

Historical Analysis of Airborne Beryllium Concentrations at a Copper Beryllium Machining Facility (1964–2000)

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Received 24 October 2008; in final form 6 March 2009; published online 21 April 2009

Copper beryllium alloys are the most commonly used form of beryllium; however, there have been few studies assessing occupational exposure in facilities that worked exclusively with this alloy versus those where pure metal or beryllium oxide may also have been present. In this paper, we evaluated the airborne beryllium concentrations at a machining plant using historical industrial hygiene samples collected between 1964 and 2000. With the exception of a few projects conducted in the 1960s, it is believed that >95% of the operations used copper beryllium alloy exclusively. Long-term (>120 min) and short-term (<120 min) personal and area samples were collected during a variety of activities including machining of copper beryllium-containing parts, as well as finishing operations (e.g., deburring and polishing) and decontamination of machinery. A total of 580 beryllium air samples were analyzed (311 personal and 269 area samples). The average concentration based on area samples (1964–2000) was $0.021 \mu\text{g m}^{-3}$ (SD $0.17 \mu\text{g m}^{-3}$; range $0.00012\text{--}2.5 \mu\text{g m}^{-3}$); 68.8% were below the analytical limit of detection (LOD). The average airborne beryllium concentration, based on all personal samples available from 1964 through the end of 2000 ($n = 311$), was $0.026 \mu\text{g m}^{-3}$ (SD $0.059 \mu\text{g m}^{-3}$; range $0.019\text{--}0.8 \mu\text{g m}^{-3}$); 97.4% were below the LOD. Personal samples collected from machinists ($n = 78$) had an average airborne concentration of $0.021 \mu\text{g m}^{-3}$ (SD $0.014 \mu\text{g m}^{-3}$; range $0.019\text{--}0.14 \mu\text{g m}^{-3}$); 97.4% were below the LOD. Airborne concentrations were consistently below the Occupational Safety and Health Administration permissible exposure limit for beryllium ($2 \mu\text{g m}^{-3}$). Overall, the data indicate that for machining operations involving copper beryllium, the airborne concentrations for >95% of the samples were below the contemporaneous occupational exposure limits or the 1999 Department of Energy action level of $0.2 \mu\text{g m}^{-3}$ and, in most cases, were below the LOD.

Keywords: beryllium; copper beryllium alloy; exposure assessment; industrial hygiene

INTRODUCTION

Beryllium is a lightweight, strong metal that has been used to manufacture a wide variety of products, including satellites, X-ray tubes, automotive air bag impact detectors, missiles, and aircraft. The most commonly used form of beryllium is copper beryllium (CuBe) alloy, which typically contains ~2% beryllium. As of 2001, products containing beryllium had an estimated market value of \$700 million per year (Kolan, 2001).

CuBe alloys have high electrical and thermal conductivity, high strength and hardness, are non-magnetic and resist corrosion (Stonehouse and Zenczak, 1991; Kolan, 2001). Yet, the alloy is ductile and can be machined. Because of these characteristics, copper beryllium alloys are found in many products, including electronic equipment and electrical components. There are two forms of CuBe alloys: high strength and high conductivity. High-strength alloys contain 1.6–2.0% beryllium and a small amount of cobalt or nickel, while high-conductivity alloys contain as much as 0.7% beryllium (Copper Development Association, 2008).

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During the production of CuBe alloys, beryllium oxide is reduced in the presence of carbon and copper in an arc furnace. After melting and cooling, unreduced beryllium oxide and other reaction products float to the surface and are removed as dross. The dross can contain high levels of beryllium, and is therefore removed by mechanical scalping and acid pickling (Stonehouse and Zenczak, 1991; Kent *et al.*, 2001; Kolan, 2001). The master alloy may be hot rolled or extruded, and the heat required for these processes can produce beryllium oxide on the surface of the metal. This master alloy typically contains 4% beryllium and is cast as ingots, bars or rods (Brush Wellman, 2007). The final alloy, used in most machine shops, contains ~2% beryllium (Kolan, 2001).

The occupational hazards of inhalation exposure to beryllium were recognized in Germany and Russia in the 1930s and were described in the United States in the 1940s, when cases of acute beryllium disease were reported in beryllium workers (Gelman, 1936; Van Ordstrand *et al.*, 1945). In 1946, chronic beryllium disease (CBD) was described in fluorescent lamp workers by Hardy and Tabershaw (1946). Reports of both acute and chronic disease in beryllium workers caused the Atomic Energy Commission (AEC), led by Dr. Merrill Eisenbud, to set exposure limits for beryllium in 1949 (Eisenbud, 1998). This recommended occupational exposure limit (OEL), $2 \mu\text{g m}^{-3}$ as a daily time-weighted average, was ultimately permanently adopted after numerous annual reviews by an AEC committee (Eisenbud, 1998; Borak, 2006). By 1972, this standard had been adopted by the American Conference of Governmental Industrial Hygienists (ACGIH), the American Industrial Hygiene Association, the American National Standards Institute, the Occupational Safety and Health Administration (OSHA) and the National Institute of Occupational Safety and Health (NIOSH) (Kolan, 2001; Borak, 2006).

In 1999, ACGIH proposed decreasing the threshold limit value (TLV) for beryllium to $0.2 \mu\text{g m}^{-3}$ (ACGIH, 1999). During that same year, the US Department of Energy (DOE) also published the final ruling for their Chronic Beryllium Disease Prevention Program, which mandated an action level of $0.2 \mu\text{g m}^{-3}$ (DOE, 1999). The 1999 TLV was based on a study by Kreiss *et al.* (1996) in which workers exposed to $0.1\text{--}0.6 \mu\text{g m}^{-3}$ total beryllium had sensitization prevalence of 3.6%. In 2005, based on additional studies conducted in the 2000s, ACGIH proposed a TLV value of $0.02 \mu\text{g m}^{-3}$ (ACGIH, 2005). This proposal was largely based on a study that found no cases of CBD or sensitization among 22 workers with lifetime-weighted average exposures $<0.02 \mu\text{g m}^{-3}$. However, 20 of 235 workers with lifetime-weighted average exposures between 0.024 and $0.6 \mu\text{g m}^{-3}$ were sensitized (Kelleher

et al., 2001). In 2007, ACGIH revised the proposed TLV again to $0.05 \mu\text{g m}^{-3}$ (ACGIH, 2007). This proposal was based on the inhalable particulate mass and was primarily based on two studies that found that five workers with a lifetime-weighted average exposure between 0.1 and $0.2 \mu\text{g m}^{-3}$ were sensitized and that four workers with subclinical CBD had lifetime-weighted average exposures between 0.21 and $0.5 \mu\text{g m}^{-3}$ (Kelleher *et al.*, 2001; Madl *et al.*, 2007). This proposed TLV of $0.05 \mu\text{g m}^{-3}$ respirable beryllium was expected to protect sensitive populations because very low incidences of sensitization or CBD had been observed at this level of exposure; however, it has not yet been adopted (ACGIH, 2007).

Over the past 15–20 years, the majority of beryllium used in manufacturing processes has been CuBe alloy, and many more workers are exposed to beryllium alloys than to beryllium metal or beryllium oxide (Richter, 2002). However, until recently, there has been limited study of the typical airborne beryllium concentrations in facilities that use beryllium alloys exclusively, primarily because the airborne concentrations were thought to be rather low and because the toxicity of CuBe was thought to be much less than beryllium oxide. Most studies have reported cases of CBD in plants in which workers were exposed to more than one form of beryllium, including ore, metal or oxides (Cotes *et al.*, 1983; Cullen *et al.*, 1987; Kreiss *et al.*, 1993, 1996, 1997; Stange *et al.*, 1996; Viet *et al.*, 2000; Henneberger *et al.*, 2001; Kelleher *et al.*, 2001; Newman *et al.*, 2001; Rosenman *et al.*, 2005). As a result, a number of professionals inferred that it was the metal or the oxide that was the predominant cause of the disease.

It was not until 2005 that the first large study evaluated airborne concentrations of beryllium, as well as CBD and beryllium sensitization rates were conducted in a CuBe alloy strip and wire finishing facility (Schuler *et al.*, 2005). This facility did not routinely process pure beryllium metal or beryllium oxide, and 99% of all samples were below the OSHA permissible exposure limit (PEL) of $2 \mu\text{g m}^{-3}$. Moreover, 93% of samples were below the DOE action level ($0.2 \mu\text{g m}^{-3}$). The authors reported that workers who were likely to be exposed to concentrations $>0.2 \mu\text{g m}^{-3}$ beryllium were more likely to develop CBD or beryllium sensitization than workers with less exposure (Schuler *et al.*, 2005). CBD prevalence was significantly higher ($P < 0.05$) among those who had worked in rod and wire production, particularly among those who worked in the wire annealing and pickling processes (Schuler *et al.*, 2005). There remains a paucity of data regarding typical exposure levels of workers handling only beryllium alloys under a variety of conditions or operations. Therefore, the objective of this work was to characterize historical airborne concentrations in a facility that primarily machined CuBe alloys.

Background

Industrial hygiene records were analyzed from a facility that machined a variety of metals, including steel, brass, aluminum, copper and, until recently, CuBe alloys. The facility did not produce the alloy and did not machine beryllium oxide or pure beryllium metal. The CuBe alloy was supplied to this facility as a bar stock (typically 2.5 inch diameter), which was then machined in several iterations to make a valve housing. This intricate machining consisted of first removing the bulk material and then making several passes to remove small bits until the part was properly shaped using grinders, lathes and screw machines. Machining was typically performed using flood coolant, except during the initial setup of the machine when very small cuts were made to verify the settings for accuracy. Flood coolant was used to help prevent dust from becoming airborne, to preserve the part and tool life, and to reduce heat in the part.

Industrial hygiene and sampling records from 35 years of operations were analyzed to determine exposure. Several specific job tasks were analyzed separately as one of four categories: (i) machining, (ii) machining dry, (iii) grinding and (iv) deburring. These tasks were considered to have the potential for the greatest amount of exposure at the facility. In the manufacturing industry, the term 'machining' generally covers a wide range of tasks. It can refer to work on large mills (up to 1.5 stories tall) that are used on larger valve housings, for example, or it can refer to working on smaller benchtop applications like lathes and screw machines. This type of work was often performed at the facility in the 1970s and 1980s, and to a lesser extent in the 1990s. Machining dry primarily referred to work done on a lathe where the part spins and very small amounts of material are removed from an internal cavity. As it is very delicate work, it was performed dry so that the operator could clearly observe the part. Grinding refers to the crude removal of metal from a part with a grinding wheel. It was frequently performed on a freshly welded part to smooth out the edges of the weld, and was typically performed dry so that the operator could visualize the part. Deburring refers to removal of very small chips or bits of metal or rough edges after machining was completed. At this facility, several workers performed deburring in one area and all deburring was performed dry. Deburring was performed with fine sand paper, emery boards, Dremel tools (motorized hand tool with brush or fabric) or small motorized wheels with a fine metal brush attached. Because of strict quality control specifications, deburring was done entirely by hand, and had to be closely scrutinized, sometimes under a microscope, making it very tedious work that was often performed in close proximity to the operators' breathing zone.

METHODS

Creation of electronic database of air sampling results

The available industrial hygiene data were compiled by reviewing thousands of pages of historical corporate records pertaining to beryllium operations at the plant. The first samples were collected in 1964, when beryllium operations began at the facility. In total, 580 personal and area air samples collected between 1964 and 2000 were identified and analyzed. Samples were collected during a variety of work activities, including machining, deburring and beryllium decontamination projects.

Industrial hygienists at the plant created an electronic database of the industrial hygiene samples, including beryllium. This database was populated as sampling was conducted. In the 2000s, industrial hygienists added historical sampling data as they were discovered through a search of archival records. Based on historic sampling sheets and internal memos, the database contained 500 personal and area air samples analyzed for beryllium between 1964 and 2000. The database included information regarding the sample date, department, beryllium concentration, sampling time, sample code, sampling method and process code for the activity that was occurring during sampling. In many cases, internal memos were generated in conjunction with beryllium sampling; these were included in the review as they sometimes contained additional information about the circumstances under which sampling occurred.

The database was reviewed and considered a starting point for this analysis. As part of an overall quality assurance/quality control process, hard copies of the sampling data sheets were compared with the electronic database to ensure that the various fields were entered correctly into the database. Hard copy backup information was not provided for 23 of the samples contained in the database (<5%), so the accuracy of these data could not be verified. In total, 477 of the database entries were checked for accuracy. An error was considered critical if it involved the sample result (concentration, lab result, units or qualifier) or sample type (personal/area). All other errors, including typographical errors, were considered non-critical given they would not lead to miscalculation of the airborne concentration. Overall, there were eight samples containing critical errors (<1.7%) in the database, and all errors were in the concentration entry. All errors found during the verification process were corrected in the database.

The database currently consists of all industrial hygiene air samples that were taken at the plant from 1964 through 2000. Documentation was found for 88 samples that had not been included by industrial hygiene personnel; however, these samples were entered

into the electronic database and incorporated into this analysis. In total, 580 personal and area air samples were considered (Fig. 1). Eight area samples with reported very low detection levels ($10^{-6} \mu\text{g m}^{-3}$) were excluded based on discussions with industrial hygiene personnel and an additional review of the plant's records. The records for these samples, taken in the 1960s, were limited, and the detection limits could not be verified. Personal samples accounted for 311 of the total samples, while the remaining 269 were area samples. Within each group, the air sampling results were categorized by sample duration. All air monitoring data were divided into short-term (≤ 120 min), long-term (> 120 min), or unknown sample duration (Fig. 2). A large portion of the short-term samples spanned the duration of a specific task. These values represent only a portion of the total workday.

Data analysis

The data were moderately to severely left-censored, and in some groups 100% of the samples were below

the limit of detection (LOD). If the LOD of a sample was not given, and a simple non-detect (ND) or '0' was reported, an LOD was estimated using the reported sample time and flow rate. For samples collected after 1981, the database indicated that NIOSH 7300 method was followed, and therefore the LOD was calculated using a detection limit of $0.005 \mu\text{g}$. However, no collection methods were recorded in the database for area samples collected prior to 1981. Based on the flow rate (between 10 and 57 l min^{-1}) and, in some cases, very long sampling time (i.e., 4700 min), it seems likely that these were fixed airhead samples. Flame atomic absorption was a popular method of beryllium detection in the 1960s and 1970s (Kolan *et al.*, 1999); therefore, the detection limit for flame atomic absorption of $0.1 \mu\text{g}$ was used to calculate the LOD when necessary for these samples. Because of the high flow rates and long sampling times, some of the LODs for the area samples are very low (Table 2).

Because of the exceedingly high percentage of samples that were below the LOD, and because they

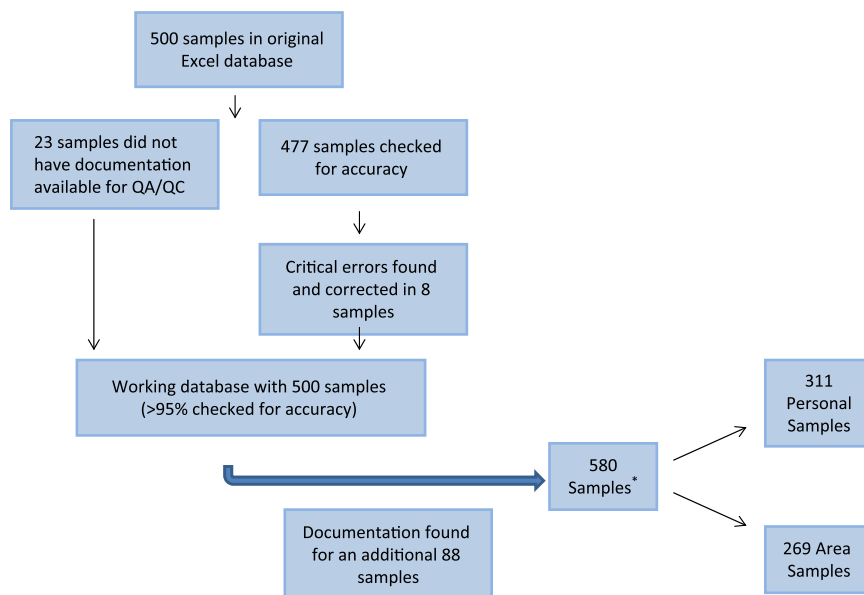


Fig. 1. Overview of quality assurance/quality control of all beryllium samples collected between 1964 and 2000. A total of 311 personal samples and 269 area samples were included in the final analysis. *Eight samples were removed from the analysis because reported detection limits were unusually low and could not be verified ($10^{-6} \mu\text{g m}^{-3}$ beryllium).

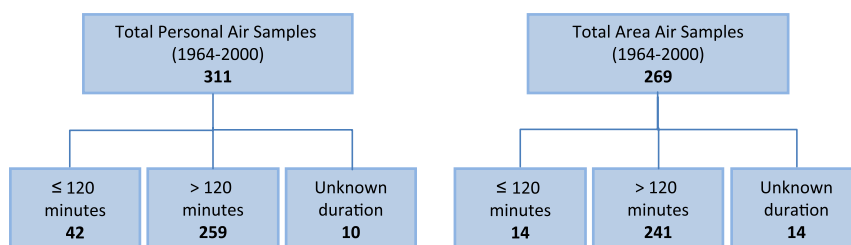


Fig. 2. Summary of personal ($n = 311$) and area ($n = 269$) samples included in the analysis. Long-term and short-term samples were also analyzed separately.

did not follow a discernable distribution, the analysis was conducted using ProUCL 4.0 software, which implements the Kaplan–Meier method (Singh and Singh, 2007). No substitution methods, such as LOD/2 or LOD/ $\sqrt{2}$, were applied (Helsel, 2005a; Singh and Singh, 2007).

The Kaplan–Meier method, based on the product limit estimate (PLE), is a non-parametric method capable of handling left-censored data with multiple limits of detection. A thorough description of the PLE can be found in a report by Bechtel Jacobs Company LLC (2000), which provides mathematical and graphical descriptions of the PLE. Briefly, to estimate the PLE mean, the data are arranged in order of decreasing concentration, with the LOD used for ND samples. The numbers of detect and ND samples at each concentration are then tallied, and their difference is used to estimate the PLE at each concentration. Ultimately, PLE values are plotted, and the area between the resulting curve and a horizontal line at PLE = 1 represents the mean value of the PLE. The mean values of the PLE are the mean concentrations of CuBe alloy reported in the following datasets.

The 95th percentile upper confidence limit (UCL) of the data was calculated with ProUCL software, version 4.0. ProUCL software is used to assess UCLs in fully censored and left-censored datasets with multiple detection limits, as is the case in this dataset. Exceedance fractions were calculated using IHDaataAnalyst software, version 1.0.1. (Exposure Assessment Solutions Inc., 2007). The exceedance fraction is the percentage of samples predicted to exceed the exposure limit (PEL or action level). Censored data analysis was conducted using robust log-probit regression for multiple LODs and Kaplan–Meier method (She, 1997; Helsel, 2005b). Compliance statistics, including exceedance fractions and confidence limits, were recorded. For datasets that were 100% censored, hypothesis testing was conducted for the 95th percentile of the OEL assuming a maximum probable geometric standard deviation (SD) of two.

RESULTS

The total number of beryllium samples collected by the industrial hygiene staff at the plant varied considerably by decade (Table 1). In the 1960s, when beryllium operations were first implemented, 4 personal and 174 area samples were collected. Fifty-four samples (2 personal and 52 area) were collected during the 1970s, 10 samples were collected during the 1980s (all personal), 148 samples were collected during the 1990s (110 personal and 38 area) and 190 samples (185 personal and 5 area) were collected during the year 2000. This trend, in which area samples were more prevalent historically but personal samples have been preferred more recently, has been observed in

many industrial hygiene datasets at facilities that handled significant quantities of beryllium. The trend may be because high-volume samples needed to be collected in early years to identify and control the point source in attempts to satisfy OSHA or other regulatory bodies, rather than conduct so-called ‘compliance sampling’ of the workers. Large sample volumes were also needed in the industry to obtain measurements above the LOD (Kolanz *et al.*, 2001).

Area air samples

Results for the area samples are presented in Table 2 and Fig. 3. Between 1964 and 2000, 68.8% of the 269 area samples were below the LOD for beryllium. The average airborne beryllium concentration in the area samples was $0.021 \mu\text{g m}^{-3}$ (SD $0.17 \mu\text{g m}^{-3}$; range $0.00012\text{--}2.5 \mu\text{g m}^{-3}$). The 95% UCL of airborne beryllium was $0.066 \mu\text{g m}^{-3}$. The exceedance fraction was 0.004 [95% confidence interval (CI): $<0.001\text{--}0.019$]. The lognormal continuous distribution of the data (Fig. 3) shows that the long-term samples were lower than the short-term samples, as would be expected. The samples, especially the long-term samples, were well below the OEL. There were five samples calculated as having concentrations of $2 \mu\text{g m}^{-3}$; however, in most cases, these levels were driven by the LOD for these samples. Four of the samples were reported to be $<2 \mu\text{g m}^{-3}$, so the LOD ($2 \mu\text{g m}^{-3}$) was used in our analysis of the range of beryllium reported. There was one long-term sample collected in 1992 that contained $2.5 \mu\text{g m}^{-3}$ beryllium, which was above the OEL of $2.0 \mu\text{g m}^{-3}$. This sample was reportedly taken during the preparation, application and teardown of components. The location of this sample relative to the position of workers performing the tasks in the area and any use of respiratory protection by workers in this area is unknown. No other samples were above the PEL during this time; in fact, the next highest sample recorded was $0.147 \mu\text{g m}^{-3}$.

The average airborne beryllium concentration from the long-term samples (>120 min, $n = 241$) was $0.023 \mu\text{g m}^{-3}$ (SD $0.179 \mu\text{g m}^{-3}$). The 95% UCL of the mean beryllium concentration was $0.074 \mu\text{g m}^{-3}$, and the exceedance fraction was 0.004 ($<0.001\text{--}0.020$). Samples taken in the area

Table 1. Number of personal and area samples of beryllium collected by decade

	Personal	Area
1960–1969	4	174
1970–1979	2	52
1980–1989	10	0
1990–1999	110	38
2000	185	5
Total	311	269

Table 2. Area samples collected for beryllium from 1964 through 2000

	<i>n</i>	Below LOD (%)	Minimum LOD ($\mu\text{g m}^{-3}$)	Maximum LOD ($\mu\text{g m}^{-3}$)	Minimum detect ($\mu\text{g m}^{-3}$)	Maximum detect ($\mu\text{g m}^{-3}$)	Mean ^a ($\mu\text{g m}^{-3}$)	SD ^a ($\mu\text{g m}^{-3}$)	95% UCL ^b ($\mu\text{g m}^{-3}$)	Exceedance fraction (95% CI)
All area samples ^c	269	68.8	0.00015	2.0	0.00012	2.5	0.021	0.17	0.066	0.004 (<0.001–0.019)
1–120 min	14	92.9	0.020	0.72	0.00012	0.00012	NA ^d	NA ^d	NA ^d	NA ^d
>120 min	241	66.4	0.00015	2.0	0.00012	2.5	0.023	0.179	0.074	0.004 (<0.001–0.020)
Unknown sample time	14	85.7	0.0006	0.083	0.0029	0.04	0.0058	0.010	0.023	NA ^d
Machinist area samples	8	100.0	0.007	0.08	NA ^e	NA ^e	NA ^e	NA ^e	NA ^e	NA ^e
1–120 min	—	—	—	—	—	—	—	—	—	—
>120 min	8	100.0	0.007	0.08	NA ^e	NA ^e	NA ^e	NA ^e	NA ^e	NA ^e
Unknown sample time	—	—	—	—	—	—	—	—	—	—

NA = Not applicable.

^aEstimated using the Kaplan–Meier method for censored datasets.

^bEstimated using the Kaplan–Meier method and the Chebyshev inequality.

^cExcluded 1 sample with abnormally low detection ($0.0000008 \mu\text{g m}^{-3}$).

^dCould not be calculated due to small number of detectable samples.

^eAll ND samples.

of machinists were analyzed separately. All eight area samples taken near machinists and analyzed for beryllium resulted in beryllium concentrations below the LOD (range <0.007 to $<0.08 \mu\text{g m}^{-3}$).

Personal air samples

Personal samples were analyzed to estimate the mean airborne concentration, SD, and range for the typical worker. As is standard practice, these samples were collected on a worker's lapel during machining of CuBe alloy components and during maintenance and decontamination activities. The results are reported in Table 3. The vast majority (97.4%) of the personal samples did not detect beryllium in the air surrounding the worker (i.e. results were below the analytical LOD). All personal samples, including short-term samples, were well below OSHA's beryllium PEL of $2 \mu\text{g m}^{-3}$. In total, 97.4% of the personal samples taken from 1964 through 2000 ($n = 311$) were below the LOD. The range of airborne beryllium was 0.019 – $0.8 \mu\text{g m}^{-3}$. The mean beryllium concentration was $0.026 \mu\text{g m}^{-3}$ (SD $0.059 \mu\text{g m}^{-3}$) and the 95% UCL was $0.042 \mu\text{g m}^{-3}$. The exceedance fraction was 0.0025 (95% CI: 0.001–0.005). This value may be somewhat conservative (i.e., overestimates the actual exposure) because it is based upon all available samples, including short-term and task-based samples. For long-term samples (>120 min, $n = 259$), the airborne beryllium mean concentration was $0.021 \mu\text{g m}^{-3}$ (SD $0.027 \mu\text{g m}^{-3}$), the 95% UCL was $0.030 \mu\text{g m}^{-3}$. The exceedance fraction could not be determined because of the low number of detectable samples. In total, 98.1% of the long-term samples were below the analytical LOD. However, the lognormal continuous distribution of the data (Fig. 3) shows that these samples were well below the OEL.

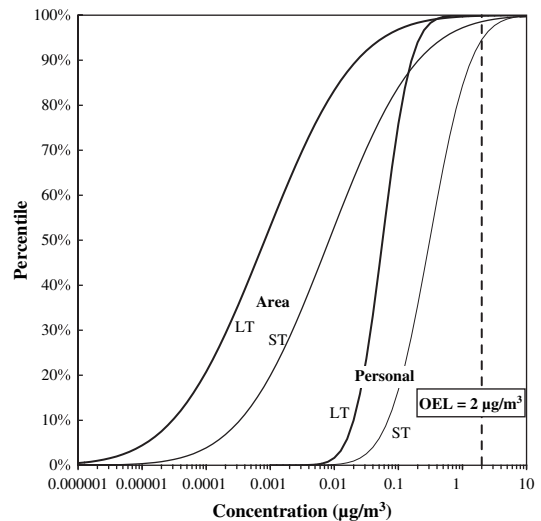


Fig. 3. Lognormal continuous distributions of long-term (heavy curves) and short-term (light curves) area and personal samples. The vertical dashed line represents the OEL of $2 \mu\text{g m}^{-3}$.

In January 2000, the DOE action level of $0.2 \mu\text{g m}^{-3}$ was adopted. A total of 185 personal samples were collected in 2000 as part of a plant-wide survey, none of which exceeded the new action level (Table 3). Long-term personal samples collected in 2000 ($n = 177$) were all below detection limits (range <0.04 to $<1.0 \mu\text{g m}^{-3}$), and therefore the exceedance fractions could not be calculated. Hypothesis testing rejected the hypothesis that the true 95th percentile is $\geq 0.2 \mu\text{g m}^{-3}$ ($P = 0.000114$). Assuming that the testing was adequate and representative, which was the view of the hygienists, it is very unlikely that airborne beryllium levels exceeded the DOE action level of $0.2 \mu\text{g m}^{-3}$ during that year.

Task-based samples

As is the general practice in industrial hygiene, the bulk of the sampling was focused on those tasks where exposures were considered the highest. An analysis of tasks that have historically been associated with higher levels of exposure was performed using all available

samples from 1964 through 2000 (Table 4). For example, an analysis of 145 personal samples taken during decontamination activities found that 100% of the samples were below the LOD (range <0.05 to <1 $\mu\text{g m}^{-3}$). Hypothesis testing of the 130 long-term personal samples taken during decontamination activities indicated that

Table 3. Personal samples collected for beryllium between 1964 and 2000

	<i>n</i>	Below LOD (%)	Minimum LOD ($\mu\text{g m}^{-3}$)	Maximum LOD ($\mu\text{g m}^{-3}$)	Minimum detect ($\mu\text{g m}^{-3}$)	Maximum detect ($\mu\text{g m}^{-3}$)	Mean ^a ($\mu\text{g m}^{-3}$)	SD ^a ($\mu\text{g m}^{-3}$)	95% UCL ^b ($\mu\text{g m}^{-3}$)	Exceedance fraction (95% CI)
All personal samples ^c	311	97.4	0.007	2	0.019	0.8	0.026	0.059	0.042	0.0025 (0.001–0.005)
1–120 min ^c	42	97.6	0.060	2	0.51	0.51	NA ^d	NA ^d	NA ^d	NA ^d
>120 min	259	98.1	0.007	1.6	0.019	0.34	0.021	0.027	0.030	NA ^d
Unknown sample time	10	80.0	0.01	1	0.14	0.8	0.223	0.218	0.698	0.0018 (<0.001–0.051)
Personal samples from 2000	177	100	0.04	1.0	NA ^e	NA ^e	NA ^e	NA ^e	NA ^e	NA ^e

NA = Not applicable.

^aEstimated using the Kaplan–Meier method for censored datasets.

^bEstimated using the Kaplan–Meier method and the Chebyshev inequality.

^cTwo outlying samples were omitted because they involved the release of beryllium oxide.

^dCould not be calculated due to small number of detectable samples.

^eAll ND samples.

Table 4. Task-based personal samples (1964–2000) collected for beryllium

	<i>n</i>	ND (%)	Minimum LOD ($\mu\text{g m}^{-3}$)	Maximum LOD ($\mu\text{g m}^{-3}$)	Minimum detect ($\mu\text{g m}^{-3}$)	Maximum detect ($\mu\text{g m}^{-3}$)	Mean ^a ($\mu\text{g m}^{-3}$)	SD ^a ($\mu\text{g m}^{-3}$)	95% UCL ^b ($\mu\text{g m}^{-3}$)	Exceedance fraction (95% CI)
Decontamination	145	100.0	0.05	1	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
1–120 min	14	100.0	0.2	1	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
>120 min	130	100.0	0.05	0.2	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
Unknown sample time	1	100.0	0.5	0.5	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
Machining	78	97.4	0.007	0.5	0.019	0.14	0.021	0.014	0.031	NA ^d
1–120 min	8	100.0	0.06	0.5	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
>120 min	68	98.6	0.007	0.1	0.019	0.019	NA ^d	NA ^d	NA ^d	NA ^c
Unknown sample time	2	50.0	0.02	0.02	0.14	0.14	NA ^d	NA ^d	NA ^d	NA ^c
Dry machining	5	100.0	0.061	0.544	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
1–120 min	1	100.0	0.061	0.061	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
>120 min	3	100.0	0.071	0.544	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
Unknown sample time	1	100.0	0.354	0.354	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
Grinding	8	87.5	0.001	1	0.51	0.51	NA ^d	NA ^d	NA ^d	NA ^d
1–120 min	4	75.0	0.001	1	0.51	0.51	NA ^d	NA ^d	NA ^d	NA ^d
>120 min	3	100.0	0.05	0.06	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
Unknown sample time	1	100.0	0.30	0.30	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
Deburring	3	100.0	0.15	0.68	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
1–120 min	3	100.0	0.15	0.68	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c	NA ^c
Machining, deburring, grinding, machining dry	94	97.8	0.001	1.0	0.019	0.51	0.51	0.052	0.544	NA ^d
1–120 min	12	91.7	0.001	1.0	0.51	0.51	NA ^d	NA ^d	NA ^d	NA ^d
>120 min	78	98.7	0.007	0.68	0.019	0.019	NA ^d	NA ^d	NA ^d	NA ^d
Unknown sample time	4	75	0.02	0.5	0.14	0.14	NA ^d	NA ^d	NA ^d	NA ^d

NA = Not applicable.

^aEstimated using the Kaplan–Meier method for censored datasets.

^bEstimated using the Kaplan–Meier method and the Chebyshev inequality.

^cAll ND samples.

^dCould not be calculated due to small number of detectable samples.

the hypothesis that the true 95th percentile of airborne beryllium is $>0.2 \mu\text{g m}^{-3}$ was rejected ($p = 0.00127$).

Machining of CuBe (as opposed to pure beryllium) has historically been considered a task that did not produce significant concentrations of airborne beryllium. In this study, personal samples of machinists ($n = 78$) had a mean beryllium concentration of $0.021 \mu\text{g m}^{-3}$ (SD $0.014 \mu\text{g m}^{-3}$) and a range of $0.019\text{--}0.14 \mu\text{g m}^{-3}$. In total, 97.4% of personal machinist samples were below the LOD and the airborne beryllium 95th UCL was $0.031 \mu\text{g m}^{-3}$. The exceedance fraction could not be calculated because of the low number of detectable samples. Stratified by sample duration, there were eight short-term beryllium samples (<120 min) collected during machining, and these were all below the LOD (range <0.06 to $<0.5 \mu\text{g m}^{-3}$). Long-term samples (>120 min, $n = 68$) ranged from <0.007 to $<0.1 \mu\text{g m}^{-3}$ beryllium, and only one sample was above the LOD ($0.019 \mu\text{g m}^{-3}$). There was one additional detectable sample from machining that was collected for an unknown period of time ($0.14 \mu\text{g m}^{-3}$). There were also five personal samples taken during dry machining, assumed to be during machine setup. These samples were all below the LOD, which ranged from <0.061 to $<0.544 \mu\text{g m}^{-3}$. Personal samples taken during deburring ($n = 3$) were all below the LOD (range <0.15 to $<0.68 \mu\text{g m}^{-3}$). During grinding, only one of eight personal samples was above the LOD— a short-term sample with a beryllium concentration of $0.51 \mu\text{g m}^{-3}$. All the long-term samples were below the LOD for grinding.

Personal samples taken during machining, deburring, grinding, and dry machining were also analyzed as a group ($n = 94$). The average beryllium concentration for these samples was $0.51 \mu\text{g m}^{-3}$ (SD $0.052 \mu\text{g m}^{-3}$), with a range of $0.019\text{--}0.51 \mu\text{g m}^{-3}$. In total, 97.8% of the samples were below the LOD (range <0.001 to $<1.0 \mu\text{g m}^{-3}$) and the 95th UCL was $0.544 \mu\text{g m}^{-3}$. The exceedance fraction could not be calculated because of the low number of detectable samples. When stratified by time, the short-term samples ($n = 12$) ranged from <0.001 to $<1.0 \mu\text{g m}^{-3}$, and only one sample was above the LOD ($0.51 \mu\text{g m}^{-3}$). The long-term samples ($n = 78$) had one detectable sample at $0.019 \mu\text{g m}^{-3}$. The remaining samples (98.7%) were below the LOD, with a range from <0.007 to $<0.68 \mu\text{g m}^{-3}$ beryllium.

DISCUSSION

Based on the historical data collected at this facility, airborne concentrations of beryllium during machining of CuBe alloys were well below the OSHA PEL and DOE action level for the 40 years this operation was studied. For more than two-thirds of all samples, airborne concentrations of beryllium were below analytical LODs, particularly during the later

years (post-1980). In total, 68.8% of area samples and 97.4% of personal samples were below the LOD. A shift from predominantly area samples in the 1960s and 1970s to collection of personal samples was evident in this analysis, and is consistent with the general evolution of industrial hygiene programs during this time period.

Although there are relatively few records providing significant detail of industrial hygiene controls prior to 1990 at this facility, this analysis indicates that the airborne concentrations would not have been considered a significant occupational hazard at the time. This finding is consistent with what has been reported elsewhere (Kolaniz, 2001). By and large, concern about the health hazards of beryllium increased during the 1990s in the industry and work practices improved. Accordingly, documentation of sampling conditions at this facility improved considerably by 1990 and sample sheets clearly described the use of industrial hygiene control and personal protective equipment (PPE) after 1990 and 1998, respectively. By the late 1990s, local exhaust ventilation was installed in all areas using CuBe, flood coolant was used during the vast majority of machining operations, and use of PPE was common during decontamination procedures.

It has been noted previously that the use of good housekeeping and wet methods during machining of CuBe alloys can keep airborne beryllium concentrations well below the current PEL ($2 \mu\text{g m}^{-3}$) (Rossman *et al.*, 1991; Schuler *et al.*, 2005). However, what has been considered a 'safe' or tolerable airborne concentration of beryllium has evolved over time, and especially since 1999, there has been concern that perhaps any measurable concentration can increase the risk of sensitization in susceptible individuals.

Historically, machining of beryllium alloys has been considered much less hazardous than other operations because there is considerably reduced potential for exposure to respirable particles (Hoover *et al.*, 1990; Kreiss *et al.*, 1997). For example, the total aerosol production rate during milling or sawing of beryllium alloys is 10-fold lower than milling or sawing beryllium metal, possibly due to the brittle nature of the pure metal. This, coupled with the lower percentage of beryllium in the alloy (2–4%) compared to pure beryllium metal (100%), results in a much lower hazard (>500 -fold less) for the alloyed forms of beryllium (Hoover *et al.*, 1990). Beryllium alloy machining operations that are considered to have little exposure potential include drawing, stamping, bending, sawing, turning, tapping, boring, drilling, milling or reaming. The use of industrial hygiene controls such as flood coolant or local exhaust ventilation has been known for many years to significantly reduce airborne beryllium concentrations during operations such as sanding, grinding, polishing, honing, abrasive sawing and lapping (Rossman *et al.*, 1991).

Industrial hygiene controls varied over time at this facility, as is consistent with industry as a whole. Based on industrial hygiene sample sheets, it is clear that from ~1990 to the present, most machining and finishing operations were conducted using local exhaust ventilation and/or wet methods or, in some cases, were performed in some sort of enclosed housing. Local exhaust was used for some deburring or polishing operations. However, given the lack of detail in the earlier sample documentation, it is not certain precisely when these controls were implemented. The frequency of the use of PPE, in particular respirators and protective clothing, increased over time, especially after ~1990. By and large, the actual exposure of workers was less than reported here, especially for samples collected after ~1990, when respirator use was more common, particularly for decontamination activities.

This study summarizes airborne beryllium concentrations in a facility that machined CuBe alloys. With the possible exception of one small project in the early 1960s, the facility did not machine other forms of beryllium. The industrial hygiene records described here were collected over 3½ decades and provide a relatively large dataset for analysis ($n = 580$), including area, personal and task-based samples collected during a variety of tasks such as deburring, decontamination, machining and grinding. To date, there have been few studies that have documented exposure levels to workers handling CuBe exclusively, despite the fact that this is the primary form of beryllium encountered in the workplace today. Although this dataset is somewhat limited because of the large percentage of samples that were below the LOD, it nonetheless is valuable for those who seek to understand historical exposure conditions under certain scenarios, and, in many workplaces, the information may still be relevant. Changes in industrial hygiene practices (as well as the nature of record keeping) over time at this facility are consistent with trends in the industrial hygiene community as a whole. Furthermore, the increase in sample collection was consistent with the realization in the 1990s that the PEL may not be as protective as previously thought, as well as with the implementation of DOE's Chronic Beryllium Disease Prevention Program.

CONCLUSION

The analysis of personal and area historic beryllium samples at a facility that machines copper beryllium alloys indicates that exposure to beryllium was well below the OSHA PEL from the start of operations in 1964 through 1999. In 2000, the DOE imposed an action level of $0.2 \mu\text{g m}^{-3}$, and the samples taken in 2000 were all below this new guideline. This analysis confirms that flood coolant and ventilation can maintain concentrations of airborne beryllium below both his-

toric and current exposure guidelines during typical machining operations involving copper beryllium alloy.

FUNDING

Funding for the quality assurance/quality control of this database and analysis of the industrial hygiene sampling data was provided by Honeywell Federal Manufacturing & Technologies LLC; preparation of this manuscript was funded by ChemRisk.

Acknowledgements—The database used for this analysis was created and maintained by Honeywell Federal Manufacturing & Technologies LLC. One of the authors (D.J.P.) has served as an expert witness in litigation associated with occupational exposure to beryllium. The authors would also like to acknowledge Jeff Clarke for his assistance with data entry and quality assurance/quality control of the database.

The manuscript has been authored with the assistance of, and contains data provided by, Honeywell Federal Manufacturing & Technologies LLC, under Contract No. DE-AC-04-01AL66850 with the US DOE. Honeywell Federal Manufacturing & Technologies LLC retains a copyright in this manuscript. The US Government retains, and the publisher, by accepting the article for publication, acknowledges that the US Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or to allow others to do so, for US Government purposes.

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