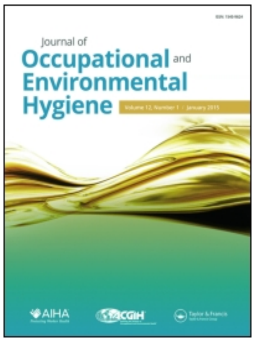

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Case Studies
Identification of Potential Sources of Arsenic Exposure During Scrapyard Work at a Former Uranium Enrichment Facility

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In 2002, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation from union workers and management of a former uranium enrichment facility in Ohio, one of two in the United States operated by a nongovernment contractor and subcontractors.(1,2) Work had recently begun on dismantling the components of the gaseous diffusion process cascade, and during that process, employees and management detected a previously unknown inorganic arsenic (As) contamination.(3) Further investigation found that not only was the entire work area contaminated but that arsenic was present on the inner surfaces of the workers' respirators and in their urine. This case study describes how the NIOSH investigator and the contractor identified the source of that contamination and the recommendations that were made to reduce worker exposure.

IDENTIFICATION OF ARSENIC SOURCES

When routine air monitoring for metals during scrapyard torch cutting unexpectedly revealed high concentrations of arsenic, efforts to identify its source led to the discovery of blocked instrument lines that contained a yellow-white, viscous, hygroscopic material.(4) Analysis of that material by the facility's laboratory staff indicated the material was arsenic oxide, and that the original substance may have been either chlorylarsenic hexafluoride ($ClO_2 \cdot AsF_6$) or arsenic tetrachloride-arsenic hexafluoride $[AsCl_4+] \cdot [AsF_6-]$.(5) A second deposit, though somewhat different in appearance, was found in another cell and was also believed to be either $ClO_2 \cdot AsF_6$ or $[AsCl_4+] \cdot [AsF_6-]$.

X-ray diffraction analysis of the residue revealed hydrogen arsenate and copper arsenate. Apparently, arsenic had reacted with the copper instrument lines to form the copper arsenate compound.(6,7) Laboratory personnel from a similar facility in another state suggested that the material may have been arsenic pentafluoride that had formed a complex with hydrofluoric acid (HF), a metal, or other unidentified compounds.

Arsenic may have entered the system either as an impurity in the uranium hexafluoride (UF_6) feed material or as a contaminant of fluoride-bearing ore used to generate HF or fluorine (F_2) during fluorination of uranium tetrafluoride, or uranium octoxide. Since the facility used a system to remove impurities from F_2, it was eliminated as a source of the arsenic contamination. However, process engineers determined that the UF_6 feedstock entering the facility in the 1980s was contaminated with arsenic.(8)

Exposure to inorganic arsenic can produce dermatitis, keratoses, peripheral neuropathies, and peripheral vascular diseases, and can cause cancer of the skin, liver, and lungs. Though it can be absorbed dermally it is primarily absorbed via inhalation and ingestion.(9) Ingestion of arsenic from contaminated hands may also result in absorption of toxicologically significant amounts of arsenic.(10)

Inorganic arsenic is eliminated from the body through metabolism and urinary excretion. About 60% of an absorbed arsenic dose can be eliminated in urine. The biological half-life of arsenic in humans is 24 to 36 hours. Inorganic metabolites appear in urine shortly after the start of exposure and rise slowly during the first days then tend to level off.(11,12) If workers are exposed to arsenic on subsequent days, their urinary arsenic concentration may increase throughout the week and decrease over the weekend or other nonwork periods when there is no additional exposure.

Nonoccupational sources of arsenic include drinking water, food, polluted air and cigarette smoke (12 to 42 μg/cigarette).(13,14) Therefore, arsenic can be found in the urine of people who have had no occupational exposure to it. Concentrations of inorganic arsenic and its urinary metabolites in the general population of European countries are usually below 10 μg/L (about 8.9 μg/g creatinine), but concentrations are slightly higher in the United States.(9,10)

SCRAPYARD TORCH CUTTING

There were 27 workers in the scrapyard: 7 welders, 8 maintenance mechanics, 4 laborers, 5 chemical operators, and 3 vehicle drivers, whose principal function was to reduce the size of the metal parts of the cascade system either by mechanical shearing or torch cutting using an oxy-acetylene cutting torch. Once the parts were reduced in size they were removed by forklift and placed in shipping containers.

To reduce worker exposure to fumes during torch cutting, one of the chemical operators positioned a local exhaust ventilation (LEV) apparatus fitted with a high-efficiency particulate air (HEPA) filter close to the source of emissions. The system included a 10″ by 20″ unflanged hood equipped with a metal spark arrester grill connected by a 6″ flexible plastic duct to a fan motor assembly designed to move 2100 cubic feet of air per minute. The entire apparatus was on wheels so it could be maneuvered as needed to capture fumes during torch cutting. During inclement weather torch cutting occurred in a covered area; six of those LEV units were used to provide general building exhaust ventilation.

All torch cutting workers wore respiratory protective devices consisting of a full face-piece air purifying respirator (FFAPR) fitted with HEPA P-100 filter cartridges. The respirators were removed after cutting was finished. In addition, workers wore anticontamination coveralls; flame retardant head, shoulder, and shoe covers; total body coveralls; safety shoes; leather welding aprons, and leather gloves with latex undergloves.

According to the contractor, the size reduction activity in the scrapyard had begun in 2000. In 2001 the contractor collected personal breathing zone air samples from workers exposed to metal fumes in the torch cutting plumes. Analysis of 16 samples revealed that arsenic concentrations ranged from 2–12 μg arsenic/m^3 of air, 6 samples (37.5%) exceeded the arsenic action level of 5 μg/m^3 as an 8-hour time-weighted average, and 2 samples (12.5 5%) exceeded the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) of 10 μg/ m^3.(15,16) In response to those findings, an "arsenic control plan" was put into effect to reduce worker exposure to arsenic and to determine, through a medical surveillance program, whether workers were incurring an arsenic exposure.

The medical surveillance program included a physical examination and collection of urine for the determination of urinary inorganic/organic arsenic. The results from those samples were compared with the American Conference of Governmental Industrial Hygienists' (ACGIH®) biological exposure index (BEI®) of 35 μg/L of urine, which was established by ACGIH as an indication of the amount of arsenic that would be expected in the urine of a worker exposed at the threshold limit value of 10 μg arsenic/m^3 of air.(11,12)

INVESTIGATION AND ANALYTICAL METHODS

Though the scrapyard workers wore appropriate respiratory protection and clothing, concern remained that they might be exposed to arsenic when they removed their respirators and outer garments. A meeting was held with the workers, union representatives, and management officials to discuss their concerns and discuss potential sources of exposure. Based on those discussions it was decided to: (1) observe all work practices to identify any that could lead to arsenic exposure; (2) review the contractor's industrial hygiene and biological monitoring data; (3) evaluate respirator cleaning and maintenance procedures; observe the use of the LEV during torch cutting operations; and (5) collect wipe samples from various objects that the workers routinely came in contact with for the subsequent analysis for arsenic.

Wipe samples for arsenic determination were collected according to NIOSH Method 9100 using Ghost Wipes® to swab surfaces.(17) Because the only intent of the wipe sampling was to determine whether arsenic had entered the inside of the respirators, the surface area of the irregularly shaped surfaces was not calculated; thus, the results from those samples were presented only in terms of μg/wipe and not μg/cm^2. Wipe samples were analyzed for arsenic according to NIOSH Method 7901, modified to enable microwave sample digestion by: (1) transferring the sample to a clean microwave digestion vessel; (2) adding 10 mL of 1:1 (volume:volume) American Society for Testing Methods (ASTM) type II water:concentrated nitric acid; (3) sealing the vessel and placing it in a microwave oven (CEM, MARS System, Matthews, N.C.) that was operated at a preset program as described in the addendum to NIOSH Method 7300; and (4) transferring an aliquot of the sample to a 25-mL volumetric flask and diluting it to 25 mL with ASTM type II water. Analysis was performed using a PerkinElmer Zeeman 5100 (PerkinElmer, Boston, Mass.) graphite furnace atomic absorption spectrophotometer. The analytical limit of detection (LOD) for this method was found to be 0.1 μg/wipe and the limit of quantitation (LOQ) was 0.4 μg/wipe. No arsenic was found on any of three media blanks submitted for analysis.

Based on the NIOSH results, industrial hygienists from the contractor conducted additional wipe sampling to determine the efficacy of the respirator cleaning program. To do this, 13 newly issued FFAPRs were randomly selected from issued stocks at the Don/Doff Trailer respirator storage area. The FFAPRs had been recently disassembled, washed, reassembled, inspected, and sealed in plastic bags at the on-site respirator cleaning facility. FFAPRs were removed from their sealed bags and wipe samples were collected over various surfaces including a combination of the exterior of the facepiece, the entire interior of the facepiece, the filter cartridge holder interior, and the circumference of the inner facepiece seal. Measurements of interior and exterior surface dimensions of a medium and a large sized FFAPR were taken to estimate surface wipe areas. The two different sized FFAPRs had about the same surface area. Samples were collected using Ghost Wipe® prewetted wipes and NIOSH Method 9100 and immediately placed into labeled, capped vials.(16) Field and media blank samples were also collected.

Wipe samples were analyzed on site using a modification of NIOSH Method 7300 for analysis of elemental metals by inductively coupled plasmaatomic absorption spectroscopy.(16) An analytical LOQ of 0.170 μg arsenic/wipe was reported and was used for wipe samples that were found to be nondetectable. Wipe sample results were not blank-corrected.

NIOSH investigators also observed work practices in the scrap yard to ascertain if any, alone or in combination, may have contributed to an arsenic exposure. The observations were recorded by digital photography and written records.

RESULTS

NIOSH Wipe Sampling Findings

Of 11 wipe samples collected and analyzed by NIOSH, five were found to contain detectable amounts of arsenic including 0.6 and16 μg/wipe on the outside of two respirator facepieces. Another wipe sample taken from inside the facepiece of a "freshly cleaned" respirator yielded 1.0 μg. All field blank samples were below the LOD of the instrument. Laboratory studies to validate the collection efficiency of the wipe sampling method using Ghost Wipe for arsenic were not performed.

Contractor Findings

Based on the NIOSH results, the contractor initiated a wipe sampling effort. However, detectable inorganic arsenic was found on field and media blanks analyzed by the contractor's laboratory, making interpretation of their findings difficult. The greatest amount of inorganic arsenic surface contamination, .015 μg arsenic/cm^2 (or 2.45 μg arsenic/wipe), was found on the interior of the filter cartridge housings of one FFAPR. The inner facepiece seal of this same respirator had an arsenic surface contamination level of 0.014 μg arsenic/cm^2, (or 2.58 μg arsenic/wipe). On visual inspection, this respirator had no distinguishable discoloration, soiling, or damage. For reference, the floor area of the Don/Doff Trailer where samples were collected revealed an inorganic arsenic surface contamination of 0.02 μg arsenic/cm^2 (or 2.03 μg arsenic/wipe).

According to the contractor's industrial hygienist, detectable amounts of inorganic arsenic were found on all 13 wipe samples collected from various FFAPR surfaces. Nine of the 13 results were less than the LOQ of the analytical method but greater than or equal to the analytical LOD.

DISCUSSION AND RECOMMENDATIONS

The basis for conducting urinary monitoring for arsenic was the serendipitous finding of airborne arsenic during torch cutting operations. Consequently, the contractor implemented routine arsenic air monitoring and a biological monitoring program that required collection of a urine specimen at the end of each work week as specified by the ACGIH BEI guidelines.

Unfortunately, at the start of this program the contractor did not collect any urine from potentially exposed workers at the beginning of the week when their urinary arsenic levels would be expected to be at or near background levels. Further, arsenic exposures were sporadic and therefore it was not possible to correlate airborne exposures with urinary arsenic concentration. Furthermore, several workers who appeared to have urinary arsenic concentrations that approached the BEI (range: 3.40–29.51 μg arsenic/g creatinine; $N = 273$) were found to have unusually low urinary creatinine concentrations. For example, values of 0.28, 0.6, and 0.24 g creatinine/L of urine were found in workers whose urinary arsenic concentrations were 38.46, 16.67, and 41.67 μg arsenic/g creatinine, respectively. Thus, it is not possible to draw any conclusions regarding the relative contribution of inhalation, ingestion, or dermal absorption to the workers' arsenic body burden, nor is it possible in this case to use biological monitoring to determine if airborne exposures were exceeding the NIOSH recommended exposure limit (2 μg/m^3) or the OSHA PEL-TWA (10 μg/m^3).(15,17,18)

Nevertheless, after accounting for other potential sources of arsenic, these data, taken with the airborne arsenic concentrations and the finding of arsenic on the inner surfaces of the workers' respirators, demonstrate that workers were incurring an arsenic exposure as a result of torch cutting.

In addition to having established a pathway of exposure, further investigation revealed that procedures for the appropriate donning/doffing of personal protective equipment (PPE) were loosely enforced. Since workers have the potential for arsenic exposure when near the torch cutting operation, workers should not doff any of their PPE until they reach the Don/Doff trailer. Rules regarding donning/doffing PPE must be followed and each worker should conduct an inspection of their respirator assembly each time it is used. Each wearer must be familiar with respirator inspection criteria and those personal hygiene issues that could adversely affect the proper respirator fit and seal. Respirator wearers identifying an inspection deficiency should report that deficiency to their frontline manager and ensure that the respirator is removed from service.

Finding 16 μg arsenic on a wipe sample taken from a "clean" respirator facepiece indicates that the cleaning procedure being used was not adequate and given the failure to follow proper donning and doffing procedures indicates that handling the respirators is a potential source of arsenic exposure. Unfortunately, the site did not have any new, unused respirators; thus it impossible to make comparisons with data collected from "freshly cleaned" respirators to evaluate the effectiveness of the washing process. Despite the fact that the current respirator cleaning and sanitizing operation was consistent with the recommended respirator cleaning practices from Annex A of ANSI Z88.2-1992, *American National Standard for Respiratory Protection*, steps to improve the effectiveness of the process appear warranted. The washing solution (pH 14) may have inhibited the complete removal of arsenic surface contamination indicating the need for a more effective detergent.

The LEV system used to control the welding fume was not properly maintained and was in poor working order. The unflanged hood appeared to provide little fume control since the spark arrester grating on the face of the hood was partially clogged. Those findings highlight the need for regular inspection and cleaning of the LEV components including the hood, grate, duct work, and fan motor assembly. Installing appropriate flanging around the perimeter of the exhaust hood can increase capture velocity by nearly 40%.(18) Also, the spark arresting gratings were found to be partially clogged and must be kept clean to ensure the maximum capture efficiency of the hood. Furthermore, at times the hood was properly located approximately 1–2 feet from the torch but at other times it was as far as 6 feet from the torch. The LEV should be positioned as close as possible to the cutting torch (within 1–2 feet).(18)

Alternatively, an overhead canopy-style hood system that would take advantage of the natural convective properties of the fume plume could be used. If an articulated arm were used, it would allow the hood to be placed directly over the plume and capture efficiency would be greatly enhanced. However, if such a system were to be employed, welders must be aware of its location and ensure that they do not position themselves between the fume source and the LEV.

Finding arsenic in the contractor's blank samples requires a review to validate their wipe sampling and analytical techniques. While it is possible that the blank samples could have been contaminated by improper handling before, during, or after the sample was collected, it is also possible that the contamination occurred in the laboratory.

Overall, the contractor's current arsenic control plan, including air monitoring workers and urine sampling, should be continued to evaluate the effectiveness of the recommended changes made in equipment and work practices. Most importantly, an effort should be made to determine each worker's baseline urinary arsenic concentration.

CONCLUSIONS

The essence of this case study was the search for the source of an unexpected arsenic contamination. The discovery of that contamination caused the contractor to take several steps including more intensive air monitoring for arsenic, monitoring of respirator and other surfaces for arsenic, collection of urine for determination of arsenic body burden, improvement of the local exhaust ventilation system, and an overall revamping of the current worker exposure protection policies and procedures.

There were several issues that complicate a detailed understanding of the magnitude and extent of the arsenic contamination. First, airborne arsenic exposures were variable and not predictable. Second, while the workers' respirators and other surfaces were clearly contaminated with arsenic, there were problems with the contractor's laboratory procedures that made interpretation of the data difficult at best. Third, the variability and lack of predictability of airborne exposures and concerns about the contractor's laboratory procedures, coupled with the failure to obtain baseline urine arsenic concentrations, do not allow a cogent conclusion concerning the amount of arsenic that may have been absorbed by the workers and its relation to either airborne or dermal exposure.

However, that failure is of little consequence to the final determination that an unexpected arsenic exposure existed and that there was a problem with the ventilation system in use at the time. Despite the fact that the wipe samples taken from the respirator interiors are only qualitative, the finding of any arsenic on the interior surfaces demonstrates that the workers were not adequately protected and were incurring arsenic exposure.

In a perfect world, the collection and analysis of air, wipe, and urine samples and specimens would be well planned and flawless. However, when exposure sources are unknown and exposures are variable and unpredictable with regard to occurrence and magnitude, and there are problems with the analysis of samples, the best that one can hope to achieve is identification of the source and enhancement of procedures to control it.

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