

**HETA 94-0077-XXXX**  
**April 1996**  
**Lockheed Martin Utility Services, Inc.**  
**Piketon, Ohio 45661**

**NIOSH INVESTIGATORS:**  
**Steven H. Ahrenholz, Ph.D., CIH**

### **SUMMARY**

On November 30, 1993, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a Health Hazard Evaluation (HHE) to evaluate worker exposures to arsenic in the uranium enrichment process of the Lockheed Martin Utility Systems, Inc. (LMUS), gaseous diffusion plant in Portsmouth, Ohio. The request sought evaluation of arsenic exposure which may occur when opening process equipment, or working on equipment removed from the process. Arsenic was first determined in process equipment in October 1993. Worker representation was provided by the Oil, Chemical, and Atomic Workers and United Plant Guard Workers of America unions.

NIOSH investigators conducted an industrial hygiene survey to address potential arsenic exposures March 1-4, 1994. A limited number of area air samples were obtained for uranium and radon. Opening and closing conferences were held with both management and labor representatives. Arsenic results and recommendations were distributed in an interim report to all parties June 28, 1994.

Arsenic samples were collected in the process building where arsenic has been known to accumulate in the production equipment. Additional samples were obtained in a maintenance facility where welding was performed on equipment removed from the process. The time weighted average (TWA) results over the sampling period for seven area samples ranged from below detectable levels (nondetectable or ND) up to 0.7  $\mu\text{g}/\text{m}^3$  of arsenic. Fourteen worker personal breathing zone (PBZ) exposure samples ranged from ND to 109  $\mu\text{g}/\text{m}^3$  of arsenic. Only six PBZ samples were above detectable levels with an average of 25  $\mu\text{g}/\text{m}^3$  of arsenic. All six of these workers wore protective clothing and supplied-air respirators required for their task. The NIOSH recommended exposure limit is 2  $\mu\text{g}/\text{m}^3$ , and to maintain levels as low as feasible due to its classification as an occupational carcinogen.

Four uranium area samples were also collected on-site. TWA results over the sampling period ranged from 0.1 to 1.1  $\mu\text{g}/\text{m}^3$  of total uranium. The NIOSH REL for soluble uranium, the form present, is 50  $\mu\text{g}/\text{m}^3$ . NIOSH regards uranium as an occupational carcinogen and recommends that airborne levels be maintained as low as feasible.

Recommendations include: continued exposure monitoring and exposure control aimed at keeping exposures as low as feasible; a re-evaluation of the suitability of using an air-purifying respirator for work on arsenic contaminated equipment that has been radiologically decontaminated; and avoiding the re-use of personal protective equipment that is not radiologically contaminated but may be contaminated with arsenic compounds.

The results of this NIOSH HHE demonstrate that the potential for worker exposures to arsenic in excess of the NIOSH REL of 2  $\mu\text{g}/\text{m}^3$  exists for personnel involved directly with performing maintenance activities on the uranium enrichment equipment in the X-326 process building. All workers encountering elevated airborne arsenic concentrations were using protective clothing and supplied-air respiratory protection. Protective measures in use against radiological contamination are considered adequate against the arsenic exposures encountered. Recommendations pertaining to exposure evaluation efforts and protective equipment considerations are provided on pages 18-19 of this report.

**KEYWORDS:** SIC 2819 (industrial inorganic chemicals, not elsewhere classified), gaseous diffusion, uranium enrichment, arsenic (CAS# 7440-38-2), uranium (CAS# 7440-61-1, 24678-82-8), uranium hexafluoride (CAS# 7783-81-5), hydrogen fluoride (CAS# 7664-39-3), contaminated process feed materials.

## **INTRODUCTION**

On November 30, 1993, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a Health Hazard Evaluation (HHE) to evaluate worker exposures to arsenic contamination present in the uranium enrichment equipment at the Lockheed Martin Utility Systems, Inc. (LMUS), Portsmouth, Ohio, gaseous diffusion plant. (Note that at the time of the HHE request submission, the facility was Martin Marietta Utility Systems.) Worker representation was provided by the two bargaining units at this site, Local 3-689 of the Oil, Chemical, and Atomic Workers Union International (OCAW) and Local 66 of the United Plant Guard Workers of America (UPGWA). The request primarily concerned the activities of the OCAW membership involved in operations and maintenance work on the uranium enrichment process equipment. Job titles identified to be of concern included: process operators, welders, maintenance mechanics, instrument mechanics, and chemical operators. The presence of arsenic in the process equipment on-site was first discovered in October 1993.

The LMUS Portsmouth Gaseous Diffusion Plant (PORTS) located in Piketon, Ohio, came under the jurisdiction of the Department of Labor's Occupational Safety and Health Administration (OSHA), from the Department of Energy (DOE) as a result of the Energy Policy Act of 1992.<sup>1</sup> This act mandated that on July 1, 1993, the DOE-owned gaseous diffusion plants be transferred to the United States Enrichment Corporation (USEC), a congressionally-established government-owned corporation which will operate the United States' uranium enrichment facilities.<sup>1</sup> Because the PORTS facility became subject to the OSHA Act, the workforce could submit a request for a HHE to NIOSH under section 20 (a) (6) of this act. NIOSH investigators conducted a site visit to evaluate worker exposures to arsenic March 1-4, 1994. Opening and closing conferences were held with management and labor representatives March 1 and 4, 1994, regarding the HHE activities. Limited sampling for uranium was also performed during this survey as a part of background work applicable to a separate NIOSH mortality study in progress at the site, under a Memorandum of Understanding between DOE and the Department of Health and Human Services (DHHS)-NIOSH.<sup>2</sup> An interim report presenting the arsenic sampling results along with recommendations was distributed to LMUS management, OCAW Local 3-689, and UPGWA Local 66 representatives June 28, 1994.

## **BACKGROUND**

The LMUS PORTS is one of two operating uranium enrichment production facilities in the United States. LMUS operates PORTS located in Piketon, Ohio and the Paducah Gaseous Diffusion Plant (PGDP) located in Paducah, Kentucky under contract to the USEC. Each plant utilizes the gaseous diffusion process to enrich uranium from a natural state of 0.7% <sup>235</sup>U up to higher concentrations of <sup>235</sup>U which historically have ranged from 2% to greater than 97%. The LMUS PORTS has discontinued high assay <sup>235</sup>U production and currently produces a product that is in the range of 2 to 5% for use as fuel rods in commercial nuclear power generation.<sup>3</sup> The assay of the material is the determination of the amount by weight of fissionable material (<sup>235</sup>U) present in the enriched uranium by physical or chemical measurements.<sup>4</sup>

### **Process**

Production of enriched uranium at PORTS began in 1955. The two gaseous diffusion plants (PORTS and PGDP) have been operated in a complementary mode. The Paducah facility performs the initial enrichment of uranium up to about 1 to 2% <sup>235</sup>U. This material serves as a feedstock for PORTS. The PORTS facility also utilizes the same feed materials supplied by the uranium conversion facilities that PGDP receives. The uranium enrichment process uses uranium in the form of gaseous uranium hexafluoride (UF<sub>6</sub>). The uranium enrichment process used at this facility, also referred to as gaseous diffusion, uses a physical separation process. Lighter molecules of UF<sub>6</sub> containing the <sup>235</sup>U atom or isotope diffuse more rapidly through a porous barrier in the system, leaving behind a gas stream with a slightly higher concentration of UF<sub>6</sub> molecules containing the <sup>238</sup>U atom. The degree of isotope separation at any one stage of the process is very small because of the small difference in molecular weight of the two uranium hexafluoride isotopes (349 vs 352).

The process equipment is an assembly of thousands of separative stages. The separative equipment consists of a compressor, converter, and motor which comprises a stage arrangement; a number of stages are assembled into a "cell", containing between eight and 12 stages. Between 10 and 20 cells are assembled to form a functional unit. These cells are linked together in series completing the formation of the "cascade" for uranium enrichment. The PORTS' several thousand stages are housed in three interconnected buildings. Each cascade building has two floors, each floor covering approximately 1.5 million square feet.<sup>3,5</sup> The overall configuration results in a flow of increasingly enriched UF<sub>6</sub> (<sup>235</sup>U) toward the top of the process. Depleted UF<sub>6</sub> (<sup>238</sup>U) flows toward the bottom or "tails" end of the process.

Uranium hexafluoride is delivered to and shipped from the facility in the solid phase. Because UF<sub>6</sub> is a solid at room temperature, the diffusion plant must be operated at temperatures and pressures that maintain the material in the gaseous state. Product withdrawal involves the condensation of gaseous UF<sub>6</sub> into cylinders for shipment.

### **Process Contaminants: Sources**

PORTS has been in continuous operation since 1955. Various contaminants and "light" gases have entered the process from a variety of sources over time. Acidic gases (e.g., fluorine, chlorine trifluoride, etc.) enter the cascade through process equipment maintenance activities. Chlorofluorocarbon (CFC) from the cascade cooling system equipment also escapes into the process. The presence of contaminants in process feed materials, and originating as a part of the decay series of uranium, may also contribute to the chemical agents present within the cascade process equipment.

The UF<sub>6</sub> in gaseous or liquid form, is extremely reactive with water, and slightly corrosive to most common metals. It is incompatible with organic materials such as lubricating oils.<sup>6</sup> The introduction of moisture into the system through small leaks (e.g., pinhole) results in the

formation of solid deposits within the system because of the reaction of various fluoride containing compounds due to the combination of water vapor and process gas (PG), another term for UF<sub>6</sub>.

### **Discovery of Arsenic in the Cascade:**

Arsenic and arsenic-containing compounds were not among the chemicals historically evaluated in the feed UF<sub>6</sub> analyses, within process samples, in tests of purged process equipment for residual gases, or in the gases from the process released to the atmosphere. Arsenic-containing materials present within the uranium enrichment process equipment were first discovered when blocked copper instrument lines from the X-25-7-2 cell in the X-326 building were opened revealing a pale yellow-white viscous material similar to butter or taffy. The material released a green smoke upon exposure to atmospheric moisture. The remaining residue was highly hygroscopic. Analyses of the material by the PORTS on-site laboratory indicated that the original deposit may have been ClO<sub>2</sub>·AsF<sub>6</sub> (chlorylarsenic hexafluoride) or [AsCl<sub>4</sub><sup>+</sup>][AsF<sub>6</sub><sup>-</sup>] (arsenic tetrachloride-arsenic hexafluoride). The hygroscopic reaction product was identified to be an arsenic oxide, e.g., As<sub>2</sub>O<sub>5</sub>. A second deposit in cell X-27-1-15 appeared as a light green material that released a white smoke upon exposure to atmospheric moisture. This second deposit, when immersed in water in the lab, reacted vigorously while forming an acidic solution (pH = 2). The PORTS laboratory reported that the compounds contained high levels of copper and chlorine. Although this second deposit differed in some respects from the first deposit in the X-25-7-2 instrument line, the material was also considered to be potentially ClO<sub>2</sub>·AsF<sub>6</sub> or [AsCl<sub>4</sub><sup>+</sup>][AsF<sub>6</sub><sup>-</sup>].<sup>7</sup>

X-ray diffraction analyses were performed by PORTS' on-site laboratory on the solids remaining from these initial samples after the hydrolyzed material had been dried at ~90 °C. The diffraction patterns for each residual solids sample were similar. The crystalline material was identified as H<sub>5</sub>As<sub>3</sub>O<sub>10</sub> (hydrogen arsenate) and Cu<sub>2</sub>As<sub>2</sub>O<sub>7</sub> (copper arsenate). Solid material from a valve in cell X-25-7-2 and a copper tube from X-27-1-15 was identified as Cu<sub>2</sub>As<sub>2</sub>O<sub>7</sub>.<sup>8</sup> Copper was considered to be a "getter" for arsenic, thus the accumulation of arsenic-containing compounds in copper process components.<sup>9</sup> Gettering is the absorption of gas by a getter film. The getter film may be a metallic deposit on a surface.<sup>10</sup>

Laboratory personnel at PGDP, which provides feed UF<sub>6</sub> for PORTS, indicated that PORTS was probably seeing AsF<sub>5</sub> (arsenic pentafluoride) complexed with HF, a metal, or other compound.<sup>7</sup> A high AsF<sub>5</sub> concentration was identified in the cascade process equipment in the X-326 building in the vicinity of high CFC concentrations, near the top end of the cascade process. The highest concentration of AsF<sub>5</sub> identified inside of the process equipment was 3800 parts per million (ppm) at the X-25-7-9 cell in X-326.<sup>11</sup> This level at this point inside the system represents an arsenic concentration of several hundred milligrams of arsenic per cubic meter (mg/m<sup>3</sup>) of gas. This conversion to a milligram value for arsenic assumes cell operating conditions of an internal pressure of 1.2 pounds per square inch absolute, a 200 °F operating temperature, and an average process power consumption of 1900 Megawatts.<sup>6</sup>

**Arsenic in the Cascade Process-An Unsuspected Contaminant:**

PORTS process engineers have determined that arsenic entered the cascade process as an impurity in the UF<sub>6</sub> feed material. Arsenic would have been introduced into the UF<sub>6</sub> produced through the fluorination of UF<sub>4</sub> (uranium tetrafluoride) or U<sub>3</sub>O<sub>8</sub> (uranium octoxide) with arsenic contaminated fluorine (F<sub>2</sub>). The arsenic would have been present in the fluoride-bearing ore used to produce the HF and F<sub>2</sub> with incomplete removal of the arsenic. The introduction of the arsenic contaminated UF<sub>6</sub> is suspected to have occurred during the 1980's. On-site generated F<sub>2</sub> is considered to be arsenic free even if arsenic has been present in HF received by the site since in-line trapping of contaminants would remove arsenic compounds prior to the F<sub>2</sub> use by the site. This latter potential source has been evaluated and is not considered a contributor to arsenic contamination in the cascade process. The supplier of feed material that had shipped UF<sub>6</sub> containing significant arsenic during the 1980's reportedly took action to improve operations and reduce arsenic contamination by 1990.<sup>7</sup> The site also implemented testing of incoming PGDP product UF<sub>6</sub> to determine if arsenic was being fed into the cascade in measurable quantities.<sup>11</sup>

Arsenic compounds are also considered to reside in solid UO<sub>2</sub>F<sub>2</sub> (uranyl fluoride) deposits within the cascade equipment. These deposits would volatilize arsenic during the course of cell treatments to remove uranium residues.<sup>12</sup> PORTS has sought to identify other locations and equipment throughout the cascade process that may have potential for arsenic contamination and worker exposures. Concerns regarding the presence of arsenic in sludges from heavy metal recovery and microfiltration in the decontamination building were also raised. PORTS determined that this material did not present a hazard because the material was not likely to become airborne and contained a very low concentration of arsenic (less than 0.003% by weight).<sup>11,13</sup>

**Engineering and Personal Protective Equipment Controls:**

The primary activities associated with potential exposures to arsenic are opening PG systems for maintenance, dismantling process equipment, and working on arsenic contaminated equipment. The cascade process is a closed process. Equipment taken off line for maintenance or cell treatment is purged of its contents prior to work being performed. Sampling is conducted on the residual gases present within the off stream equipment to assure that the purging process has been adequate.

The presence of radioactive contaminants and the generation of HF vapor when residual UF<sub>6</sub> combines with moisture in the air requires personal protective equipment (PPE) against these hazards. Supplied-air respirators, full-face mask or hood, anticontamination (anti-Cs) coveralls, polyvinyl chloride (PVC) or rubber gloves, and PVC booties were worn by workers performing maintenance activities on the cascade process. Additional PPE included plastic coated Tyvek™ coveralls, welder's hood, flame retardant coveralls, and self-contained breathing apparatus available for use depending upon the activity and location on the process equipment.

LMUS-PORTS requirements for PPE change when equipment with potential arsenic-containing deposits (as well as other materials) has been wet-decontaminated (decontaminated) or exposed to atmospheric moisture. If the release or generation of significant gaseous arsenic compounds or high levels of particulate arsenic is unlikely, the following minimum PPE is recommended by PORTS: an MSA full-face mask with GMHF-C HEPA/acid gas canister (used routinely for protection against UF<sub>6</sub>); anti-C's (routinely used for protection from radionuclides); rubber gloves; and, booties. PORTS notes that the MSA full-face mask with GMHF-C canister is not only effective against radionuclides and HF, but is also effective against arsenic (in gaseous and particulate forms).<sup>7</sup> A written opinion from MSA indicates that this respirator would be effective against the contaminants for which use of the GMHF-C canister was proposed. MSA identified in a letter to LMUS that the Occupational Safety and Health Administration (OSHA) in Table II of the inorganic arsenic standard (29 CFR 1910.1018) permits the use of gas masks equipped with a high efficiency filter and acid gas canister for inorganic arsenicals with significant vapor pressure.<sup>14</sup> Airborne inorganic arsenic concentrations under these conditions of use may not exceed 500 µg/m<sup>3</sup>.<sup>15</sup>

## **EVALUATION METHODS**

### **Airborne Chemical Contaminants:**

The NIOSH site visit conducted March 1-4, 1994, consisted of personal exposure and area air monitoring for total arsenic and uranium. A coinciding NIOSH mortality study had provided the NIOSH investigators previous opportunities to conduct walk-through surveys of the areas of interest. Security access limitations and logistics, health physics surveys of sampling equipment and samples for radiological contamination before and after sample collection, and the identification of maintenance work activities necessitated additional on-site survey preparation time. The potential for radiological contamination of NIOSH equipment required that additional measures be taken prior to, during, and after the sampling activities to permit the removal of equipment and samples from the site. De-briefing of NIOSH investigators, a review of information collected with the site classification officer, and arrangements for the handling and shipment of radiologically-contaminated industrial hygiene samples were conducted at the completion of the survey. Sampling was conducted during the first and second shifts on March 2 and 3, 1994. A LMUS industrial hygiene technician conducted parallel sampling for a number of the personal and area samples collected by NIOSH investigators.

### **Total Arsenic:**

Preparatory information obtained from the site regarding the arsenic compounds potentially present indicated that arsenic may be present as several different chemical species, in both the gaseous and particulate phases. LMUS had been using NIOSH Sampling and Analytical Method 7901 with modifications to assess airborne arsenic exposures.<sup>16</sup> NIOSH Method 7901 collects particulate arsenic compounds and arsenic trioxide vapor.<sup>17</sup> The analyte evaluated is total arsenic. Because a gaseous form of arsenic, AsF<sub>5</sub>, was possibly present, several area samples

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were collected incorporating NIOSH Method 6001 for arsine. This method also measures total arsenic and may collect other arsenic compounds besides arsine, present in the gaseous state or an aerosol form.<sup>17</sup> The specifics regarding the two methods are presented in the following paragraphs along with the descriptions of the sampling trains.

### **Arsenic: NIOSH Methods 7901 and 6001**

#### **Sampling Train Description:**

All PBZ exposures for arsenic compounds were evaluated using a sampling train that consisted of an SKC<sup>®</sup> 224-PCXR8 Personal Sampling Pump operating at a flow rate of approximately 3.6 liters per minute (Lpm) and a sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) impregnated 0.8 micrometer (μm) cellulose ester membrane filter and backup pad. The Millipore<sup>®</sup> filter and backup pad were impregnated and tested for the passage of air through the treated filters by the NIOSH Measurement Research Support Branch laboratory. Filter cassettes were connected to the sampling pump by a length of Tygon<sup>®</sup> tubing. All pumps (personal and area samplers) were placed inside plastic ZipLoc<sup>®</sup> bags or wrapped in plastic to reduce the possibility of radiological surface contamination. Pumps were secured to a belt or in a pocket of the worker's coveralls inside of the Anti-C clothing. Only the cassette and the several inches of tubing at the cassette end of the sampling train were placed outside of the workers' protective clothing on their lapels.

Area air samples for arsenic compounds utilized the same sampling pump as the personal exposure samples, but with an average flow rate of 2 Lpm. This allowed for equal flow rates for the filter-only sampling train (equivalent to that worn by the workers) and the sampling train which included a standard coconut shell charcoal tube (100 milligram (mg)/50 mg front/backup sections) in-line directly behind the impregnated filter cassette. This second sampling train, as previously mentioned, was intended to explore the possibility of gaseous arsenic compounds passing through the impregnated filter. All area sample filters were mounted between four and six feet above surrounding walking surfaces.

#### **NIOSH Method 7901: Arsenic Trioxide as As**

All filter samples for arsenic were digested and analyzed according to NIOSH Method 7901.<sup>17</sup> These samples were analyzed using a Perkin-Elmer Zeeman 5100 Graphite Furnace Atomic Absorption (AA) Spectrophotometer.

The following modifications of the sample preparation were utilized. Fifteen milliliters (mL) of concentrated nitric acid were added to each beaker after filters were transferred to 125 mL Phillips beakers. The samples were heated and reduced on hotplates to approximately 1 mL in volume. Six mL of 30% hydrogen peroxide was added to each beaker. The samples were heated and reduced on hotplates. The samples were then brought to volume in 25 mL volumetric flasks. Quality control samples (QCs) and preparation blanks were also digested by this process. The QCs and preparation blanks were analyzed with this set. Note that the samples submitted for arsenic analyses were analyzed in two different sets. This was due to restrictions on the handling

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and shipment of a portion of the samples because of the presence of radiological contamination. The outside of all cassettes were screened by DataChem Laboratories for radiological contamination upon receipt. Sample cassettes sent directly by LMUS to DataChem had all security tape seals placed upon them by NIOSH investigators intact upon receipt at the Data Chem laboratory in Salt Lake City, Utah.

The analytical limit of detection (LOD) for arsenic for the two filter sets was 0.07 and 0.1 microgram per filter ( $\mu\text{g}/\text{filter}$ ). The analytical limit of quantitation (LOQ) for arsenic was between 0.23 and 0.31  $\mu\text{g}/\text{filter}$ . Results that fell between the LOD and the LOQ are semi-quantitative in nature and are reported in the results table as trace. This denotes that the contaminant was determined to be present, but at a value possessing greater variability and interpretative limitations than is associated with results above the LOQ.

### **Arsenic: NIOSH Method 6001-Arsine as As**

The charcoal tube samples were prepared and analyzed according to NIOSH Method 6001.<sup>17</sup> These samples were analyzed using a Perkin-Elmer Zeeman 5100 Graphite Furnace AA Spectrophotometer.

The following modifications were incorporated in the preparation of the samples. The front and back portions of each sorbent tube were placed in separate 14 mL centrifuge tubes. Two mL of 0.01 Molar (M) nitric acid were added to each centrifuge tube. The samples were then sonicated for 30 minutes in a 25 °C ultrasonic water bath. Samples were then centrifuged for 10 minutes at 3000 revolutions per minute. Preparation blanks were also prepared by this process. The concentrations of the front and back portion of the samples were added together to give the total concentration of the sample. Since the calculated LOD/LOQ is for only the front or back portions of the sample, the calculated LOD/LOQ were doubled to account for the concentrations of the front and back portions of the sample being added together.

The LOD for arsenic in the charcoal tube samples was 0.02  $\mu\text{g}/\text{sample}$ . The LOQ for arsine measured as arsenic is 0.065  $\mu\text{g}/\text{sample}$ . Results from the sorbent tube samples were combined with the respective filter sample and reported as one sample result.

### **Uranium: Kinetic Phosphorescence Analysis**

Area samples for total uranium were collected using Gilian<sup>®</sup> Aircon-2 Constant Flow Air Samplers set at an average sampling flow rate of 10 Lpm. The uranium was collected on an untreated Millipore<sup>®</sup> 0.8  $\mu\text{m}$  pore size mixed cellulose ester membrane filter. All sample durations were at least for the time period of the work activity under evaluation. This ranged from 67 to 324 minutes over all samples collected. Sampling pump operation could not be terminated until the equipment had been surveyed out of the radiation contamination area by the LMUS-PORTS health physics technician.

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Uranium filter samples were analyzed using kinetic phosphorescence analysis (KPA) following DataChem Laboratories Standard Operating Procedure (SOP) WR-DC-342.<sup>18</sup> This method is used for the measurement of low-levels of elemental uranium. Appendix A briefly presents the theory pertaining to kinetic phosphorescence. This method involves the addition of a proprietary phosphate-based buffer to the liquid samples to produce uranyl phosphate. The samples are then exposed to the beam from a nitrogen laser. The decay rate of the phosphorescence of the uranyl phosphate is subsequently measured. Interferences common to this method include fluorescent interferences from organic compounds and quenchers in the form of common metals.

Sample preparation required the placement of the filters into 150 mL Griffin beakers. The walls of the filter cassettes were not washed into the sample. The filters were dissolved in nitric acid and further oxidized with three successive nitric/hydrogen peroxide wet ashes. The samples were brought to near dryness and then dissolved in 10 mL of 0.8 M nitric acid. A blank and QC were both prepared with the samples. Initial analyses of the sample solutions indicated the need to reduce the influence of quenching agents in the samples. This was done with a ten-fold dilution on all samples except the blank. The samples were reanalyzed and values observed fell within the acceptable ranges specified by the DataChem SOP.<sup>18</sup>

Reported uranium results were calculated from the raw data and converted from  $\mu\text{g/L}$  to  $\mu\text{g/filter}$ . Raw data reports showed that the lifetimes (of the phosphorescent signal per sample) were acceptable for all of the samples. The correlation coefficient ( $R^2$ ) calculated to determine the linearity of the phosphorescence decay curve and which also indicates possible method interferences was acceptable for all of the samples that were not blank. The reagent blank result was found to be below the calibration background, and below the detection limit of 0.001  $\mu\text{g/filter}$ , which may be equated for industrial hygiene terminology to the LOD. The quality control filter result was 19.2  $\mu\text{g/filter}$ . The true concentration was 20  $\mu\text{g/filter}$ , indicating a 96% recovery of U.

Because the analyses for U were conducted by the DataChem Radiochemistry Lab following procedures and techniques differing from the industrial hygiene procedures used to analyze metals, each sample result is reported with a total propagated uncertainty (TPU) calculated at the 95% confidence level. The TPU, taking into consideration all preparation and analysis errors, was determined to be  $\pm 20\%$  of the reported value for each sample. A further explanation of the determination method for TPU is presented in Appendix A.

### Special Handling Considerations

The presence of the contaminant Technetium ( $^{99}\text{Tc}$ ) and other radionuclides associated with the uranium enrichment process (e.g.,  $^{235}\text{U}$ ) necessitated a health physics assessment to determine radiological contamination levels of the air sample filters and cassettes before they could be released for unrestricted use from the site. LMUS health physics surveyed sample cassettes and filters of LMUS parallel samples for surface alpha contamination and beta activity. A determination of the Nuclear Regulatory Commission licensing restrictions for both NIOSH and

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DataChem Laboratories was also required before any samples exceeding unrestricted use levels could be released from the site or shipped for analysis. Samples left in the custody of LMUS for shipment directly to DataChem Laboratories for analysis were secured with tamper indicating devices (TID) (wrapped with a serially numbered and embossed brittle plastic adhesive tape). DataChem was provided with the TID numbers for verification upon receipt. Industrial hygiene samples approved by LMUS health physics for unrestricted release accompanied the NIOSH investigators upon their departure from the site for subsequent submission to DataChem.

All sampling pumps were pre- and post-calibrated daily. The placement of equipment inside of the restricted access radiation contamination zones (both personal and area sampling trains) precluded periodic checks for equipment operation once it was in place. The use of disposable coverings over sampling equipment further impaired sampling equipment access and observation.

### **Quality Control Samples for Arsenic**

The modifications used by DataChem in the analysis of arsenic samples were provided to LMUS. This enabled LMUS to analyze the parallel samples for arsenic following the same analytical procedures as were applied to the NIOSH samples. Quality control (QC) samples were also included in the NIOSH submission of arsenic samples. Subsequent to the disclosure of arsenic results to LMUS and labor representatives in June 1994 some additional QC samples generated by the NIOSH laboratory were submitted for analysis to DataChem.<sup>19</sup> QC samples were also provided to LMUS for submission to their analytical laboratory. These results reinforced confidence in the NIOSH arsenic results. A question had been raised concerning arsenic recoveries by LMUS representatives following the initial reporting of the survey results.

## **EVALUATION CRITERIA AND TOXICOLOGY SUMMARIES**

### **General Guidelines**

As a guide to the evaluation of exposures to chemical and physical agents in the workplace, NIOSH investigators employ criteria which are intended to represent levels of (airborne) contaminant exposure to which most workers may be exposed up to ten hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is important to note that *not all* workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). Some hazardous substances may also act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even though occupational exposures are controlled at the levels set by the evaluation criteria. Some substances are absorbed by direct contact with the skin and mucous membranes, or by ingestion, increasing the overall exposure above measured airborne

concentrations. Evaluation criteria may change over time as new information on the toxic effects of an agent become available.

The primary sources of evaluation criteria for the workplace are: NIOSH Criteria Documents and recommended exposure limits (RELs),<sup>20</sup> the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs<sup>®</sup>),<sup>21</sup> and Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs).<sup>15,22</sup> These values are usually based on a time-weighted average (TWA) exposure, which refers to the average airborne concentration of a substance over a specified time period. Frequently the time period of interest associated with TWAs is the complete 8-hour (PELs, TLVs<sup>®</sup>) or up to 10-hour (RELs) workday. Short-term exposure limits or ceiling limits also exist for some substances and are intended to supplement the TWA limits where there are recognized toxic effects from short-term exposures.

To compare results with the NIOSH, OSHA, and ACGIH criteria that are TWAs, an extrapolation of results from a sampling time of less than eight hours up to an 8-hour TWA value may be calculated. This calculation may be performed using one of two assumptions. The first assumption involves no other exposure to the compound(s) of interest over the unsampled period of the 8-hour workshift. Depending upon the contaminant, the work environment, and the individual worker's job activities this may or may not be a less conservative approach. This was the approach used in calculating 8-hour TWA values for this HHE. A second and more conservative approach to handling the unsampled time period when calculating an 8-hour TWA is to assume the exposure during the unsampled period was equal to the time period covered by the sampling process. This latter approach produces a value equivalent to dividing the sample concentration by the sample time.

A caveat regarding the evaluation criteria is that the limits *are not* fine lines between safe and dangerous concentrations of contaminants nor are they a relative index of toxicity. Recommended exposure criteria are recommendations (with the exception of OSHA PELs which are legally enforceable exposure limits) and should be used as guidelines for good practices in the workplace. Although serious injury is not believed to be likely as a result of exposures to contaminants at concentrations up to the evaluation criteria, the best practice is to maintain concentrations of all atmospheric contaminants as low as is practical.<sup>21</sup> The NIOSH recommendation concerning exposures to occupational carcinogens is to limit exposure levels to the lowest feasible concentrations.<sup>23</sup>

### **Arsenic**

Exposure to inorganic arsenic can produce dermatitis (skin inflammation), keratoses (horny growths on the skin), peripheral neuropathies (diseases of the nerves of the extremities), peripheral vascular diseases (diseases of the arteries and veins of the extremities), and cancer of the skin, liver, and lungs.<sup>24</sup> Arsenic is absorbed primarily via inhalation and ingestion. Oral ingestion from contaminated hands may result in absorption of toxicologically significant amounts of arsenic.<sup>25</sup>

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Inorganic arsenic is eliminated from the body through metabolism and urinary excretion. The total amount excreted in urine accounts for about 60% of the absorbed amount. Inorganic arsenic metabolites appear in urine shortly after the start of exposure. The concentration rises slowly during the first days of the exposure, and then levels off.<sup>24</sup> The biological half-life of arsenic in man is 24 to 36 hours.<sup>26</sup> If a worker's exposure on following days is similar, the arsenic concentration in urine remains more or less the same.

The ACGIH has proposed a Biological Exposure Index (BEI) for arsenic. The BEI is 50 micrograms per gram ( $\mu\text{g/g}$ ) of creatinine for inorganic arsenic and its metabolites in urine measured in workers at the end of the workweek.<sup>24</sup> The current ACGIH TLV-TWA of  $10 \mu\text{g/m}^3$  for arsenic and inorganic compounds is based on the prevention of systemic effects due to the inhalation of arsenic and its inorganic compounds and the clinical and epidemiological evidence for inorganic arsenic to cause lung and skin cancer.<sup>23,26</sup> Both NIOSH and OSHA [29 CFR 1910.1018] consider inorganic arsenic to be a potential occupational carcinogen.<sup>15,20</sup> The NIOSH REL (ceiling limit) is  $2 \mu\text{g/m}^3$ , and the OSHA PEL-TWA is  $10 \mu\text{g/m}^3$ . Table I presents the numerical occupational exposure evaluation criteria for airborne contaminants evaluated in this HHE, including arsenic. The carcinogen classification is also presented where applicable.

Sources of non-occupational exposure to arsenic are drinking water, food and polluted air.<sup>27</sup> Cigarette smoking is also a source of exposure to arsenic ( $12$  to  $42 \mu\text{g/cigarette}$ ).<sup>28</sup> Therefore, arsenic is found in the urine of people who have no occupational exposure to arsenic. Concentrations of inorganic arsenic and its metabolites in the urine of the general population are usually below  $10 \mu\text{g/L}$  (generally equivalent to  $\mu\text{g/g}$  creatinine) in European countries, but slightly higher in the United States.<sup>29</sup> Given the NIOSH REL for arsenic, biological monitoring by urinalysis is of little value in determining whether or not workers' arsenic exposures exceeded the REL, as normal levels of arsenic in urine could easily mask the contribution of occupational exposures near the REL.

### Uranium

The release of  $\text{UF}_6$  into the air results in a rapid reaction with water vapor to produce  $\text{UO}_2\text{F}_2$  (uranium oxyfluoride or uranyl fluoride) and HF. The reaction:



This toxicity discussion and the cited occupational exposure criteria will primarily address the adverse effects associated with U through its chemical activity. This HHE did not address radiological hazards associated with the uranium enrichment process at Portsmouth. No radiation exposure criteria will be presented for exposures to U.

Exposure to insoluble compounds of uranium produces respiratory irritation, whereas soluble compounds are toxic to the kidneys.<sup>30</sup> High doses of soluble uranium cause tissue damage in the kidneys leading to functional loss as indicated by the failure to resorb urinary protein, glucose,

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catalase, phosphate, citrate, and creatinine. High doses of uranium also affect the blood vasculature throughout the body. Uranium may damage capillary membranes and is also known to induce damage to liver and muscle tissue. The effects of uranium on the nervous system may be similar to those associated with poisoning by other heavy metals. Transient renal injury, which occurs when one or more of the chemical components of urine indicates that there has been some structural change within the kidney, is reversible. In this situation the loss of reserve renal capacity is regarded to be small with the chemical composition of the urine quickly returning to normal ranges.<sup>31</sup>

Accidental exposure of workers to a mixture of UF<sub>6</sub> (uranium hexafluoride), UO<sub>2</sub>F<sub>2</sub> (uranyl fluoride), HF (hydrofluoric acid), and live steam caused lacrimation, conjunctivitis, shortness of breath, paroxysmal cough, rales in the chest, nausea, vomiting, skin burns, transitory albuminuria, and elevation of blood urea nitrogen. Two fatalities occurred among the most heavily exposed. Urinary abnormalities continued for several weeks. Injury effects observed on the skin, eyes, and respiratory tract were caused by the irritant action of the hydrofluoric acid, whereas the transient renal changes were attributed to the uranium.<sup>30</sup>

Excess illness from chronic respiratory disease has been reported in epidemiologic studies of uranium mill workers. Excess mortality due to tumors of the lymphatic and hematopoietic systems, other than leukemia, have also been reported for uranium mill workers. Standardized mortality ratios for lung or bone cancer, leukemia or other respiratory or genitourinary disease were not observed to be higher among those workers with the highest mean exposures to uranium dust.<sup>32</sup> A series of studies at a uranium enrichment plant between 1943 and 1947 noted an excess of lung cancer deaths and central nervous system deaths. This study examined the risk of dying of lung cancer in men receiving radiation exposure to the lungs due to the inhalation of uranium or uranium containing dusts.<sup>33</sup>

The current ACGIH TLV-TWA of 200 µg/m<sup>3</sup> has been recommended for elemental uranium and its soluble and insoluble compounds since 1969. In 1969 the TLV-TWA was raised from 50 µg/m<sup>3</sup> to the present level based upon an absence of evidence linking occupational uranium exposures during a 25 year period that were in excess of the 1969 limit with renal, hematopoietic, or other injury. An ACGIH Short Term Exposure Limit (STEL) of 600 µg/m<sup>3</sup> was added in 1976. This TLV is reportedly undergoing re-evaluation by the ACGIH TLV Committee regarding the appropriateness of the TLV for carcinogenic potential due to biological actions of the agent associated with properties other than that of the nonradioactive element.<sup>32</sup> OSHA has a PEL-TWA of 50 µg/m<sup>3</sup> measured as U for soluble compounds of uranium and a PEL-TWA of 250 µg/m<sup>3</sup> measured as U for insoluble compounds.<sup>22</sup> The OSHA basis for these exposure limits was that these levels would protect workers exposed to uranium from significant risks of kidney or blood disorders and radiological damage potentially associated with exposure to these compounds at levels above the PELs.<sup>32</sup> The NIOSH REL for soluble uranium is 50 µg/m<sup>3</sup> and the REL for insoluble uranium compounds is the same as the ACGIH's TLV<sup>®</sup>.<sup>20,21</sup> NIOSH also recommends that uranium compounds be treated as a potential occupational carcinogen.<sup>20</sup> The uranium evaluation criteria presented here are also listed in Table I.

Uranium absorption from the respiratory tract is the most important route of entry in occupational settings. Although soluble uranium salts may be absorbed through the skin, this is considered to have a minimal contribution to the overall amount of uranium entering the body due to occupational exposures. Pulmonary absorption of uranium in humans may be as high as 20%. Ten to 30% of the uranium that reaches the circulatory system from acute exposures is bound irreversibly to bone; 10 to 20% is deposited in the kidneys; and 60 to 70% is excreted in urine during the first 24 hours after an intake.<sup>32</sup>

## **RESULTS**

### **Arsenic**

Samples were collected at three different locations within the X-326 process building and at one location in the X-700 converter maintenance facility. All area and personal exposure samples obtained in the X-700 building during placement and welding of back-up strips onto a converter were below detectable levels. Area and personal exposure samples for workers replacing P-nut valves on cell X-27-3-12 on the cell floor of X-326 were also all below detectable levels.

Area and personal exposures during the alumina trap changeout of top purge traps A, B, and C on the operating floor of X-326 ranged from below detectable levels up to  $0.3 \mu\text{g}/\text{m}^3$  of total arsenic. Overexposures were documented during the removal of a valve on the evacuation booster station located at the top end of the process in building X-326. The two area samples located in the immediate proximity of the removal process demonstrated an airborne arsenic concentration of  $0.7 \mu\text{g}/\text{m}^3$ . The overhead crane operator's arsenic exposure was below detectable levels. Personal exposure levels to arsenic for the four workers performing the valve removal ranged from 1 to  $109 \mu\text{g}/\text{m}^3$  of arsenic. The average exposure for these four workers was  $37 \mu\text{g}/\text{m}^3$ , with a standard deviation of  $50 \mu\text{g}/\text{m}^3$ . The chemical operator conducting the decontamination after removal of the valve had the highest exposure. All values presented previously in this paragraph represent time-weighted averages over the actual sampling periods which were less than eight hours in duration.

Table II lists individual sample results calculated as both a TWA over the sampling period (first TWA column) as well as an 8-hour TWA with the assumption of zero exposure during the unsampled time period (second TWA column). Eight-hour TWAs calculated for all samples ranged from below detectable levels up to  $22 \mu\text{g}/\text{m}^3$  of arsenic. Table I presents the evaluation criteria for airborne arsenic.

Samples collected by the LMUS industrial hygiene technician at the same locations or for the same workers as those monitored by NIOSH investigators are presented in the Notes column of Table II. The airborne concentrations calculated both as a TWA over the sampling period as well as for an 8-hour TWA, assuming zero exposure during the unsampled time period, are presented. This information is provided for the reader's reference. LMUS sampling produced results above as well as below the NIOSH results. This provides some indication of the variability associated

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with environmental sampling and reinforces the caveat that evaluation criteria are not to be interpreted as a fine line separating acceptable and unacceptable worker exposures.

One should note that all workers wore personal protective clothing including airline supplied-air respiratory protection. All work was performed inside of delimited radiation contamination zones. Samples were collected outside of the workers' protective clothing.

Quality control samples were submitted along with the arsenic samples collected at the PORTS following the site visit. The mean recovery for these six QC samples for arsenic accompanying the original field samples was 96% and were regarded to be within the analytical control criteria. Subsequent to this field survey and the receipt of the survey sample results, another set of quality control samples spiked with known quantities of arsenic were submitted at the request of LMUS-PORTS. LMUS-PORTS expressed interest in evaluating their site laboratory analytical capabilities for arsenic following the same analytical method with modifications as the NIOSH contract laboratory.

This request arose in light of the fact that NIOSH samples documented some of the highest arsenic exposures evaluated to date at the facility. LMUS-PORTS had followed the same sampling and analytical procedures, with modifications, as used by DataChem for the NIOSH survey samples. Table III presents previous company data for arsenic. Table IV presents the quality control sample results for both DataChem Laboratories (the NIOSH contract laboratory), and the PORTS on-site laboratory. Results are identified for arsenic QC samples provided by two sources, PORTS and NIOSH.

### **Uranium**

Area samples for uranium were obtained at four locations in the plant and at one off-site reference location. TWA results for uranium over the sampling period for samples obtained on-site ranged from 0.1 to 1.1  $\mu\text{g}/\text{m}^3$ ; 8-hour TWA values for the same samples ranged from 0.05 to 0.8  $\mu\text{g}/\text{m}^3$ . A reference sample obtained in one of the NIOSH investigators hotel rooms in Portsmouth measured 0.01  $\mu\text{g}/\text{m}^3$  for an 8-hour TWA. The results of airborne uranium sampling are presented in Table V. All airborne concentrations of uranium, measured as uranium, were less than one fiftieth of the applicable industrial hygiene exposure evaluation criteria for soluble uranium compounds.

## **DISCUSSION AND CONCLUSIONS**

### **Arsenic**

The sampling data confirms LMUS findings that potential arsenic exposures occur with activities involved in opening uranium enrichment process equipment. All workers evaluated for personal exposure to arsenic compounds, with the exception of one individual, wore supplied-air respiratory protection. One worker overseeing the P-nut valve replacement was outside of the

radiation contamination zone. This removed him from the immediate vicinity of the work that required the higher levels of personal protective equipment. Workers wore flame retardant anti-Cs (protective coveralls), poly vinyl chloride (PVC) gloves, and shoe covers. Workers involved in the valve removal at the evacuation booster station in X-326 wore polyethylene coated Tyvek<sup>R</sup>-QC disposable coveralls in addition to the other protective gear for protection against technetium. The personal protective equipment utilized by the individuals whose exposures were evaluated should have effectively prevented any exposure to the observed airborne concentrations of arsenic. The respiratory protection table (Table 2) in the OSHA arsenic standard indicates that a supplied air respiratory with a full facepiece, hood, or helmet or suit operated in positive pressure mode offers acceptable protection up to a concentration of 20,000  $\mu\text{g}/\text{m}^3$  for inorganic arsenic containing compounds possessing significant vapor pressure. A front or back mounted gas mask equipped with high-efficiency filter and acid gas canister may be used for respiratory protection against airborne inorganic arsenicals at concentrations below 500  $\mu\text{g}/\text{m}^3$ .<sup>15</sup> Airborne levels of total arsenic evaluated during this survey were well below both of these concentrations.

A review of the available arsenic sampling results collected by the LMUS-PORTS industrial hygiene department indicates that for a number of activities where potential arsenic exposures may occur, the levels are low (below 5  $\mu\text{g}/\text{m}^3$ ) or nondetectable. Table III presents some historic worker exposure monitoring data conducted by the LMUS-PORTS industrial hygiene department at locations and for work similar to that conducted by NIOSH investigators March 2-3, 1994. The LMUS-PORTS results were subject to the same difficulty experienced by the NIOSH investigators in that work tasks of short duration and thus limited sampling periods may result in minimum quantifiable concentrations (MQCs) higher than the NIOSH REL. The NIOSH sample results demonstrated two exposures in excess of any observed by LMUS-PORTS as of February 25, 1994. These samples were collected at or near the segment of the cascade process referred to as the "arsenic bubble". The uranium enrichment process is a physical separation process and appears to result in the collection of different process impurities at differing points within the equipment. Company data identified arsenic concentrations inside the process up to almost 4,000 parts per million in onstream cells (several hundred  $\text{mg}/\text{m}^3$  of arsenic). (A cell is an assembly of stages, each stage being the smallest complete separatory unit within the process.)

A modification of the sampling train used to evaluate airborne arsenic was incorporated into the area sampling conducted during this survey. An initial question was whether a filter sample for arsenic captured all of the arsenic present. A standard charcoal tube was placed in line behind the air sampling cassette in an effort to determine whether gaseous arsenic compounds may also be captured. Although the number of these samples was limited, all of the sorbent tubes were nondetectable for arsenic. The arsenic values for these two part samples, if above detectable levels, were due to the contaminant collected on the filter.

This evaluation did not involve assessing worker exposures during work conducted on equipment or equipment lines that contained visible deposits of arsenic-containing materials. The NIOSH data applies primarily to the tasks evaluated on the process equipment and an example of work

performed on a purged, cleaned, and isolated converter. The company has located tasks and work locations that present greater potential for excessive arsenic exposures based upon their body of previously collected exposure information. The routine required personal protective equipment (clothing and respiratory protection) used to prevent exposure to radiological contamination, the process gas ( $UF_6$ ), and HF also offers substantial protection against arsenic compounds present in the process as a contaminant.

The workers should be adequately protected from arsenic hazards when utilizing the protective equipment required in radiological contamination zones; however, supplied-air respiratory protection and protective clothing should also be worn when working on arsenic-contaminated equipment in the absence of radiological contamination. LMUS documents indicate that a Mine Safety Appliances air purifying respirator may be acceptable to provide protection under these latter conditions. NIOSH does not currently approve any air purifying respirators for protection against arsenic exposures, except for the limited application of emergency escape purposes.<sup>34</sup>

### **Uranium**

The area air sample results for uranium in the X-700 and X-326 buildings during the NIOSH survey did not identify any elevated exposures (i.e., approaching current occupational exposure limits) when evaluating airborne uranium concentrations as a nonradioactive element. The presence of uranium in the process in the form of  $UF_6$  will result in the formation of other hazardous and toxic contaminants upon mixing with atmospheric moisture (see page 13). Soluble forms of uranium are considered to be the primary uranium compounds present at PORTS. Low airborne uranium concentrations were not indicative of low airborne arsenic concentrations for the limited number of samples collected. The location of the samples collected in the X-326 building, which is at the product or enriched end of the process and contains a higher concentration of  $^{235}U$ , presents radiological health hazards due to uranium which are not adequately addressed with the mass per volume airborne concentrations. The data collected during this survey, along with the personal protective equipment in use by the workers (presented in the arsenic discussion), does not indicate a chemical health hazard to uranium.

### **RECOMMENDATIONS**

Exposure monitoring and exposure control for arsenic at the LMUS Piketon Gaseous Diffusion Plant should aim at reducing and maintaining arsenic exposures at the lowest level feasible. The OSHA PEL and Action Level may be used as guides in addressing exposures although measureable airborne arsenic concentrations below a target level of  $5 \mu\text{g}/\text{m}^3$  does not denote the absence of an occupational health hazard. This is because of the concerns regarding the carcinogenicity of arsenic compounds.

The amount and type of monitoring for arsenic exposures should be modified by LMUS-PORTS to focus efforts on characterizing high level or ill-defined arsenic exposures. Monitoring on a less intense basis should be continued for tasks previously evaluated and demonstrating

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negligible arsenic exposures to insure they remain unchanged. Exposure monitoring conducted to evaluate airborne arsenic contaminants should strive to evaluate levels below the most restrictive evaluation criteria.

The workers appear to be adequately protected from arsenic hazards when utilizing the protective equipment required in radiological contamination zones; however, supplied-air respiratory protection and protective clothing should also be worn when working on arsenic- contaminated equipment in the absence of radiological contamination. LMUS-PORTS documents indicated that a Mine Safety Appliances air purifying respirator may be acceptable to provide protection under these latter conditions.<sup>13</sup> NIOSH does not currently approve any air purifying respirators for protection against arsenic exposures, except for the limited application of emergency escape purposes.<sup>34</sup>

The re-use of personal protective clothing that may have become contaminated with arsenic containing dusts should be avoided. This did not appear to be a problem for the tasks evaluated by NIOSH because of the extensive use of disposable clothing. This could become a potential problem in instances where tasks involving arsenic-contaminated materials are being worked on, but which are not subject to the constraints (and accompanying disposable protective clothing) associated with handling radiologically contaminated equipment.

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**AUTHORSHIP AND ACKNOWLEDGEMENTS**

Report Prepared by: Steven H. Ahrenholz, Ph.D., CIH  
Research Industrial Hygienist  
Exposure Assessment Section  
Health-related Energy Research  
Branch  
Division of Surveillance, Hazard  
Evaluations, and Field Studies

Field Assistance: John J. Cardarelli II, M.S.  
Research Health Physicist  
Exposure Assessment Section  
Health-related Energy Research  
Branch  
Division of Surveillance, Hazard  
Evaluations, and Field Studies

Laboratory Analyses: Dave A. Reddish  
Boyd E. Neilson  
DataChem Laboratories  
Salt Lake City, Utah

Originating Office: Hazard Evaluations and Technical  
Assistance Branch  
Division of Surveillance, Hazard  
Evaluations and Field Studies  
National Institute for Occupational  
Safety and Health  
4676 Columbia Parkway  
Cincinnati, Ohio 45226

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1. Lockheed Martin Utility Services, Inc., Piketon, Ohio
2. OCAW-Local 3-689
3. OCAW International
4. UPGWA-Local 66
5. Confidential requestors
6. Occupational Safety and Health Administration, Region V

For the purposes of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Table I (continued)  
Occupational Exposure Evaluation Criteria for Airborne Contaminants

HETA 94-0077  
Lockheed Martin Utility Services Uranium Enrichment Plant  
Piketon, Ohio

Country	Agent	Forms of Agent Specifically Identified with the Evaluation Criteria	Occupational Exposure Limit <sup>A</sup>		Carcinogenicity Notation <sup>B</sup>
			TWA in ug/m3	STEL in ug/m3	
USA: ACGIH <sup>C</sup>	Arsenic	Elemental and inorganic compounds (except arsine) as arsenic	10		Confirmed human carcinogen
USA: NIOSH <sup>C</sup>		Total inorganic arsenic		2	Occupational carcinogen (Maintain lowest feasible level)
USA: OSHA <sup>C</sup>		Inorganic arsenic	10 (Action Level 5)		Carcinogen
Australia			50		Established human carcinogen
Federal Republic of Germany		D	none	none	Established human carcinogen
United Kingdom		Arsenic and compounds, except arsine (D)	100		
USA: ACGIH <sup>C</sup>	Uranium	Elemental uranium, soluble and insoluble compounds; as uranium	200	600	Not currently established
USA: NIOSH <sup>C</sup>		Soluble compounds as uranium;	50	-	Occupational carcinogen (Maintain lowest feasible level)
		insoluble compounds as uranium	200	600	
USA: OSHA <sup>C</sup>		Soluble compounds as uranium;	50		-
		insoluble compounds as uranium	250		
Australia		Natural, soluble, and insoluble; as uranium	200	600	-
Federal Republic of Germany		Uranium compounds, total dust, as uranium	250	2500 (30 minutes; 1X/shift)	Due to natural radioactivity the tolerance values identified in the "Strahlenschutzverordnung" (radiation protection guidelines) of 10/13/76 are to be followed

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Table I (continued)  
Occupational Exposure Evaluation Criteria for Airborne Contaminants

HETA 94-0077  
Lockheed Martin Utility Services Uranium Enrichment Plant  
Piketon, Ohio

Country	Agent	Forms of Agent Specifically Identified with the Evaluation Criteria	Occupational Exposure Limit <sup>A</sup>		Carcinogenicity Notation <sup>B</sup>
			TWA in ug/m3	STEL in ug/m3	
United Kingdom		Natural, soluble compounds; as uranium	200	600 (10 minute STEL)	
	Radon				

- A: Limits are presented as Time-Weighted Averages (TWAs) calculated over a workshift (usually 8 hours) or as Short-Term Exposure Limits (STELs) calculated over a shorter (usually 15 minute) time period. A ceiling concentration denotes a level that is not to be exceeded. The OSHA Action Level denotes an exposure level at which selected protective actions within the OSHA occupational exposure standard, 29 CFR 1910.1018, must be implemented. Concentrations are given in micrograms per cubic meter of air (ug/m3).
- B: Carcinogenicity notation represents that designation for the agent by the respective country (and source) identified in the International Labour Office reference: Occupational Exposure Limits for Airborne Toxic Substances. 3ed. Occupational Safety and Health Series No. 37, International Labour Organisation, Geneva, (1991). The ACGIH value is from ACGIH [1993]. 1993-1994 threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Industrial Hygienists. The NIOSH limit is taken from NIOSH [1975]. Criteria for a recommended standard: occupational exposure to inorganic arsenic-new criteria-1975. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health; DHEW (NIOSH) Publication No. 75-149 and the OSHA limits from 29 CFR 1910.1018.
- C: ACGIH= American Conference of Governmental Industrial Hygienists; NIOSH= The National Institute for Occupational Safety and Health; OSHA= The Occupational Safety and Health Administration. OSHA standards are mandatory exposure limits in the United States.
- D: Source for these two entries is ACGIH [1994]. Documentation of the arsenic, elemental and inorganic compounds (except arsine) TLV. [Unpublished]. ACGIH; 1330 Kemper Meadow Dr.; Cincinnati, OH 45240.

TABLE II (continued)

Arsenic Air Sampling Results in the X-326 Process Building and X-700 Converter Maintenance

HETA 94-0077  
 Lockheed Martin Utility Services Uranium Enrichment Plant  
 Piketon, Ohio

March 2-3, 1994

Sample Date	Building Location	Sample Type Area or Personal <sup>A</sup>	Sample Period (min)	Sample Volume (m <sup>3</sup> ) <sup>B</sup>	Airborne Concentration in ug/m <sup>3</sup> <sup>C</sup>		Job Title or Area Sample Location <sup>ED</sup>	Notes <sup>F</sup> (LMUS results in ug/m <sup>3</sup> )
					TWA over sample period	8-hour TWA		
3/2/94	X-326, Operat-ing Floor, Top Purge Traps A,B,C	Area	See Notes	-	-	-	At vacuum unit exhaust, on cart	Pump faulted; invalid sample LMUS Duplicate Sample Result (LMUS-Dup): S-TWA 0.4 8-hr TWA 0.2
****		Area	216	0.444	0.2	0.1	At vacuum unit exhaust, on cart	Alumina trap changeout LMUS-Dup: S-TWA <i>ND</i> 8-hr TWA <i>ND</i>
		Area	209	0.416	0.3	0.1	Column R-101, Operating Floor	Stationary sample location LMUS-Dup: S-TWA 0.5 8-hr TWA 0.2
		Area	See Notes	-	-	-	Column R-101, Operating Floor	Pump faulted; invalid sample LMUS-Dup: S-TWA 0.5 8-hr TWA 0.2

TABLE II (continued)

Arsenic Air Sampling Results in the X-326 Process Building and X-700 Converter Maintenance

HETA 94-0077  
 Lockheed Martin Utility Services Uranium Enrichment Plant  
 Piketon, Ohio

March 2-3, 1994

Sample Date	Building Location	Sample Type Area or Personal <sup>4</sup>	Sample Period (min)	Sample Volume (m <sup>3</sup> ) <sup>5</sup>	Airborne Concentration in ug/m <sup>3</sup> <sup>C</sup>		Job Title or Area Sample Location <sup>ED</sup>	Notes <sup>F</sup> (LMUS results in ug/m <sup>3</sup> )
					TWA over sample period	8-hour TWA		
		Personal	127	0.465	T	T	Chemical Operator; Col L-101	Alumina trap replacement LMUS-Dup: S-TWA 0.6 8-hr TWA 0.2
		Personal	136	0.494	ND	ND	Chemical Operator; at Col L-101	Same as above
		Personal	137	0.494	T	T	Chemical Operator; at Col L-101	Same as above LMUS-Dup: S-TWA 0.7 8-hr TWA 0.1
	X-326 Product with-drawal (PW)	Personal	110	0.399	ND	ND	Security Guard; PW exclusion zone; in guard house	Worker in adjacent area to alumina trap changeout

TABLE II (continued)

Arsenic Air Sampling Results in the X-326 Process Building and X-700 Converter Maintenance

HETA 94-0077  
 Lockheed Martin Utility Services Uranium Enrichment Plant  
 Piketon, Ohio

March 2-3, 1994

Sample Date	Building Location	Sample Type Area or Personal <sup>A</sup>	Sample Period (min)	Sample Volume (m <sup>3</sup> ) <sup>B</sup>	Airborne Concentration in ug/m <sup>3</sup> <sup>C</sup>		Job Title or Area Sample Location <sup>ED</sup>	Notes <sup>F</sup> (LMUS results in ug/m <sup>3</sup> )
					TWA over sample period	8-hour TWA		
3/2/94	X-700 Converter Maintenance	Area	See Notes	-	-	-	Area, mounted on work platform railing; Inside columns A-4,B-4 A-5,B-5	Pump faulted; invalid sample LMUS-Dup: S-TWA 0.03 8-hr TWA 0.02
		Area	287	0.591	ND	ND	Back-up strips being welded in place on converter	Pump faulted at 287 minutes terminating sample LMUS-Dup: S-TWA 1.6 8-hr TWA 1.1
		Personal	306	1.123	ND	ND	Converter Mechanic	Clamping backup strips onto converter prior to welding LMUS-Dup: S-TWA ND 8-hr TWA ND

TABLE II (continued)

Arsenic Air Sampling Results in the X-326 Process Building and X-700 Converter Maintenance

HETA 94-0077  
 Lockheed Martin Utility Services Uranium Enrichment Plant  
 Piketon, Ohio

March 2-3, 1994

Sample Date	Building Location	Sample Type Area or Personal <sup>4</sup>	Sample Period (min)	Sample Volume (m <sup>3</sup> ) <sup>B</sup>	Airborne Concentration in ug/m <sup>3</sup> <sup>C</sup>		Job Title or Area Sample Location <sup>ED</sup>	Notes <sup>F</sup> (LMUS results in ug/m <sup>3</sup> )
					TWA over sample period	8-hour TWA		
		Personal	5 (See Notes)	0.019	ND	ND	Welder	Welding patch on converter shell, Ni & steel welding using MIG and stick; pump faulted, terminating sample LMUS-Dup: S-TWA <i>ND</i> 8-hr TWA <i>ND</i>
3/3/94	X-326 Cell Floor	Area	67	0.135	ND	ND	Midway between columns P-27 & P-30, cell floor, along cell 12 of unit 27-3	Two workers replacing P-nut valves on seal feed on cell 12 LMUS-Dup: S-TWA <i>ND</i> 8-hr TWA <i>ND</i>
		Area	68	0.139	ND	ND	Same as above	Same as above LMUS-Dup: S-TWA <i>ND</i> 8-hr TWA <i>ND</i>
		Personal	57	0.209	ND	ND	Instru-ment Mechanic	Changed out 6 P-nut valves; anti C's worn

TABLE II (continued)

Arsenic Air Sampling Results in the X-326 Process Building and X-700 Converter Maintenance

HETA 94-0077  
 Lockheed Martin Utility Services Uranium Enrichment Plant  
 Piketon, Ohio

March 2-3, 1994

Sample Date	Building Location	Sample Type Area or Personal <sup>A</sup>	Sample Period (min)	Sample Volume (m <sup>3</sup> ) <sup>B</sup>	Airborne Concentration in ug/m <sup>3</sup> <sup>C</sup>		Job Title or Area Sample Location <sup>ED</sup>	Notes <sup>F</sup> (LMUS results in ug/m <sup>3</sup> )
					TWA over sample period	8-hour TWA		
		Personal	59	0.218	ND	ND	Instru-ment Mechanic	Changed out 6 P-nut valves; anti C's worn
		Personal	56	0.207	ND	ND	Instru-ment Mechanic	Monitored work from outside contamination zone, no respiratory protection worn
3/3/94	X-326, cell floor, Evacuation Booster Station	Area	324	0.645	0.7	0.5	Located in work area where cutting out and removal took place, Columns B-60,B-61,C-60,C-61	Removal of EEB7 valve on booster station connected to surge drum LMUS-Dup: S-TWA 3.7 8-hr TWA 1.4
		Area	324	0.616	0.7	0.5	Same as above	Same as above LMUS-Dup: S-TWA 1.3 8-hr TWA 0.8

TABLE II (continued)

Arsenic Air Sampling Results in the X-326 Process Building and X-700 Converter Maintenance

HETA 94-0077  
 Lockheed Martin Utility Services Uranium Enrichment Plant  
 Piketon, Ohio

March 2-3, 1994

Sample Date	Building Location	Sample Type Area or Personal <sup>4</sup>	Sample Period (min)	Sample Volume (m <sup>3</sup> ) <sup>B</sup>	Airborne Concentration in ug/m <sup>3</sup> <sup>C</sup>		Job Title or Area Sample Location <sup>ED</sup>	Notes <sup>F</sup> (LMUS results in ug/m <sup>3</sup> )
					TWA over sample period	8-hour TWA		
		Personal	52	0.185	ND	ND	Mainten-ance Mechanic	Overhead crane operator wore SCBA LMUS-Dup: S-TWA <i>ND</i> 8-hr TWA <i>ND</i>
		Personal	322	1.176	33	22	Welder	Burned out valve bonnet using a carbon arc, PPE incl anti Cs and airline respirator LMUS-Dup: S-TWA 2.7 8-hr TWA 0.9
		Personal	321	1.172	1	0.7	Mainten-ance Mechanic	Assisted in pulling out valve and wrapping it, PPE as above LMUS-Dup: S-TWA 1.1 8-hr TWA 0.7

TABLE II (continued)

Arsenic Air Sampling Results in the X-326 Process Building and X-700 Converter Maintenance

HETA 94-0077  
 Lockheed Martin Utility Services Uranium Enrichment Plant  
 Piketon, Ohio

March 2-3, 1994

Sample Date	Building Location	Sample Type Area or Personal <sup>4</sup>	Sample Period (min)	Sample Volume (m <sup>3</sup> ) <sup>B</sup>	Airborne Concentration in ug/m <sup>3</sup> <sup>C</sup>		Job Title or Area Sample Location <sup>ED</sup>	Notes <sup>F</sup> (LMUS results in ug/m <sup>3</sup> )	
					TWA over sample period	8-hour TWA			
		Personal	313	1.145	5	3	Mainten-ance Mechanic	Pulled out valve and closed lines, PPE as previous two LMUS-Dup: S-TWA 2.8 8-hr TWA 1.3	
		Personal	35	0.129	109	8	Chemical Operator	Decontamination of pipe after removal of valve, wore bubble suit	
NIOSH Analytical Method 7901 Limits of Detection and Quantitation for Sample Sequence 7981					Limit of detection/filter: 0.07-0.1 ug Limit of quantitation/filter: 0.23-0.31 ug				
Evaluation Criteria					Airborne Occupational Exposure Limit <sup>F</sup>		Carcinogen Status <sup>G</sup>		
NIOSH Recommended Exposure Limit (REL)					2 (15 minute ceiling) Lowest Feasible Level		Occupational Carcinogen		

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TABLE II (continued)

Arsenic Air Sampling Results in the X-326 Process Building and X-700 Converter Maintenance

HETA 94-0077  
 Lockheed Martin Utility Services Uranium Enrichment Plant  
 Piketon, Ohio

March 2-3, 1994

Sample Date	Building Location	Sample Type Area or Personal <sup>A</sup>	Sample Period (min)	Sample Volume (m <sup>3</sup> ) <sup>B</sup>	Airborne Concentration in ug/m <sup>3</sup> <sup>C</sup>		Job Title or Area Sample Location <sup>D</sup>	Notes <sup>E</sup> (LMUS results in ug/m <sup>3</sup> )
					TWA over sample period	8-hour TWA		
<b>OSHA Inorganic Arsenic Permissible Exposure Limit (PEL)</b>					<b>10 (8-hr TWA; 5 ug/m<sup>3</sup> for Action Level)</b>		<b>Carcinogen</b>	

\*\*\*\* Shaded cells denote that the same sample date and building location apply to the identified sample.

A: Area samples were located in the work area within the contamination zone as close to the work location as possible. Area samples were placed by individuals inside the contamination zone at the direction of the NIOSH investigators. Personal samples were placed on the individual workers at a location approximating the collar and outside of the respiratory protection gear.

B: Sample volume is given in cubic meters of air. - denotes not applicable.

C: Airborne concentration of total arsenic is presented in micrograms per cubic meter of air sampled. Two values are presented: the Time-Weighted Average (TWA) calculated only for the sampling period and an 8-hour TWA calculated over a full 8 hour workshift incorporating an assumed zero exposure during the unsampled time period outside of the time period actually sampled. T indicates that arsenic was identified to be present in the sample but was below the analytical limit of quantitation. (This was less than an 8-hr TWA for this sample set of 0.1 ug/m<sup>3</sup>.) ND indicates that the concentration of arsenic, if present, was below the analytical limit of detection for those samples. (Calculated 8-hour TWA values for the ND samples ranged from below 0.5 ug/m<sup>3</sup> to below 0.1 ug/m<sup>3</sup>.) The reader is referred to the discussion on the sampling and analytical methods used for evaluating arsenic exposures.

D: Job Title represents the job title of the individuals sampled, area sample location provides a more specific definition of where the stationary samplers were located. Area samples were generally located at a level of between three and five feet above the floor or surrounding walking surfaces. Column designations within buildings are given by letter and number.

E: Notes: Several invalid samples associated with pump failures are listed for completeness. The placement of sampling equipment inside of the contamination zones precluded access to equipment during its operation inside of these zones. Workers within the zones were instructed on equipment placement and the starting/stopping of sampling. Most sampling periods are longer than that required for task performance since equipment had to remain inside of the contamination zone after work was completed and until it was surveyed for radiological contamination by the health physics department and approved for release into uncontaminated areas. Lockheed Martin Utility Services-Portsmouth (LMUS-PORTS) conducted duplicate sampling at some of the locations and in the breathing zones of some of the workers selected by the NIOSH investigators. These sample results from the LMUS-PORTS industrial hygiene department are noted as LMUS-Duplicate sample) with the results given as time-weighted averages (TWAs) over both the sampling period (S-TWA) and calculated out for an 8 hour TWA (8-hr TWA), assuming zero exposure during the unsampled time period. All values are presented as micrograms per meter cubed of air. The ND for none detected is italicized to denote that the samples were below the company's analytical limit of detection, not the NIOSH limit of detection listed at the end of the table.

PPE: (Personal Protective Equipment) Anti-Cs denote anticontamination protective clothing. Work inside of contamination zones evaluated for arsenic exposures, with the exception of the evacuation booster station valve replacement, required workers to wear flame retardant yellow Tyvek coveralls, booties, shoe covers, gloves, and a bubble hood connected to an air line. Workers

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on the evacuation booster station valve removal wore additional white plastic coated Tyvek coveralls to protect against technitium exposures, welders hoods over full face supplied air line respirators, and welder lenses. The crane operator wore a selfcontained breathing apparatus (SCBA) because of mobility requirements associated with climbing and accessing the overhead crane cab. Workers outside of contamination zones wore company issued blue cotton coveralls, shoes, and possibly disposable latex gloves (task and area dependent).

- F:* Airborne Occupational Exposure Limits are presented. The NIOSH recommended exposure limit (REL) represents a ceiling concentration which is not to be exceeded at any time, measured over any 15 minute sampling period during a workshift. NIOSH recommends that engineering controls be used to the maximum extent to maintain exposure levels at the lowest level possible. Supplementary use of personal protective equipment may be necessary to achieve this goal but represents the last choice for protection. The OSHA Permissible Exposure Limit represents an enforceable standard for exposures which would occur if the employee were not using a respirator. An Action Level represents the exposure level at which specific requirements must be implemented as required in the OSHA Inorganic Arsenic standard, 29 CFR 1910.1018.
- G:* Carcinogen status represents the classification of arsenic as a cancer producing substance. Arsenic is identified by both OSHA and NIOSH as a carcinogen.

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Table III  
Comparison of Previous Company Sampling Data for Arsenic to NIOSH Results

HETA 94-0077  
Lockheed Martin Utility Services Uranium Enrichment Plant  
Piketon, Ohio

Building	Location	Sample Type	Previous Company Samples		NIOSH Samples	
			Sample Dates	Arsenic Concentration (ug/m3) <sup>A</sup>	Sample Date	Arsenic Concentration (ug/m3) <sup>A</sup>
X-326	Purge Traps	Area	11/3/93	ND	3/2/94	0.2
X-326	Guard Shack	Area	11/3/93	ND	Not Applicable	-
X-700	Converter Maintenance	Area	11/3/93	ND	3/2/94	ND
X-700	Converter Maintenance	Personal	11/3/93, 12/7/93	ND-0.5	3/2/94	ND
X-326	Replace Peanut Valves	Personal	12/21/93	ND	3/3/94	ND
X-326	Evacuation Booster Station	Personal	11/9/93, 11/11/93	ND-6	3/3/94	1-109

A: Contaminant concentrations are presented in micrograms per cubic meter of air. ND denotes that arsenic concentrations in the sample fell below the analytical limit of detection for the specific sample. Nondetectable values obtained from previous company sampling results indicates that airborne nondetectable levels of arsenic ranged from below 0.05 ug/m<sup>3</sup> to less than 0.1 ug/m<sup>3</sup>. The nondetectable levels for the NIOSH samples ranged from below 0.09 ug/m<sup>3</sup> to less than 5 ug/m<sup>3</sup>. Note that the environmental limit of detection is influenced by sample size (total air volume sampled).

TABLE IV

Summary of Mean Recoveries of Arsenic in Quality Control (QC) Samples Obtained from Two Sources and Submitted to Laboratories Used by NIOSH and PORTS

HETA 94-0077  
Lockheed Martin Utility Services Uranium Enrichment Plant  
Piketon, Ohio

QC Source <sup>A</sup>	Laboratory <sup>B</sup>	No. Samples <sup>C</sup>	Percent Recovery of Spiked Arsenic			Analytical Method <sup>D</sup>
			Range	Mean	Std. Deviation	
PORTS Contract Lab	PORTS Contract Lab	20	43-94	78	15	Atomic Absorption
	PORTS On-site Lab	4	71-82	76	4	Atomic Absorption
	PORTS On-site Lab	7 <sup>C</sup>	83-170	112	25	Inductively Coupled Plasma
	NIOSH Contract Lab	8	93-110	98	6	Atomic Absorption
NIOSH In-house Lab	PORTS On-site Lab	8	64-85	79	7	Atomic Absorption
	NIOSH Contract Lab	8	100-110	102	3	Atomic Absorption

- A:** Samples spiked with arsenic were obtained from two sources, the PORTS contract laboratory (American Analytical Laboratory, Akron, OH) and the NIOSH Division of Physical Sciences and Engineering.
- B:** The two analytical laboratories under comparison were the PORTS on-site analytical laboratory and the NIOSH contract laboratory (DataChem, Salt Lake City, UT). The expected recoveries for the spikes provided by American Analytical were determined from the analyses of 20 paired samples prepared at the same time as those supplied to PORTS for this comparison with the NIOSH contract lab.
- C:** Number of samples analyzed by each lab from the source identified in the first column. This excludes blanks which were also submitted. The total number represents equal samples at each of the four spike levels of arsenic: 1, 3, 7, and 10 micrograms. For the PORTS on-site lab analyzing samples from the PORTS contract lab by inductively coupled plasma, one sample result at the 1 microgram level was reported as a less than and was excluded from these values presented here.
- D:** PORTS reported results for two different analytical methods which the site uses. Inductively coupled plasma analysis is PORTS preferred analytical method for arsenic.
- NOTE:** The mean recovery for six QC samples originally submitted with the NIOSH arsenic samples collected during the survey had a mean recovery of 96% which was reported by the lab to be in control.

TABLE V (continued)  
 Uranium Air Sample Results for Areas in X-326 Process Building and X-700 Converter Maintenance  
 HETA 94-0077  
 Lockheed Martin Utility Services Uranium Enrichment Plant  
 Piketon, Ohio  
 March 2-3, 1994

Sample Date	Building Location	Sample Period (min) <sup>A</sup>	Sample Volume (m <sup>3</sup> ) <sup>B</sup>	Analytical Concentration <sup>C</sup>		Airborne Concentration in ug/m <sup>3D</sup>		Area Sample Location <sup>E</sup>	Notes
				ug/ filter	± TPU error in ug	TWA over sample period	8-hour TWA		
3/1- 3/2/94	Hotel room	581	5.824	0.07	0.016	0.01	0.01	On table in NIOSH investi-gator's room	-
3/2/94	X-326, Operat- ing Floor, Top Purge Traps A,B,C	209	2.103	0.3	0.061	0.1	0.06	Column R-101, Operating Floor	Notes <sup>F</sup>
3/2/94	X-700 Conver- ter Main- tenance	277	2.867	2.5	0.490	0.9	0.5	Area, mounted on stand on work platform; Inside columns A-4,B-4 A-5,B-5	Notes <sup>F</sup>
3/3/94	X-326 Cell Floor	60	0.624	0.2	0.047	0.4	0.05	Midway between columns P-27 & P-30, cell floor, along cell 12 of unit 27-3	Two workers replacing P-nut valves on seal feed on cell 12 Notes <sup>F</sup>

TABLE V (continued)  
 Uranium Air Sample Results for Areas in X-326 Process Building and X-700 Converter Maintenance  
 HETA 94-0077  
 Lockheed Martin Utility Services Uranium Enrichment Plant  
 Piketon, Ohio  
 March 2-3, 1994

Sample Date	Building Location	Sample Period (min) <sup>A</sup>	Sample Volume (m <sup>3</sup> ) <sup>B</sup>	Analytical Concentration <sup>C</sup>		Airborne Concentration in ug/m <sup>3D</sup>		Area Sample Location <sup>E</sup>	Notes
				ug/ filter	± TPU error in ug	TWA over sample period	8-hour TWA		
3/3/94	X-326, cell floor, Evacuation Booster Station	321	3.248	3.7	0.740	1.1	0.8	Located in work area where cutting out and removal took place, Columns B-60,B-61,C-60,C-61	Removal of EEB7 valve on booster station connected to surge drum Notes <sup>F</sup>
DataChem Laboratories Standard Operating Procedure: Total Uranium by Kinetic Pulsed-Laser Phosphorimetry(ref#)				Limit of detection/filter: 0.001 ug					
Evaluation Criteria Source				Airborne Occupational Exposure Limit <sup>G</sup>				Carcinogen Status <sup>H</sup>	
NIOSH Recommended Exposure Limits (REL)				Soluble compounds as Uranium: 50 ug/m <sup>3</sup> Insoluble compounds as Uranium: 200 ug/m <sup>3</sup> Maintain Exposures at Lowest Feasible Level				Occupational Carcinogen	
OSHA Uranium Permissible Exposure Limits (PEL)				Soluble compounds as Uranium: 50 ug/m <sup>3</sup> Insoluble compounds as Uranium: 250 ug/m <sup>3</sup>				-	

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- A:* All sample periods presented in minutes (min).
- B:* Sample volumes are presented as total volume in cubic meters of air (m<sup>3</sup>).
- C:* Analytical concentrations reported as total uranium are reported in micrograms (ug) per filter. The second column accompanying the concentration of uranium per filter is the error value associated with each respective filter analysis. This is identified as the Total Propagated Uncertainty (TPU) and is presented at the 95% confidence level. This error term provides for a range of result values specific to an individual sample and is provided with radiochemistry data. The error value takes into consideration all preparation and analysis errors. The TPU for these results was determined to be plus or minus 20% of the result value.
- D:* Airborne concentration of total uranium is presented in micrograms per cubic meter of air sampled. Two values are presented: the Time-Weighted Average (TWA) calculated only for the sampling period and an 8-hour TWA calculated over a full 8 hour workshift incorporating an assumed zero exposure during the unsampled time period outside of the time period actually sampled. The µg/filter analytical concentration was used to calculate airborne concentrations. The TPU has not been incorporated into the results in the Airborne Concentration columns.
- E:* Area samples were located in the work area within the contamination zone as close to the work location as possible. Area samples were placed by individuals inside the contamination zone at the direction of the NIOSH investigators. Area samples were generally located at a level of between three and five feet above the floor or surrounding walking surfaces. Column designations within buildings are given by letter and number.
- F:* Notes: The placement of sampling equipment inside of the contamination zones precluded access to equipment during its operation inside of these zones. Workers within the zones were instructed concerning equipment placement and the starting/stopping of sampling. Most sampling periods are longer than that required for task performance since equipment had to remain inside of the contamination zone after work was completed and until it was surveyed for radiological contamination by the health physics department and approved for release into uncontaminated areas.
- G:* Airborne Occupational Exposure Limits are presented. The NIOSH recommended exposure limit (REL) represents a full-shift 8-10 hour TWA. NIOSH recommends that engineering controls be used to the maximum extent to maintain exposure levels at the lowest level possible. Supplementary use of personal protective equipment may be necessary to achieve this goal but represents the last choice for protection. The OSHA permissible exposure limit represents an enforceable standard.
- H:* Carcinogen status represents the classification of uranium as a cancer producing substance. Uranium is identified by NIOSH as a carcinogen.

## Appendix A

### Total Propagated Uncertainty

*(The following information is extracted from the DataChem Laboratory report for total uranium results prepared by Dave A. Reddish.<sup>35</sup>)*

The total propagated uncertainty (TPU) is an error term (range of results). TPU generally is provided with radiochemistry data and allows the comparison of a given result to health protection or environmental protection standards with an understanding of the range the result may encompass.

In radiochemistry counting (e.g., alpha or gamma spectrometry, proportional counting, liquid scintillation counting, etc.), most errors are "normally" distributed due to the nature of counting events. Therefore, errors may be determined based on the number of counting events observed, and assumptions do not have to be made about error, as a percentage of results. The absolute counting errors may be calculated based on observations, and these errors are summed in quadrature with systematic errors.

The total uranium analysis is the only non-counting type analyses performed by the DataChem Laboratories (DCL) Radiochemistry Lab. In the kinetic phosphorescence analyzer (KPA) uranium analysis, a phosphorescence intensity decay rate is measured and mathematically extrapolated back to zero time, which represents the uranium contribution, and, therefore, concentration. The KPA software does provide an error term, but this term only represents the error in the measurement, based upon the relative intensity, decay curve slope, and decay curve correlation coefficient. This term does not take into account such errors as measurement, calibration, and separation recovery uncertainties. These terms as well as the measurement errors are addressed by measuring the population standard deviation of blanks measured over time. A comparison is also made to verify that the blank standard deviation ( $\sigma_{\text{BLK}}$ ) is consistent with the standard deviation of low-level standards (ones having a concentration nearest the detection level (MDC)). The  $\sigma_{\text{BLK}}$  is multiplied by 1.96 to determine the blank TPU at the 95% confidence level.

A TPU was determined for blanks but not for the samples. Because KPA errors would not be normally distributed but would tend to follow hyperbolic functions around the calibration curve, the estimation of error at any given concentration would be difficult. The dominant statistical question that health protection specialists, health physicists, or environmental engineers would be asking about samples results is, "Is this reported result significant (a real number)?" Therefore, a relative error is determined, based on the blank statistics and then multiplied by the result for reporting a TPU. The relative error is determined as follows:

$$\text{Relative TPU (\%)} = 1.96 (\sigma_{\text{BLK}} / \text{mean blank result}) \times 100\%$$

The reported error (TPU) follows as such:

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$$\textit{Absolute (reported) TPU} = \textit{Analyte Result X (Relative TPU/100\%)}$$

Based on control data currently maintained by DCL for blanks analyzed by KPA, the relative TPU is 20%. DCL realizes that, as the sample results increase above the MDC, their estimate for error may be too high, but, in that the analysis of the data is generally more critical near the detection level, their perception is that this methodology is appropriate to answer the data user's question as stated above.