_3 over 2 hour period, fuming with 20 mL concentrated H_2SO_4 over 40 minute period, adding 40 mL H_2O and heating over 1 hour period and reducing volume, diluting to final volume of 25 mL ~ 4.0 hour elapsed time Ghostwipe™ present	91 %	6 % n=5
8	HNO_3/H_2O_2 + H_2SO_4; 0.5 hour drying oven at 160 ° C heating ~ 1.75 hour elapsed time Ghostwipe™ present	61 %	24 % n=3
9	HNO_3/H_2O_2 + $(NH_4)_2SO_4$; no external heating ~ 0.5 hour elapsed time Ghostwipe™ present	3 %	N/A n=1
10	HNO_3/H_2O_2 + H_2SO_4 + $(NH_4)_2SO_4$; no external heating ~ 0.5 hour elapsed time Ghostwipe™ present	16 %	N/A n=1
11	HNO_3/H_2O_2 + H_2SO_4+ $(NH_4)_2SO_4$; hot plate heating ~ 0.75 hour elapsed time Ghostwipe™ present	28 %	10 % n=3
12	HNO_3/H_2O_2 + H_2SO_4+ $(NH_4)_2SO_4$; 0.5 hour drying oven heating ~ 0.75 hour elapsed time Ghostwipe™ present	35 %	24 % n=3
13	HNO_3/H_2O_2 + $NH_4{\cdot}HF$; no external heating ~ 0.25 hour elapsed time Ghostwipe™ present	14 %	N/A n=1
14	Modified LANL Method- 1 % $NH_4{\cdot}HF$ solution; ~ 0.75 hour elapsed time no Ghostwipe ™	10 %	17 % n=3
15-22	Digestion of ~0.2 g high-fired BeO with H_2SO_4 under various heating and water concentrations ~ 0.75 hour elapsed time no Ghostwipe ™	~ 100 %	N/A n=1 for each experiment
23-25	HNO_3 destruction of GHOSTWIPE ™ (the various conditions affect the % Be recovery followed by digestion of 0.2 g of high-fired BeO with hot H_2SO_4 and water addition). ~ 0.75 hour elapsed time Ghostwipe™ present	79 %, 99 %, 94 %	N/A n=1 for each experiment

5.0 Experimental

5.1 Preparation of Ground High-Fired BeO Samples (Prepared by R.L Rutherford and A.R. Jurgensen)

A sample of ceramic BeO fired at 1450 °C was obtained from Brush-Wellman Company. Approximately 0.2 g of BeO ceramic shards were weighed in a plastic weighing dish on a 4-place analytical balance. The shards were quantitatively transferred into a clean agate mortar. Ethanol was added to the mortar and ground by hand (the BeO material was so hard that mechanical grinding with Micronizer™ motorized grinder proved to be impractical). After hand grinding, the slurry was quantitatively transferred to a clean Pyrex beaker for digestion tests.

5.2 Particle Size Determination of Hand-ground BeO Sample (Performed by W.H. Smith)

One of the hand-ground samples was analyzed for particle size (see Attachment 1 for particle size distribution plots). A Microtrak-S3000 ™ analyzer was used for the measurements. The average particle diameter as a function of number % was 0.43 microns and the average particle diameter as a function of volume % was 14.8 microns.

5.3 Digestion Methods for Experiments with Nominally 824 micrograms of High-fired BeO
(Methods 1-14)

General

A Pyrex beaker containing 0.2061 g of hand-ground, high-fired BeO was quantitatively transferred to a 250 mL plastic volumetric flask. Deionized water was added to the mark to obtain a known weight of BeO per volume of water. After mixing, the slurry was transferred to a wide-mouth plastic bottle and a Teflon-coated magnetic stir bar was added. Sub-sampling was accomplished by vigorously mixing the slurry with the stir bar and removing a 1 mL aliquot that was transferred to either a 125 mL plastic bottle (for the IH Method sample preparations) or to a Pyrex beaker or Pyrex Erlenmeyer flask (for tests requiring heating with a hotplate or drying oven).

In Methods 1-13, a GHOSTWIPE™ was added and dissolved as the first step in the digestion procedure. Method 14 is the modified Los Alamos National Laboratory (LANL) digestion procedure that uses a 1 % ammonium bifluoride solution with a nitrocellulose filter. For Method 14, no nitrocellulose filter was used in our tests in order to strictly determine the effect of the 1% ammonium bifluoride solution on the high-fired BeO. The nominal 824 microgram sample of BeO was contacted in a rotator with 24 mL of 1 % ammonium bifluoride solution for 45 minutes, the mixture filtered, and the filtrate analyzed by ICP-AES to measure % Be recovery.

Condensed Procedures for Methods 1-14

5.3.1 Method #1 Procedure

Method # 1
Industrial Hygiene Procedure

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD (n=4)
yes	HCl, HF	No-the heating is done in a drying oven set at 95-105 °C	90 %	6 %

Method Steps/Explanatory Narrative

Only slight modifications to the procedure in Manual 3Q1-5 **"Hot Block Digestion of Environmental and Industrial Hygiene Samples for Metals by ICP Emission Spectroscopy", Procedure number 2024, revision 1, effective date: 9/05/02,** were used to dissolve the GHOSTWIPES ™ and BeO. The primary modification was that a drying oven was used to heat and evaporate sample rather than the Hot Block equipment, which frequently does not fit well in the normal-sized ADS fume hoods. The specific steps of the IH procedure are as follows:

1. Pre-heat the drying oven in the fume hood to 95-105 °C.
2. Place the GHOSTWIPE ™ in a 125 mL high-density polyethylene wide-mouth bottle.
3. Add 1 mL of the 0.2061 g high-fired Be0/250 mL stock slurry.
4. Add 4 mL of concentrated HNO_3 and 1 mL of concentrated HCl. Place the cap on the bottle to minimize splatter, but DO NOT CAP THE BOTTLE (the bottle could over-pressurize during the digestion of the GHOSTWIPE ™).
5. Heat the samples for 15 minutes after the temperature of the oven re-equilibrates to 95-105 °C. The GHOSTWIPE ™ should be dissolved and most of the brown NO_x gas should be dissipated.
6. Add 1 mL of concentrated HF.
7. Place the cap back on the bottle BUT DO NOT CAP TIGHTLY.
8. Heat and reflux the solution at 95-105 °C for 30 minutes without boiling.
9. Cool the sample for 5 minutes, add dropwise 2 mL of 30 % H_2O_2.
10. Place the cap back on the bottle but DO NOT TIGHTEN THE CAP. Heat the mixture for 60 minutes or until the volume is 2 mL, which ever comes first.
11. Cool the sample, add 2 mL concentrated HCl and 2 mL H_2O.
12. Heat the mixture at 95-105 °C for 15 minutes.
13. Cool the sample.
14. Quantitatively transfer the solution to a 25 mL volumetric flask and submit to ICP-AES for Be determinations.

5.3.2 Method # 2 Procedure

Method # 2
Nitric acid Dissolution of GHOSTWIPE ™ –
addition of HCl and HF (Modified IH Procedure)

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD (n=2)
yes	HCl, HF	Yes	45 %	26 %

Method Steps/Explanatory Narrative

1. Add 1 mL of the 0.2061 g high-fired Be0/250 mL stock slurry.
2. Add 5 mL concentrated HNO_3 and 5 drops 30 % H_2O_2 to dissolve GHOSTWIPE ™. Within 2 minutes (and usually immediately) the HNO_3 begins to react with the GHOSTWIPE ™ with evolution of large amounts of brown NO_x gas. The GHOSTWIPE ™ dissolution is allowed to proceed for 10 minutes. There should be no evidence of residual GHOSTWIPE ™ fragments before proceeding on with further digestion steps.
3. Add 2 mL concentrated HCl and 2 mL concentrated HF.
4. Heat flask on hotplate on the "8" setting (out of 10) for about 5 minutes until the brown fumes dissipates and the volume is about 4-5 mL.
5. Remove flask from the hotplate and set aside to cool.
6. Dilute solution to 25 mL.
7. Filter solution through a 0.45 micron porosity syringe filter before analysis.

5.3.3 Method # 3 Procedure

Method # 3
Nitric Acid Dissolution of GHOSTWIPE ™ -
No Other Acids or Treatments

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD (n=1)
yes	none	No	0.3 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 1 mL of the 0.2061 g high-fired Be0/250 mL stock slurry.
2. Add 5 mL concentrated HNO_3 and 5 drops 30 % H_2O_2 to dissolve GHOSTWIPE ™. Add a watch glass to the flask to contain splatter. Within 2 minutes (and usually immediately) the HNO_3 begins to react with the GHOSTWIPE ™ with evolution of large amounts of brown NO_x gas. The GHOSTWIPE ™ dissolution is allowed to proceed for 10 minutes.
3. Let solution cool to room temperature and dilute solution to 25 mL.
4. Filter solution through a 0.45 micron porosity syringe filter before analysis.

5.3.4 Method # 4 Procedure

Method # 4
Nitric Acid Dissolution of GHOSTWIPE ™ – Addition of Sulfuric Acid
No External Heating

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD (n=1)
yes	H_2SO_4	No	16 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 1 mL of the 0.2061 g high-fired Be0/250 mL stock slurry to a 125 mL Erlenmeyer flask.
2. Add 5 mL concentrated HNO_3 and 5 drops 30 % H_2O_2 to dissolve GHOSTWIPE ™. Add a watch glass to the flask to contain splatter. Within 2 minutes (and usually immediately) the HNO_3 begins to react with the GHOSTWIPE ™ with evolution of large amounts of brown NO_x gas. The GHOSTWIPE ™ dissolution is allowed to proceed for 10 minutes.
3. Add 3 mL concentrated H_2SO_4 dropwise to the warm solution resulting from the GHOSTWIPE ™. The temperature of the solution rose to about 80-85 °C from the dissolution of the GHOSTWIPE ™ and addition of concentrated H_2SO_4.
4. Remove flask from the hotplate and set aside to cool.
5. Dilute solution to 25 mL.
6. Filter solution through a 0.45 micron porosity syringe filter before analysis.

5.3.5 Method # 5 Procedure

Method # 5
Nitric Acid Dissolution of GHOSTWIPE ™ – Addition of Sulfuric Acid Hotplate Heating for 5 Minutes

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% Recovery of BeO	% RSD (n=3)
Yes	H_2SO_4	Yes	32 %	26 %

Method Steps/Explanatory Narrative

1. Add 1 mL of the 0.2061 g high-fired Be0/250 mL stock slurry.
2. Add 5 mL concentrated HNO_3 + 5 drops 30 % H_2O_2 to dissolve GHOSTWIPE ™ wipe. Add a watch glass to the flask to contain splatter Within 2 minutes (and usually immediately) the HNO_3 begins to react with the GHOSTWIPE ™ with evolution of large amounts of brown NO_x gas. The GHOSTWIPE ™ dissolution is allowed to proceed for 10 minutes. There should be no evidence of residual GHOSTWIPE ™ fragments before proceeding on with further digestion steps.
3. Add 3 mL concentrated H_2SO_4.
4. Heat flask on hot plate on the “8” setting (out of 10) for about 5 minutes until the brown fumes dissipate and white fumes are being emitted. After about 1 minute of additional heating, the solution begins turning an amber color.
5. Remove flask from the hotplate and set aside to cool.
6. Dilute solution to 25 mL.
7. Filter solution through a 0.45 micron porosity syringe filter before analysis.

5.3.6 Method # 6 Procedure

Method # 6
Nitric Acid Dissolution of GHOSTWIPE ™ –
Addition of Sulfuric Acid
Hot Plate Heating for 1.5 Hrs.

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% Recovery of BeO	% RSD (n=3)
yes	H_2SO_4	Yes	34 %	14 %

Method Steps/ Explanatory Narrative

Same method as # 5 except that the setting of the hot plate was reduced from “8” to “3” to achieve a 1.5 hours of boiling (longer boil time). After the brown fumes dissipated, white fumes appeared. When the solution began to turn amber from reaction of H_2SO_4 on the organic residue from the GHOSTWIPE ™, the flask was removed from the heat and allowed to cool before diluting to 25 mL.

5.3.7 Method # 7 Procedure

Method # 7
Destruction and Oxidation of GHOSTWIPE ™
with Prolonged Heating with 120 mL of HNO_3-
Dissolution of BeO with Fuming H_2SO_4/H_20

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD (N=5)
Yes	H_2SO_4	Yes	91 %	6 %

Method Steps/Explanatory Narrative

1. Add 1 mL of 0.2061 g high-fired BeO/250 mL stock slurry to a 250 mL Pyrex beaker.
2. Add 1 GHOSTWIPE ™.
3. Add 120 mL conc. HNO_3.
4. Fume for 2 hr on a hotplate with volume reduction to ~ 20 mL. Let solution cool.
5. Slowly add 20 mL of H_2SO_4.
6. Fume on hotplate for 40 minutes. Let solution cool.
7. Add 40 mL of DI water over 1 hour while fuming on a hotplate. Reduce volume to 15 mL. Cool solution.
8. Dilute to 25 mL with DI water.

5.3.8 Method # 8 Procedure

Method # 8 **Nitric Acid Dissolution of GHOSTWIPE ™ -** **Addition of Sulfuric Acid** **Heating at 160 °C in Drying Oven**				
GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD
yes	H_2SO_4	No- Heating was done in a drying oven set at 160 °C	61 %	24 %

Method Steps/ Explanatory Narrative

Same method as # 5 except that after dissolution of the GHOSTWIPE ™ with HNO_3, 3 mL of H_2SO_4 were added and the flask placed in a drying oven set at 160 °C. After dissipation of the brown fumes, the solution turned light yellow for a brief period but quickly turned dark amber and eventually black in color when the volume was reduced to 3-4 mL. The flasks were removed from the oven before dryness. The black slurry was diluted to 25 ml and then filtered through a 0.45 micron porosity filter. Several changes of syringe filters were required to filter the entire 25 mL.

5.3.9 Method # 9 Procedure

Method # 9
Nitric Acid Dissolution of GHOSTWIPE ™ - Addition of Ammonium Sulfate- No External Heating

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD (n=1)
Yes	$(NH_4)_2SO_4$	No	3 %	Not Applicable Only 1 Trial

Method Steps/ Explanatory Narrative

1. Add 1 mL of the 0.2061 g high-fired BeO/250 mL stock slurry.
2. Add 5 mL concentrated HNO_3 containing 0.2 g of $(NH_4)_2SO_4$ and 5 drops 30 % H_2O_2 to dissolve GHOSTWIPE ™. Add a watch glass to the flask to contain splatter. Within 2 minutes (and usually immediately) the HNO_3 begins to react with the GHOSTWIPE ™ with evolution of large amounts of brown NO_x gas. The GHOSTWIPE ™ dissolution is allowed to proceed for 10 minutes. There should be no evidence of residual GHOSTWIPE ™ fragments before diluting to volume.
3. Dilute to 25 mL and filter through a 0.45 micron porosity syringe filter before analysis.

5.3.10 Method # 10 Procedure

Method # 10
Nitric Acid Dissolution of GHOSTWIPE ™ –
Addition of Sulfuric Acid and Ammonium Sulfate-
No External Heating

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD (n=1)
yes	$H_2SO_4/(NH_4)_2SO_4$	No	16 %	Not Applicable Only 1 Trial

Method Steps/ Explanatory Narrative

1. Add 1 mL of the 0.2061 g high-fired Be0/250 mL stock slurry.
2. Add 5 mL concentrated HNO_3 containing and 5 drops 30 % H_2O_2 to dissolve GHOSTWIPE ™. Add a watch glass to the flask to contain splatter. Within 2 minutes (and usually immediately) the HNO_3 begins to react with the GHOSTWIPE ™ with evolution of large amounts of brown NO_x gas. The GHOSTWIPE ™ dissolution is allowed to proceed for 10 minutes. There should be no evidence of residual GHOSTWIPE ™ fragments before proceeding with additional digestion steps.
3. Add 3 mL H_2SO_4 and 0.3 g ammonium sulfate.
4. After the solution cools, dilute to 25 mL and filter through a 0.45 micron porosity syringe filter before analysis.

5.3.11 Method # 11 Procedure

Method # 11
Nitric Acid Dissolution of GHOSTWIPE ™ – Addition of Sulfuric Acid and Ammonium Sulfate Hotplate Heating

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD (n=3)
yes	$H_2SO_4/(NH_4)_2SO_4$	Yes	28 %	10 %

Method Steps/ Explanatory Narrative

1. Add 1 mL of the 0.2061 g high-fired Be0/250 mL stock slurry.
2. Add 5 mL concentrated HNO_3 and 5 drops 30 % H_2O_2 to dissolve GHOSTWIPE ™. Add a watch glass to the flask to contain splatter Within 2 minutes (and usually immediately) the HNO_3 begins to react with the GHOSTWIPE ™ with evolution of large amounts of brown NO_x gas. The GHOSTWIPE ™ dissolution is allowed to proceed for 10 minutes. There should be no evidence of residual GHOSTWIPE ™ fragments before proceeding on with further digestion steps.
3. Add 3 mL concentrated H_2SO_4 and 0.3 g ammonium sulfate.
4. Heat flask on hotplate on the “8” setting (out of “10”) for about 5 minutes until the brown fumes dissipate and white fumes are being emitted. After about 1 minute of additional heating, the solution begins turning an amber color.
5. Remove flask from the hotplate and set aside to cool.
6. Dilute solution to 25 mL.
7. Filter solution through a 0.45 micron porosity syringe filter before analysis.

5.3.12 Method # 12 Procedure

Method # 12
Nitric Acid Dissolution of GHOSTWIPE ™ – Addition of Sulfuric Acid and Ammonium Sulfate- Drying Oven Heating

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD (n=3)
yes	$H_2SO_4/(NH_4)_2SO_4$	Yes	35 %	24 %

Method Steps/ Explanatory Narrative

1. Add 1 mL of the 0.2061 g high-fired Be0/250 mL stock slurry.
2. Add 5 mL concentrated HNO_3 and 5 drops 30 % H_2O_2 to dissolve GHOSTWIPE ™. Add a watch glass to the flask to contain splatter Within 2 minutes (and usually immediately) the HNO_3 begins to react with the GHOSTWIPE ™ with evolution of large amounts of brown NO_x gas. The GHOSTWIPE ™ dissolution is allowed to proceed for 10 minutes. There should be no evidence of residual GHOSTWIPE ™ fragments before proceeding on with further digestion steps.
3. Add 3 mL concentrated H_2SO_4 and 0.3 g ammonium sulfate.
4. Place flasks in drying oven set at 160 °C for about 15 minutes until the brown fumes have dissipated and the solution in the flask is beginning to turn dark amber. The volume of solution in the flask is about 4 mL.
5. Remove flasks from the drying oven and set aside to cool.
6. Dilute solution to 25 mL.
7. Filter solution through a 0.45 micron porosity syringe filter before analysis.

5.3.13 Method # 13 Procedure

Method # 13
Nitric acid Dissolution of GHOSTWIPE ™ -
Addition of Ammonium Bifluoride-
No External Heating

GHOSTWIPE added ?	Acids used in addition to HNO_3	Heating with Hotplate ?	% recovery of BeO	% RSD (n=1)
Yes	Ammonium Bifluoride **(**$NH_4F \cdot HF$)	No	14 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1 Add 1 mL of the 0.2061 g high-fired Be0/250 mL stock slurry.
2 Add 5 mL concentrated HNO_3 and 5 drops 30 % H_2O_2 to dissolve GHOSTWIPE ™. Within 2 minutes (and usually immediately) the HNO_3 begins to react with the GHOSTWIPE ™ with evolution of large amounts of brown NO_x gas. The GHOSTWIPE ™ dissolution is allowed to proceed for 10 minutes. There should be no evidence of residual GHOSTWIPE ™ fragments before proceeding on with further digestion steps.
1\. Add 0.25 g $NH_4F \cdot HF$ crystals.
2\. After the HNO_3/ $NH_4F \cdot HF$ solution cools, dilute solution to 25 mL.
3\. Filter solution through a 0.45 micron porosity syringe filter before analysis.

5.3.14 Method # 14 Procedure

Method # 14
Modified LANL Method with Ammonium Bifluoride

GHOSTWIPE added ?	Acids used in addition to HNO_3 *Note: HNO_3 <u>is not used</u> in this method*	Heating with Hotplate ?	% recovery of BeO	% RSD
No GHOSTWIPES are not currently used at LANL. A nitrocellulose filter is used for wipes	Ammonium Bifluoride ($NH_4F \cdot HF$)	No The digestion takes place by contacting a 1 % $NH_4F \cdot HF$ solution with BeO	10 %	17 %

Method Steps/Explanatory Narrative

1. Add 1.0 mL of the 0.2061 g/250 mL stock slurry and 24 mL of a 1 % ammonium bifluoride ($NH_4F \cdot HF$) solution to a plastic bottle.
2. Place the bottle in a Toxicity Characteristic Leach Procedure (TCLP) extractor that rotates at a rate of 30 revolutions per minute and rotate for 45 minutes.
3. Filter the solution through a 0.45 micron porosity syringe filter before analysis.

5.4 Sulfuric Acid Digestion Methods for Experiments with Approximately 0.2 grams (200,000 micrograms) of High-Fired BeO (Methods 15-22)

Scoping experiments to optimize the H_2SO_4 digestion conditions for high-fired BeO were performed by A.R. Jurgensen and R.L. Rutherford. GHOSTWIPES ™ were not added in these experiments, as the focus was on determining the optimum heating times and relative amounts of H_2SO_4 and H_2O for dissolution. Method # 22, using 10 mL of both concentrated H_2SO_4 and H_2O and heating this mixture for 0.5 hour followed by addition of 20 mL of H_2O and heating for 1 hour, was the optimum method for high-fired BeO digestion in this subset of experiments. The 0.2 grams of BeO dissolved in these experiments was easily visible and it was clear (literally) when dissolution was complete. The solutions were diluted and analyzed by ICP-AES to confirm the essentially quantitative digestion and recovery of high-fired BeO by these methods.

Condensed Procedures for Methods 15-22

5.4.1 Method # 15 Procedure

Method # 15 **Beaker Tests with ~0.2 g High-BeO** **Hot H_2SO_4 Dissolution** **No GHOSTWIPE ™ Present**				
GHOSTWIPE added ?	Acid used in the digestion	Heating with Hotplate ?	% recovery of BeO	% RSD (N=1)
No	H_2SO_4	Yes	96	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.2014 g crushed BeO to the beaker.
2. Add 10 mL conc. H_2SO_4 to beaker.
3. Fume on hot plate for 4 hours.
4. Removed beaker from hotplate and cool.
5. Add 10 mL DI H_2O.
6. Placed in ultrasonic bath to break up solid cake.
7. Fume an additional 30 minutes on hotplate to dissolve.
8. Cooled and diluted to 250 mL with 2% HNO_3.

5.4.2 Method # 16 Procedure

Method # 16
Beaker Tests with ~0.2 g High-BeO
Hot H_2SO_4 Dissolution
No GHOSTWIPE ™ Present

GHOSTWIPE added ?	Acid used in the digestion	Heating with Hot Plate ?	% recovery of BeO	% RSD (N=1)
No	H_2SO_4	Yes	94	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.2017 g crushed BeO to the beaker.
2. Add 10 mL conc. H_2SO_4.
3. Fume on hot plate for 1 hour.
4. Add 20 mL of DI H_2O and 10 mL conc. H_2SO_4 over 1.5 hours.
5. Cool and dilute to 250 mL with 2 % HNO_3.

5.4.3 Method # 17 Procedure

Method # 17
Beaker Tests with ~0.2 g High-BeO
Hot H_2SO_4 Dissolution
No GHOSTWIPE ™ Present

GHOSTWIPE added ?	Acid used in the digestion	Heating with Hotplate ?	% recovery of BeO	% RSD (N=1)
No	H_2SO_4	Yes	96	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.2004 g crushed BeO to the beaker.
2. Add 20 mL conc. H_2SO_4.
3. Fume for 2.5 hour on a hotplate.
4. Add 50 mL of DI H_2O and 10 mL conc. H_2SO_4 over a 4.5 hour time period.
5. Cool and dilute to 250 mL with 2 % HNO_3.

5.4.4 Method # 18 Procedure

Method # 18
Beaker Tests with ~0.2 g High-BeO
Hot H_2SO_4 Dissolution
No GHOSTWIPE ™ Present

GHOSTWIPE added ?	Acid used in the digestion	Heating with Hotplate ?	% recovery of BeO	% RSD (N=1)
No	H_2SO_4	Yes	97 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.1984 g crushed BeO to the beaker.
2. Add 10 mL conc. H_2SO_4 + 10 mL of DI H_2O.
3. Fume for 1 hr on a hotplate.
4. Add 20 mL of DI H_2O over 1 hour.
5. Cool and dilute to 250 mL with 2 % HNO_3.

5.4.5 Method # 19 Procedure

Method # 19
Beaker Tests with ~0.2 g High-BeO
Hot H_2SO_4 Dissolution
No GHOSTWIPE ™ Present

GHOSTWIPE added ?	Acid used in the digestion	Heating with Hotplate ?	% recovery of BeO	% RSD (N=1)
No	H_2SO_4	Yes	97 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.2091 g crushed BeO.
2. Add 10 mL conc. H_2SO_4.
3. Fume for 30 min. on a hotplate,
4. Add 40 mL of DI H_2O over a 2 hour time period.
5. Cool and dilute to 250 mL with 2 % HNO_3.

5.4.6 Method # 20 Procedure

Method # 20
Beaker Tests with ~0.2 g High-BeO
Hot H_2SO_4 Dissolution
No GHOSTWIPE ™ Present

GHOSTWIPE added ?	Acid used in the digestion	Heating with Hotplate ?	% recovery of BeO	% RSD (N=1)
No	H_2SO_4	Yes	100 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.2408 g crushed BeO to beaker.
2. Add 10 mL conc. H_2SO_4.
3. Fume for 1 hour on a hotplate.
4. Add 120 mL of DI H_2O and 10 mL conc. H_2SO_4 over a 4.5 hour time period.
5. Cool and dilute to 250 mL with 2 % HNO_3.

5.4.7 Method # 21 Procedure

Method # 21
Beaker Tests with ~0.2 g High-BeO
Hot H_2SO_4 Dissolution
No GHOSTWIPE ™ Present

GHOSTWIPE added ?	Acid used in the digestion	Heating with Hotplate ?	% recovery of BeO	% RSD (N=1)
No	H_2SO_4	Yes	99 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.2045 g crushed BeO.
2. Add 10 mL conc. H_2SO_4 + 20 mL of DI H_2O.
3. Fume for 1 hour on a hotplate.
4. Add 60 mL of DI H_2O and 10 mL conc. H_2SO_4 over a 4.5 hour time period.
5. Cool and dilute to 250 mL with 2 % HNO_3.

5.4.8 Method # 22 Procedure

Method # 22 **Beaker Tests with ~0.2 g High-BeO** **Hot H_2SO_4 Dissolution** **No GHOSTWIPE ™ Present**				
GHOSTWIPE added ?	Acid used in the digestion	Heating with Hotplate ?	% recovery of BeO	% RSD (N=1)
No	H_2SO_4	Yes	99 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.2263 g crushed BeO.
2. Add 10 mL conc. H_2SO_4 + 10 mL of DI H_2O.
3. Fume for 0.5 hour on a hotplate.
4. Add 20 mL of DI H_2O over a 1 hour time period.
5. Cooled and dilute to 250 mL with 2 % HNO_3.

5.5 Digestion Methods for Experiments with Approximately 0.2 grams (200,000 micrograms) of High-Fired BeO with GHOSTWIPES ™ in the Matrix (Methods 23-25)

Experiments were performed to eliminate the problem caused by H_2SO_4 charring of the GHOSTWIPE ™ residue under certain conditions. The amount of HNO_3 used and the heating times were determined to be important to achieve complete GHOSTWIPE ™ destruction. Method 25, using 100 mL of HNO_3 and 2 hours of heating, was determined to destroy the GHOSTWIPE ™ adequately to avoid charring by H_2SO_4. Note that Method 25 is the basis of Method 7 in which 824 micrograms of BeO are added to the GHOSTWIPE ™ matrix followed by digestion of the GHOSTWIPE ™ with HNO_3 and subsequent digestion of the high-fired BeO with H_2SO_4.

Condensed Procedures for Methods 15-22

5.5.1 Method # 23 Procedure

Method # 23
Beaker Tests with ~0.2 g High-BeO
Hot H_2SO_4 Dissolution
GHOSTWIPE ™ Present

GHOSTWIPE added ?	Acids used in the digestion	Heating with Hotplate ?	% recovery of BeO	% RSD (N=1)
Yes	HNO_3- for GHOSTWIPE H_2SO_4-for BeO	Yes	79 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.1957 g crushed BeO.
2. Add GHOSTWIPE™.
3. Add 10 mL concentrated HNO_3. Sample at this point was not heated with hotplate, but the GHOSTWIPE™ was allowed to dissolve with evolution of NO_x for 20 minutes.
4. Add 10 mL H_2SO_4.
5. Fume for 0.75 hour on hotplate. Let solution cool.
6. Add 30 mL of DI H_2O over a 1.25 hr time period. Solution turned black and solids formed during this period.
7. Cool and dilute to 250 mL with 2 % HNO_3. Slurry was filtered through a 0.45 µm porosity filter prior to ICP-AES analysis.

5.5.2 Method # 24 Procedure

Method # 24
Beaker Tests with ~0.2 g High-BeO
Hot H_2SO_4 Dissolution
GHOSTWIPE ™ Present

GHOSTWIPE added ?	Acids used in the digestion	Heating with Hotplate ?	% recovery of BeO	% RSD (N=1)
yes	HNO_3- for GHOSTWIPE H_2SO_4-for BeO	Yes	99 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.1973 g crushed BeO.
2. Add GHOSTWIPE ™.
3. Add 50 mL concentrated HNO_3.
4. Fume for 3.75 hour on a hotplate to reduce volume to 20 mL. Let solution cool.
5. Add 10 mL H_2SO_4.
6. Fume for 0.75 hour on hotplate.
7. Add 20 mL of DI H_2O over a 1 hour time period. Solution turned black and solids formed during this period.
8. Cool and dilute to 250 mL with 2 % HNO_3. Slurry was filtered through a 0.45 µm porosity filter prior to ICP-AES analysis.

5.5.3 Method # 25 Procedure

Method # 25
Beaker Tests with ~0.2 g High-BeO
Hot H_2SO_4 Dissolution
GHOSTWIPE ™ Present

GHOSTWIPE added ?	Acids used in the digestion	Heating with Hotplate ?	% recovery of BeO	% RSD (N=1)
Yes	HNO_3- for GHOSTWIPE H_2SO_4-for BeO	Yes	94 %	Not Applicable Only 1 Trial

Method Steps/Explanatory Narrative

1. Add 0.1980 g crushed BeO.
2. Add GHOSTWIPE ™.
3. Add 100 mL concentrated HNO_3 over fuming time.
4. Fumed for 2 hours on hotplate to reduce HNO_3 volume to 20 mL.
5. Add 20 mL of concentrated H_2SO_4.
6. Fume on hotplate for 40 minutes.
7. Add 140 mL of DI water over 1.5 hours. Let solution cool.
8. Dilute to 250 mL.

6.0 Discussion

6.1 Evaluation of IH Digestion Procedure with High-Fired BeO

Experimental work focused on a two-phase approach to dissolving samples: (1) dissolution of the GHOSTWIPE ™ with concentrated HNO_3 and 30 % H_2O_2, or HNO_3 exclusively; (2) addition of acids or reagents to dissolve the high-fired BeO. IH samples are normally either GHOSTWIPES ™ (the vast majority of samples) or cellulose ester filters used for air sampling. Because the weight of the GHOSTWIPE ™ is about 15 times that of the air filters (~1.35 g dry weight of GHOSTWIPE ™ versus ~0.09 g weight of air filter), any organic matrix effects from the air filters would be insignificant compared to the GHOSTWIPE ™. For this reason, the recoveries of BeO were measured with an initial HNO_3/H_2O_2 or HNO_3 strike to dissolve the GHOSTWIPE ™. Our experience with GHOSTWIPES ™ was that they dissolved readily in HNO_3 within 10 minutes with no indication of undissolved strands of fiber. However, other workers have reported residual fibers indicating incomplete digestion of GHOSTWIPES ™. It is possible that subtle lot-to-lot variations in the fabrication of GHOSTWIPES ™ may explain differences in ease of destruction.

HNO_3 oxidation of the GHOSTWIPE ™ produces copious amounts of brown NO_x fumes and enough heat to increase the temperature of 5 mL of HNO_3 to about 75-80 °C. We tried to take advantage of this chemical heating by adding reagents immediately after the GHOSTWIPE ™ dissolution, but found that Be recoveries were higher when external heat was applied from a hot plate or oven to achieve boiling acid solutions.

Although the GHOSTWIPE ™ does dissolve with HNO_3 treatment, it does not completely oxidize to produce CO_2 and water and leave no organic material in the HNO_3 solution. Residual organic material was manifested as black charred solids in digestions using hot H_2SO_4. Any digestion technique that creates solids is less than propitious since the solids could sequester the analytes of interest. To avoid the charred material with hot H_2SO_4 preparations, additional heating with HNO_3 for 2 hours was required. The GHOSTWIPE ™ has a composition of polyvinyl alcohol (PVA) co-polymer (polyethylene) [see Material Data Safety Sheet-Attachment 2]. The PVA appears to react immediately with the HNO_3 during dissolution of the GHOSTWIPE ™, leaving residual polymeric material in the solution.

The IH digestion procedure produced about 90 % recoveries of high-fired BeO with good precision. The IH digestion procedure was implemented by the Analytical Development Section on 10-1-2002. IH samples analyzed after this date would have been digested with a technique that recovers at least 90 % of the high-fired BeO. Another important advantage of the IH procedure is that we have been able to routinely meet the ± 25 % of the known value of Be standards (either 0.1 or 0.2 • g Be) at the 95 % certainty level [2].

The main drawback of the IH procedure is that multiple heating and volume reduction steps result in a lengthy procedure. Approximately 5 hours are required to perform the procedure in a radiological hood. To attempt to reduce the digestion time, the same HF and HCl acids used in the IH procedure were used but with more aggressive hotplate heating. The heating time after digestion of the GHOSTWIPE ™ was 5 minutes (until the brown fumes dissipated). The average recovery with this method was only 46 %, indicating that some of the high-fired BeO particles require more heating time.

6.2 Evaluation of Hot Sulfuric Acid Digestions of High-fired BeO

Hot H_2SO_4 is used for Be analyses at both Lawrence Livermore National Laboratory [5] and at the Oak Ridge Y-12 Facility [6], prompting our tests with this reagent to determine if it would result in even better recoveries and reduced turnaround times versus the IH procedure. Tests showed that 8 M H_2SO_4 was more effective than concentrated acid for BeO because with additional water the soluble beryllium sulfate tetrahydrate forms instead of the insoluble anhydrous beryllium sulfate. Quantitative recoveries of Be were obtained even when approximately 0.2 g of BeO (0.07 g Be) or approximately 3.6 E +5 times the free release limit of 0.2 • g Be were tested in the dissolution procedures (Methods 15-22). As discussed previously, prolonged treatment of the GHOSTWIPE ™ with excess HNO_3 mitigated the organic residue problem and renders this method viable for Be samples.

6.3 Evaluation of Mixtures of Sulfuric Acid/Ammonium Sulfate for Digesting High-fired BeO

A literature source [3] states that the high-temperature form of BeO "dissolves readily only in a hot syrup of concentrated H_2SO_4 and $(NH_4)_2SO_4$". However, our tests with this mixture showed no improvement over H_2SO_4. It is likely that a formula could have been found to increase the BeO digestion rate. However, since the H_2SO_4 treatment alone was very effective in dissolving the high-fired BeO, there was little incentive in pursuing the $H_2SO_4/(NH_4)_2SO_4$ beyond a few scoping experiments. In addition, we would prefer to avoid the use of ammonium ion because digestion wastes will eventually be mixed in high-nitrate waste tanks, with the potential over time to form ammonium nitrate.

6.4 Evaluation of Ammonium Bifluoride for Digesting High-fired BeO

Ammonium bifluoride (1 % solutions) digestions are used at LANL) to prepare samples for Be determinations by a field-portable fluorescence method [4]. The LANL method uses the cellulose ester membrane filters to take samples rather than GHOSTWIPES ™. Therefore, HNO_3 is not required to destroy the GHOSTWIPE ™. Direct contact of 24 mL of the 1 % ammonium bifluoride solution with 1 mL of the slurry containing nominally 824 • g of high-fired BeO in a rotator (we used a TCLP extractor that rotates bottles end-over-end at a rate of 30 rotations per minute to test this digestion solution) produced about 10 % recovery. The recoveries did not improve significantly when a

GHOSTWIPE ™ was oxidized with HNO_3 to produce a warm solution followed by addition of solid ammonium bifluoride.

7.0 Conclusions

- Both the reference IH digestion and the H_2SO_4 were shown to be effective for high-fired BeO. Although the H_2SO_4 method is slightly faster, there is no compelling advantage perceived at this time to switch from the IH digestion to the H_2SO_4.

- Other methods tested dissolved measurable amounts of Be (at levels that would have permitted detection at the DOE free release limit of 0.2 µg Be), but the % recoveries were poorer than achieved with the IH method or with $H_2SO_{4.}$

- The hot acids used to dissolve the high-fired BeO are hazardous and, in our opinion, do not lend themselves to field methods. Sampling with GHOSTWIPES ™ complicates development of Be field methods because the large wipe must be destroyed prior to analysis with concurrent generation of hot HNO_3 solution and evolution of large amounts of toxic NO_x gas.

8.0 References

1. "Hot Block Digestion of Environmental and Industrial Hygiene Samples for Metals by ICP Emission Spectroscopy", Manual 3Q1-5, Procedure Number 2024, pp. 8-11, Revision 1, Effective Date: 9/05/02.

2. T.B. Edwards, "A Statistical Review of Measurements of Beryllium Standards", SRT-SCS-2004, 00007, February, 2004.

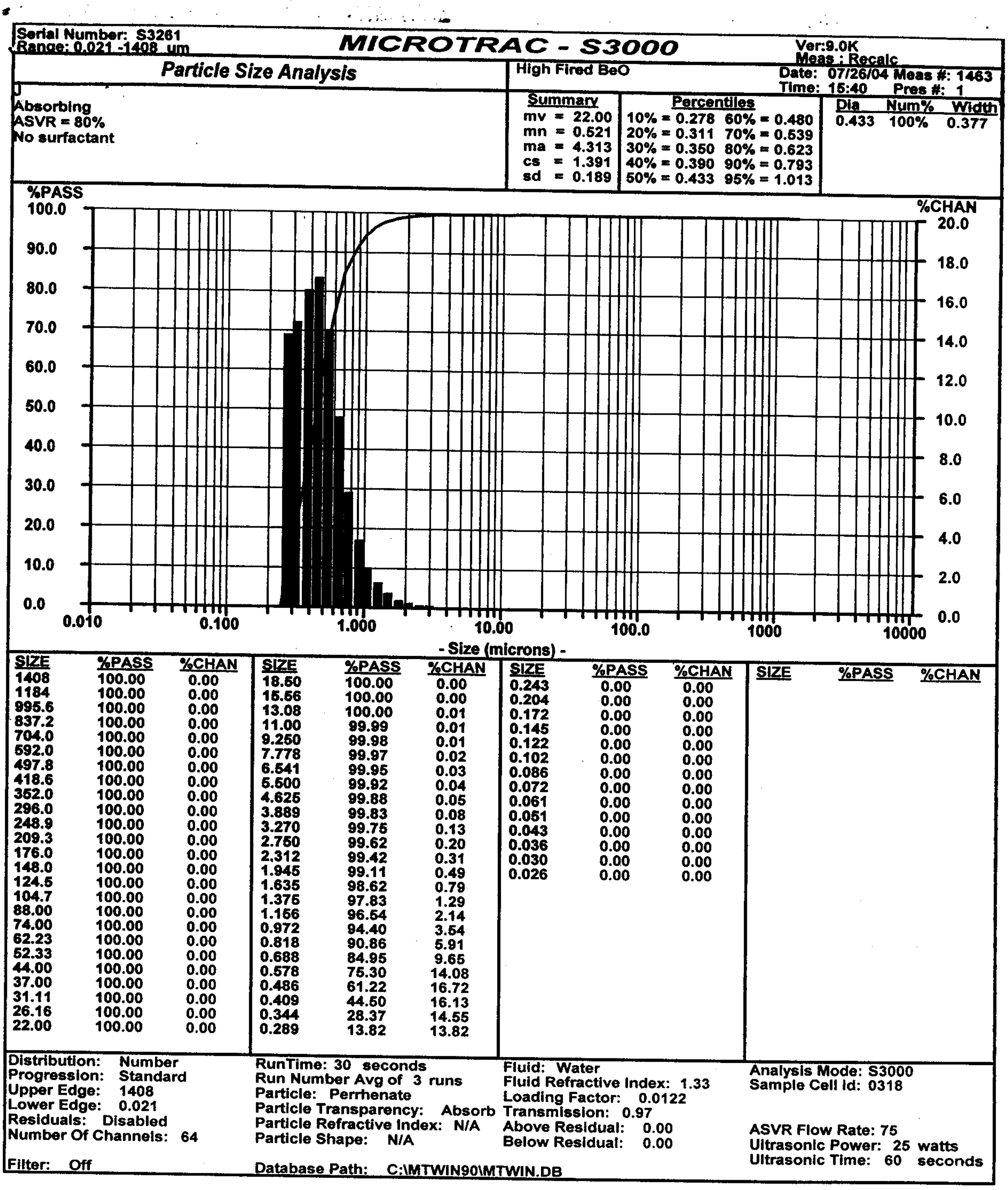
3. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", John Wiley and Sons, Publishers, page 148, 1988.

4. T.M. McCleskey, et.al., "Near Real-Time Beryllium Detection Based on Fluorescence", Presentation in the Symposium "Analytical Chemistry in Nuclear Technology" at the Spring 2004 National Meeting of the American Chemical Society, March 31, 2004.

5. "High-Fired Beryllium by ICP-AES with Microwave Digestion" LLNL Procedure # HCL-I-2010, March, 2003.

6. L.H. Collins, "Determination of Beryllium on Filter Media by ICP-OES, Y/P65-0019, Revision 0, October, 1994.

9.0.1 Attachment 1-Particle Size Analysis of Hand-Ground High-Fired BeO Used for Digestions; Particle size as Function of Number %.



Serial Number: S3261
Range: 0.021 -1408 um

MICROTRAC - S3000

Ver:9.0K
Meas : Recalc

Particle Size Analysis

High Fired BeO

Date: 07/26/04 Meas #: 1463
Time: 15:40 Pres #: 1

Absorbing
ASVR = 80%
No surfactant

Summary
mv = 22.00
mn = 0.521
ma = 4.313
cs = 1.391
sd = 0.189

Percentiles
10% = 0.278
20% = 0.311
30% = 0.350
40% = 0.390
50% = 0.433
60% = 0.480
70% = 0.539
80% = 0.623
90% = 0.793
95% = 1.013

Dia	Num%	Width
0.433	100%	0.377

SIZE	%PASS	%CHAN
1408	100.00	0.00
1184	100.00	0.00
995.6	100.00	0.00
837.2	100.00	0.00
704.0	100.00	0.00
592.0	100.00	0.00
497.8	100.00	0.00
418.6	100.00	0.00
352.0	100.00	0.00
296.0	100.00	0.00
248.9	100.00	0.00
209.3	100.00	0.00
176.0	100.00	0.00
148.0	100.00	0.00
124.5	100.00	0.00
104.7	100.00	0.00
88.00	100.00	0.00
74.00	100.00	0.00
62.23	100.00	0.00
52.33	100.00	0.00
44.00	100.00	0.00
37.00	100.00	0.00
31.11	100.00	0.00
26.16	100.00	0.00
22.00	100.00	0.00
18.50	100.00	0.00
15.56	100.00	0.00
13.08	100.00	0.01
11.00	99.99	0.01
9.250	99.98	0.01
7.778	99.97	0.02
6.541	99.95	0.03
5.500	99.92	0.04
4.625	99.88	0.05
3.889	99.83	0.08
3.270	99.75	0.13
2.750	99.62	0.20
2.312	99.42	0.31
1.945	99.11	0.49
1.635	98.62	0.79
1.375	97.83	1.29
1.156	96.54	2.14
0.972	94.40	3.54
0.818	90.86	5.91
0.688	84.95	9.65
0.578	75.30	14.08
0.486	61.22	16.72
0.409	44.50	16.13
0.344	28.37	14.55
0.289	13.82	13.82
0.243	0.00	0.00
0.204	0.00	0.00
0.172	0.00	0.00
0.145	0.00	0.00
0.122	0.00	0.00
0.102	0.00	0.00
0.086	0.00	0.00
0.072	0.00	0.00
0.061	0.00	0.00
0.051	0.00	0.00
0.043	0.00	0.00
0.036	0.00	0.00
0.030	0.00	0.00
0.026	0.00	0.00

Distribution: Number
Progression: Standard
Upper Edge: 1408
Lower Edge: 0.021
Residuals: Disabled
Number Of Channels: 64

Filter: Off

RunTime: 30 seconds
Run Number Avg of 3 runs
Particle: Perrhenate
Particle Transparency: Absorb
Particle Refractive Index: N/A
Particle Shape: N/A

Database Path: C:\MTWIN90\MTWIN.DB

Fluid: Water
Fluid Refractive Index: 1.33
Loading Factor: 0.0122
Transmission: 0.97
Above Residual: 0.00
Below Residual: 0.00

Analysis Mode: S3000
Sample Cell Id: 0318

ASVR Flow Rate: 75
Ultrasonic Power: 25 watts
Ultrasonic Time: 60 seconds

9. 0.2 Attachment 1-Particle Size Analysis of Hand-Ground High-Fired BeO Used for Digestions; Particle size as Function of Volume %.

Serial Number: S3261
Range: 0.021 -1408 um

MICROTRAC - S3000

Ver:9.0K
Meas : Original

Particle Size Analysis

High Fired BeO

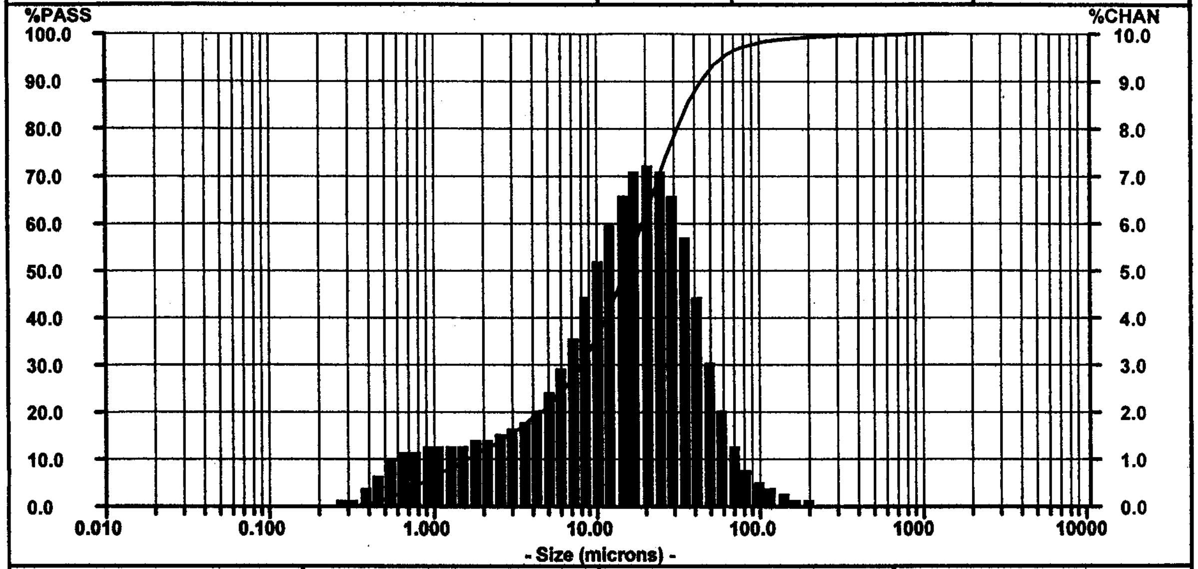
Date: 07/26/04 Meas #: 1463
Time: 15:39 Pres #: 1

Absorbing
ASVR = 80%
No surfactant

Summary
mv = 22.00
mn = 0.521
ma = 4.313
cs = 1.391
sd = 15.77

Percentiles
10% = 1.574 60% = 18.89
20% = 4.462 70% = 23.93
30% = 7.928 80% = 30.84
40% = 11.25 90% = 43.06
50% = 14.80 95% = 58.07

Dia	Vol%	Width
14.80	100%	31.54



SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN
1408	100.00	0.00	18.50	59.13	7.14	0.243	0.00	0.00			
1184	100.00	0.00	15.56	51.99	6.69	0.204	0.00	0.00			
995.6	100.00	0.00	13.08	45.30	6.04	0.172	0.00	0.00			
837.2	100.00	0.02	11.00	39.26	5.27	0.145	0.00	0.00			
704.0	99.98	0.05	9.250	33.99	4.44	0.122	0.00	0.00			
592.0	99.93	0.06	7.778	29.55	3.65	0.102	0.00	0.00			
497.8	99.87	0.07	6.541	25.90	2.98	0.086	0.00	0.00			
418.6	99.80	0.07	5.500	22.92	2.46	0.072	0.00	0.00			
352.0	99.73	0.08	4.625	20.46	2.10	0.061	0.00	0.00			
296.0	99.65	0.09	3.889	18.36	1.87	0.051	0.00	0.00			
248.9	99.56	0.12	3.270	16.49	1.72	0.043	0.00	0.00			
209.3	99.44	0.16	2.750	14.77	1.59	0.036	0.00	0.00			
176.0	99.28	0.22	2.312	13.18	1.48	0.030	0.00	0.00			
148.0	99.06	0.29	1.945	11.70	1.40	0.026	0.00	0.00			
124.5	98.77	0.39	1.635	10.30	1.35						
104.7	98.38	0.55	1.375	8.95	1.31						
88.00	97.83	0.82	1.156	7.64	1.29						
74.00	97.01	1.29	0.972	6.35	1.27						
62.23	95.72	2.06	0.818	5.08	1.26						
52.33	93.66	3.16	0.688	3.82	1.22						
44.00	90.50	4.46	0.578	2.60	1.06						
37.00	86.04	5.71	0.486	1.54	0.75						
31.11	80.33	6.66	0.409	0.79	0.43						
26.16	73.67	7.20	0.344	0.36	0.23						
22.00	66.47	7.34	0.289	0.13	0.13						

Distribution: Volume
Progression: Standard
Upper Edge: 1408
Lower Edge: 0.021
Residuals: Disabled
Number Of Channels: 64

Filter: Off

RunTime: 30 seconds
Run Number Avg of 3 runs
Particle: Perrhenate
Particle Transparency: Absorb
Particle Refractive Index: N/A
Particle Shape: N/A

Database Path: C:\MTWIN90\MTWIN.DB

Fluid: Water
Fluid Refractive Index: 1.33
Loading Factor: 0.0122
Transmission: 0.97
Above Residual: 0.00
Below Residual: 0.00

Analysis Mode: S3000
Sample Cell Id: 0318

ASVR Flow Rate: 75
Ultrasonic Power: 25 watts
Ultrasonic Time: 60 seconds

10.0 Attachment 2-Material Safety Data Sheet for Environmental Express GHOSTWIPE ™ -Page 1 of 2

MSDS: 35707 Page: 1
Mater REV: 0 . OF: 2 SDS)

Environmental Express – Ghost Wipes (Cat# SC4210 & SC4250)
(800) 353-5319
Effective date: 04/28/03

Raw Material: Environmental Express, 490 Wando Park Blvd., Mt. Pleasant, S 29464 (800)-343-5319
Chemtrec Assistance: (800) 424-9300

Section I – Product Identification

Product Name:	PVA Nonwoven Fabrics (Raw Material)	CAS Number:	None Assigned
Synonym:	Polyvinyl Alcohol Copolymer	DOT Shipping Name:	None Assigned
Chemical Family:	VinylCopolymer	DOT Hazard Class:	Not Applicable
Formula:	Proprietary Formulation	UN/NA Number:	Not Assigned

Hazardous Material Identification System (HMIS) Rating:
Health=0 Flammability=0 Reactive=0 Protective Equipment=0

Section II – Health and Safety Alert

Caution: Avoid prolonged or repeated inhalation of lints from fabrics. Do not use this product until MSDS has been read and understood.

Section III – Health Haxard Information

Eye: Mechanical irritation only
Skin: No irritation or sensitization
Ingestion: Not a probable route of entry
Inhalation: Prolonged or repeated inhalation from lints from fabrics may produce nose or throat irritation, coughing may result

Section IV – Emergency and First Aid Procedures

Eye Contact:	Flush with water for 15 minutes. Do not use chemical agents to neutralize. Seek medical aid.
Skin Contact:	Wipe or wash material from skin with soap and plenty of water.
Inhalation:	Lints from fabrics: remove from exposure and move to fresh air. Seek medical aid.
Ingestion:	Not a probable route of entry. Seek medical aid.

Section V – Fire and Explosion Hazard Information

Flash Point & Method: Not Applicable
Auto Ignition Temp: Not Applicable
Extinguishing Media: Water. CO_2, Foam
Flammable Limits: Not Applicable
Fire/Explosion Hazards: The fabrics can be ignited and burned only with difficulty. Fabric meets the specifications for Class II (NFPA702 & 19CAC 1160-1160)

Section VI – Spill, Leak, and Disposal Information

Spill/Leak: Take up with pan and broom
Waste Disposal: Dispose of waste in accordance with applicable regulations and institutional policies

Section VII – Occupational Exposure Limit Hazardous Ingredients

Exposure Limit (Product): None Established
Hazardous Ingredients: No hazardous constituents

10.0 Attachment 2-Material Safety Data Sheet for Environmental Express GHOSTWIPE ™ -Page 2 of 2

Section VIII – Personal Protection Information

Eye Protection: Safety Shield or Glasses
Skin Protection: Impervious Rubber/Plastic Gloves
Ventilation: Special ventilation not required
Respiratory Protection: NIOSH/OSHA approved air purifying or air-line respirator when dust levels exceed exposure limits ($5mg/m^3$ 8hr. respirable PEL).

Section IX – Personal Handling

Handling: No special handling required. Avoid eye contact and prolonged, excessive, or repeated skin contact or inhalation of lints from fabric.
Storage: Store in cool dry area. Keep container and package closed to prevent contamination.
Other: Not for internal use. Wash exposed areas promptly and thoroughly after contact and before eating, drinking, use of tobacco products, or use of restroom. Do not wear contacts without eye protection.

Section X – Reactivity Data

Conditions Contributing to Instability: High moisture and temperature (>200°C)
Incompatibility: Oxidizing agents (i.e. perchlorates, nitrates etc.)
Hazardous Reactions/Decomposition Products: Decomposition is insignificant if kept above 200°C but below 260°C for a short period of time. Above 220°C, Polyvinyl Alcohol yellows and decomposes into acetic acid.

Section XI – Physical Data

Boiling Point: Not Applicable
Melting Point: Approximately 200°C
Vapor Pressure: Not Applicable
pH: 5.0-7.0 (4% in water solution)
Solubility: In hot water (80°C)
Specific Gravity (g/cc): 1.3
Appearance/Odor: White Fabric/Odorless
%Volatile By Vol.: 5WT.%(H_2O)
Evaporation Rate: No Data

Section XII – Comments

Persons with a history of disease or illness involving the skin, eyes, respiratory tract or circulatory system may be at greater risk of developing adverse health effects from exposure to this product.
No known ingredients which occur at greater than 1.0% are listed as carcinogens by IARC Monographs on the evaluation of the Carcinogen Risk to humans, the NTP Annual Report on Carcinogens, or OSHA 29 CF 1910.1001-1047 Subpart Z Toxic and Hazardous Substances.

One component of this product, methanol, is reported by the manufacturer to be toxic to the developing fetus.

Notice: While the information and recommendations set forth herein are believed to be accurate as of the date hereof. Environmental Express makes no warranty claim with respect to and disclaims all liability from reliance thereon.