

Beryllium Wipe Sampling (differing methods – differing exposure potentials)

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Introduction

Beryllium was identified in its oxide form in 1798, named “Glucinium,” reduced to metallic form in 1828, renamed beryllium (Be), and began being commercially used as a hardening and toughening agent in metal alloys in 1918. Additional uses have continued to emerge. Today Be is a key ingredient in aerospace products, weapons, electronics, nuclear reactors, sports equipment and automobile accessories, springs, non-sparking tools, molds for resin injection, dental applications, golf clubs, fiber optic equipment, cellular network communication systems, bicycle frames, wheels, and precision instruments.⁽¹⁾

Beryllium Health Effects and Exposure Limitations

Evidence of negative health effects associated with Be began emerging from Europe during the 1930s but was ignored in the United States (U.S.). In the U.S., medical literature began documenting chemical pneumonia associated with occupational exposures to beryllium oxide in 1943,⁽²⁾ but controversy regarding health effects was perpetuated by faulty research reporting by the U.S. Public Health Service.⁽³⁾ Between 1947 and 1949, Be was confirmed to be the active agent associated with lung disease in Be factory workers.

In 1949 the Atomic Energy Commission (AEC), a major governmental user of Be, proposed that occupational exposures to airborne Be dust be limited to $2 \mu\text{g}/\text{m}^3$ with a maximum limit of $25 \mu\text{g}/\text{m}^3$, and a monthly average of $0.01 \mu\text{g}/\text{m}^3$ in neighborhood air around Be processing plants.^(4, 5) That limit was later adopted by the EPA as the National Emission Standard for Beryllium, which is still the clean air standard for ambient air in the vicinity of Be processing facilities.⁽⁶⁾ The recommended $2 \mu\text{g}/\text{m}^3$ limit for air inside Be processing facilities was specified in federal government contracts with Brush and was later adopted as a Threshold Limit Value by the American Conference of Governmental Industrial Hygienists (ACGIH) in 1957.^(4, 7) In addition to being extremely toxic and the cause of Chronic Beryllium Disease (CBD), Be has been determined to be a known human carcinogen with inhalation being the principle route of exposure.^(8, 9, 10, 11, 12, 13)

Beryllium Disease Prevention and Wipe Sampling

The Department of Energy (DOE), successor agency of the AEC, has remained committed to studying the health effects of Be and finding effective methods of protecting workers, their families, and the public from Be contamination. Pursuant to those obligations, the DOE promulgated 10 CFR 850 “Chronic Beryllium Disease Prevention Program,” (CBDPP) which became effective January 7, 2000.¹⁴

The CBDPP specified not-to-exceed removable surface contamination levels, but did not specify a standard sampling method.⁽¹⁵⁾ This has resulted in inconsistent sampling results and, subsequently, differing amounts of Be contamination remaining on equipment and facility surfaces. A recent survey indicated that of eighteen DOE installations, eleven used water-moistened wipe sampling materials, six facilities wipe-sampled with dry materials, and one used alcohol-moistened wipe materials.⁽¹⁶⁾

The CBDPP requires that Be work area surfaces be cleaned to assure no more than 3 $\mu\text{g Be}/100\text{ cm}^2$ removable contamination. If the work area or equipment will be released for other uses, surfaces must be cleaned so that removable contamination does not exceed 0.2 $\mu\text{g Be}/100\text{ cm}^2$. These cleanliness criteria were considered achievable based on prior experience at various DOE facilities. However, the wipe sampling methods being used at those facilities were not specified.

The removableness of surface contamination in metal machining shops is affected by oil mist residues generated when metal working fluids (MWF) are used to cool and lubricate the metal abrading/cutting processes. Oil mist aerosols generated in such metal machining shops leave somewhat tacky surface residues on walls, ceilings, shelving, and equipment that respond significantly differently to dry paper wipes than to water-moistened wipes or alcohol-moistened wipes. If a less-than-adequate method of wipe sampling is employed, erroneous decisions may be made regarding decontamination and facilities or equipment could be released with surface contamination significantly more than 0.2 $\mu\text{g Be}/100\text{ cm}^2$.

The surface sampling provisions of the CBDPP were explicitly intended to verify minimization of respiratory exposure to Be particulates.⁽¹⁷⁾ However, since the implementation of the CBDPP in 2000, an increasing body of evidence has developed implicating skin contact with Be sensitization.^(18, 19, 20, 21) Since sensitization is an integral step in the development of CBD, this raises additional issues regarding the importance of removing Be contamination from surfaces. Using dry paper or water-dampened wipes can prejudice sampling results by avoiding the collection of lipid-laced contamination residues in shops with historical use of MWF.

Purpose

The purpose of this study was to determine if there was a consistent significant relative difference in the removal efficiency of alternate wipe sampling methods being used within the DOE complex. Specifically, this research sought to establish the removal efficiency of wipe sampling with dry Whatman smear tab paper, versus wipe sampling with Ghost Wipes (water-moistened wipes), versus wipe sampling with methanol-moistened gauze wipes on a surface texture and residue typical of metal-machining shops. It was hypothesized that methanol-moistened wipe sampling would remove a greater percentage of Be surface contamination associated with metal-working fluid residue from a typical painted surface than dry or water-moistened wipe sampling.

Method

Test plates were prepared using 100 mm X 15 mm Pyrex Petri dishes having interior surfaces spray painted with a bond coat primer. To achieve uniform deposition over the test plate surface, precisely-measured aliquots of solution with known Be mass were transferred by pipette to the test plates and subsequently evaporated. A small amount of a semi-synthetic metal working fluid was added to the Be solution used to "contaminate" the test plates. Sixteen test plates were processed and wipe sampled for each wipe method (dry, water-, and methanol-moistened).

The residue applied to the painted surface of the test plates was formulated to contain $1\text{ }\mu\text{g} \pm 0.002\text{ }\mu\text{g Be}$ and 0.1 ml of a metal working fluid concentrate per 78.54 cm^2 (the equivalent of 1.25 $\mu\text{g Be}$ and 0.13 ml of a metal working fluid per 100 cm^2). The oily film resulting from fugitive MWF mist typically oxidizes after extended periods to produce a slight tackiness on shop surfaces. Test plates were baked at 230°F for 25 minutes to simulate the aging effect. Control and field blanks were collected to control for possible sources of contamination inherent in the

preparation, and sampling. All test and control plates were wiped with uniformly consistent patterns (see Figure 2) using the three wipe materials typically used at DOE facilities.

The first set of test plates to be sampled was the series wiped with dry Whatman paper. A portion of the slightly reddish-brown color of surface contamination, caused by the colored MWF, transferred onto paper when it was firmly pressed and wiped over the test plate surface. Use of the same pressure with the Ghost Wipes for the next series of plates squeezed water out of the folded wipes. Water was sopped up to avoid loss of removal efficiency and wiping pressure was moderated with the remaining moistened wipes. There was no significant visible difference between the removal accomplished by water-moistened and alcohol-moistened wipes. All used wipe materials were placed in lab vials, sealed, marked with date and time and transferred to the analytical lab with a chain of custody document. The wipe samples were analyzed using EPA method 6010B "Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES)." Analytical results were used to calculate comparative removal efficiencies, the variances of which were analyzed for statistically significant difference using one-way analyses of variance (ANOVA) and Multiple-Fs post hoc testing.

Results

The mean removal efficiency rates (n=15 for each method) were as follow:

- Dry wipes: 9.33 % (S.D.= 2.80),
- Water-moistened wipes: 22.97 % (S.D.= 6.05),
- Alcohol-moistened wipes: 50.62 % (S.D.= 9.54),

as shown on the histogram of Figure 1.

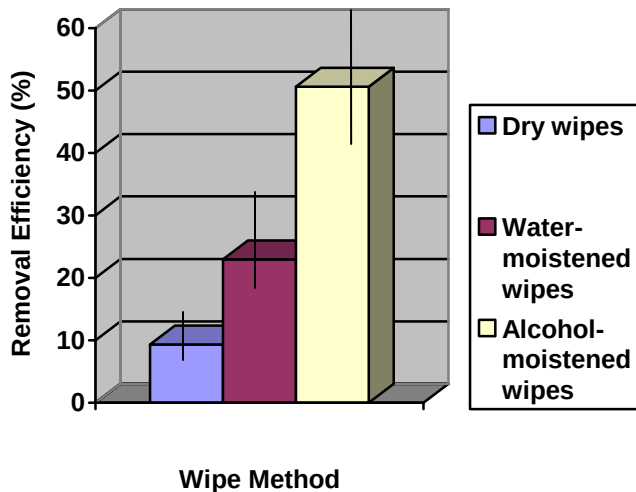


Figure 1. Mean Removal Efficiencies (%)

Removal efficiencies for dry, water-moistened, and alcohol-moistened wipe sampling were also plotted as a frequency distribution bar chart. Values along the x-axis are removal efficiency range intervals and the heights of the bars reflect the numbers of sample per range, see Figure 2. This visual aid illustrates the relatively tighter distribution (less variance) of removal efficiencies experienced with dry wipe sampling. This may be partially attributable to the fact that while moistened sampling techniques removed more of the surface contamination, they also left behind varying amounts of liquid. It would appear reasonable that the greater the solvent effect of the wetting agent, the more contaminant would be contained in the moisture left behind. Imperfect

control of wiping pressures and differing moisture content could account for variable quantities of liquid left behind and hence more diverse removal efficiencies for moistened wipe materials.

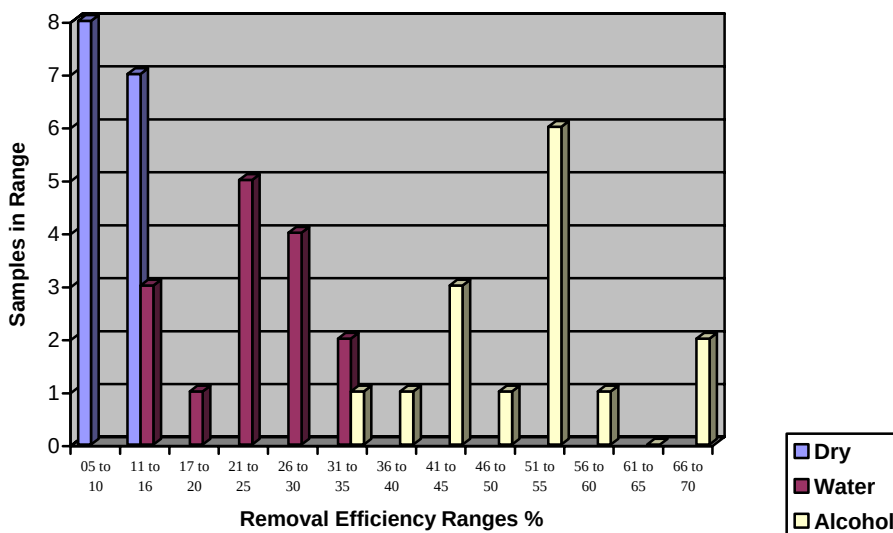


Figure 2. Frequency Distribution of Removal Efficiencies

Sampling results analyzed with single factor Analysis of Variance (ANOVA) showed that there were significant differences in the removal efficiencies of the three wipe sampling methods being compared [$F=146.87$ (2,42), $P = 1.1E-19$, SIG]. Post Hoc Multiple-F analysis of the test results demonstrated that, as predicted, water-moistened wipe sampling had significantly greater removal efficiency than dry wipe sampling, and alcohol-moistened wipe sampling had significantly greater removal efficiency than water-moistened wipe sampling ($p < 0.01$).

Discussion and Conclusions

This study was founded on the proposition that management can ill afford to ignore such excellent evidence as that provided by the research of Tinkle et al.,⁽¹⁸⁾ and the dramatic drop in sensitization experienced by Brush Wellman following implementation of skin protection policies.^(20, 21) Those responsible for decontamination of facilities and equipment in the interest of human health must give serious consideration to the possibility of skin-mediated Be-sensitization. Due to environmental sources, sensitized individuals are at greater risk of developing CBD even if not occupationally exposed to Be. The choice of wipe sample wetting agents has increased importance in light of findings that skin contact plays a valid role in Be disease conditions.

The issue of leaving behind Be in moisture remaining on surfaces sampled with moistened wipe materials could be resolved by adding a step to dry the surfaces with ashless filter paper to be included in the sample vials for digestion along with the moistened wipe materials. This modified sampling procedure would provide more consistent and accurate information regarding levels of surface contamination when making decisions regarding the need for decontamination.

Methanol-moistened wipe sampling identified twice as much machine shop Be surface contamination as compared to water-moistened wipe sampling and about five times as much as dry wipe sampling. Whereas there is no certainty that the remaining not-so-removable surface

contamination poses any real threat to unprotected users, there would probably be no ethically-supportable rationale for using less effective sampling methods.

The fact that the CBDPP cleanliness criteria were based on results from uncharacterized surface residues and unspecified wipe sampling methods raises questions about comparability and feasibility. Considering the results of this study, it could be five times more difficult to achieve the CBDPP cleanliness criteria with alcohol-moistened wipe sampling than with dry wipe sampling. The method(s), surfaces, and nature of residues used to establish the criteria given at 10 CFR 850.30 and .31 significantly influenced the values of those criteria. Good faith efforts to comply with those criteria must use the same method(s) to remove similar residues from similar surfaces, or derive equivalency factors via valid controlled comparison studies.

In the case of surfaces contaminated with Be, together with fugitive oil mist residues typical for metal working shops, this study indicates that methanol is a better wetting agent than water. Selection of inappropriate wetting agents can potentially jeopardize the health of current Be workers, as well as users of facilities or equipment released according to the provisions of CBDPP regulations.

Recommendations

Selection of water-moistened or alcohol-moistened wipe materials should be based on the historical use of the facility/equipment and the observed nature of the surface contamination. If deposits are dry and dusty, water-moistened wipes would be appropriate, whereas methanol wipes would be more appropriate if an oil film is present. Evidence for Be sensitization via skin exposure argues in favor of wipe sampling with wetting agents that provide greater residue removal efficiency.

The Department of Energy should identify the method(s), surfaces, and nature of residues used to establish the criteria given at 10 CFR 850.30 and .31 and allow for equivalency factors based on valid local-condition comparison studies.

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