GOT MERCURY?

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ABSTRACT

Many lamps used in various spacecraft contain elemental mercury, which is efficiently absorbed through the lungs as a vapor. The liquid metal vaporizes slowly at room temperature, but may be completely vaporized when lamps are operating. Because current spacecraft environmental control systems are unable to remove mercury vapors, we considered short-term and long-term exposures. Using an existing study, we estimated mercury vapor releases from lamps that are not in operation during missions lasting ≤ 30 days; whereas we conservatively assumed complete vaporization from lamps that are operating or being used during missions lasting > 30 days. Based on mercury toxicity, the Johnson Space Center’s Toxicology Group recommends stringent safety controls and verifications for any hardware containing elemental mercury that could yield airborne mercury vapor concentrations > 0.1 mg/m³ in the total spacecraft atmosphere for exposures lasting ≤ 30 days, or concentrations > 0.01 mg/m³ for exposures lasting > 30 days.

1. PROPERTIES OF MERCURY

Mercury is an element that occurs in three primary forms: 1) divalent, 2) organic, and 3) elemental [1, 2]. Divalent mercury is also known as ‘reactive’ mercury, because the charged ion reacts to form mercury salts. Perhaps the most infamous form of divalent mercury is mercuric nitrate, which was used to process animal furs in the hat-making industry. Hat makers exposed to mercury fumes often developed neurological symptoms that spurred the phrase ‘mad as a hatter’ [3]. Methymercury and ethylmercury are the most notable organic forms of mercury. Microbes in the sediment of waterbodies transform divalent mercury into methylmercury, which can bioaccumulate in aquatic food webs [4]. As a result, fish are the primary source of human exposure to methylmercury. Ethylmercury is a component of thimerosal, a preservative used in vaccines [5]. The remaining form, elemental, is the form to which crews may be exposed during spaceflight. It is therefore the focus of this evaluation.

2. ELEMENTAL MERCURY IN SPACECRAFT

Elemental mercury is a slightly volatile liquid at room temperature that is used in lamps, switches, rectifiers, and batteries [6]. Mercury-containing lamps are currently used as vehicle and payload lighting in spacecraft (Fig. 1). Mercury vapor is odorless and colorless, and no monitoring method exists to detect mercury vapor in spacecraft atmospheres at recommended limits [6]. In addition, the current environmental control systems onboard US spacecraft are unable to remove elemental mercury vapor from the air [personal communication-environmental control engineer-Marshall Spaceflight Center, Huntsville, AL]. Therefore, the National Aeronautics and Space Administration (NASA) must ensure that any potential mercury exposures are below levels that may cause adverse health effects in crew members who may experience both short-term and long-term exposure to mercury vapors.

3. PHARMACOKINETICS OF MERCURY

Mercury vapor is poorly absorbed through the skin [7], but is efficiently absorbed by the lungs. Approximately 70-80% of inhaled mercury vapor is retained in the alveoli [8]. Once inhaled, mercury is readily taken up by the blood and transported to various tissues. Mercury primarily accumulates in the brain and accumulates to a lesser extent in the kidneys [9]. The absorbed elemental
mercury is converted to the divalent form by the catalase-hydrogen peroxide complex in red blood cells and in the brain [10]. Mercury clearance occurs at different rates in different tissues, but the average half-life is 60 days for elimination from the body as a whole [8].

4. ACUTE MERCURY TOXICITY

4.1. In Animals
Relatively brief (1-30 hours) exposures of animals to high concentrations (e.g. 28 mg/m³) of mercury vapor have been reported to cause death or serious toxicity to the respiratory, gastrointestinal, and cardiovascular systems, the kidneys, brain, and liver [11]. Marked cellular degeneration with some necrosis of heart tissue was observed in rabbits following acute intermittent exposure to 28.8 mg/m³ metallic mercury vapor for periods ranging from 4 to 30 hours [12].

4.2. In Humans
The major target organs of metallic mercury vapor toxicity in humans are the kidneys and the central nervous system. Initial exposure to high concentrations of elemental mercury vapors produces a syndrome similar to "metal fume fever," which is characterized by fatigue, fever, chills, and elevated leucocyte count. Respiratory symptoms are a prominent effect of acute-duration exposure to high concentrations of metallic mercury vapors [11]. The most commonly reported symptoms include cough, dyspnea (shortness of breath), and tightness or burning pains in the chest [13-28]. X-ray analyses of the lungs have primarily shown diffuse infiltrates or pneumonitis [13, 15, 17, 24, 27-29] Other effects in humans include increases in heart rate and blood pressure, inflammation of the oral mucosa, abdominal pains, nausea, and diarrhea [11]. Concentrations of mercury vapor high enough to produce the effects listed above are not readily achievable in current manned spacecraft (except possibly within the limited volume of "space suits").

5. CHRONIC MERCURY TOXICITY
Health concerns associated with elemental mercury are not limited to acute exposure situations. Given that negligible amounts of elemental mercury vapor are removed from the spaceflight atmosphere by current air revitalization systems, chronic exposures (e.g. months to years of exposure) must also be carefully evaluated, and a comprehensive understanding of the chronic toxicity of mercury is vital to the development of acceptable spaceflight exposure limits.

In accordance with the diversity of commercial/industrial uses of mercury, a fair amount is known about the chronic toxicity of elemental mercury, and there are extensive human epidemiological reviews and laboratory animal studies within the scientific literature [6, 11]. While these studies have evaluated a variety of toxicological endpoints, it seems clear that there are two primary target organs that are especially susceptible to mercury damage following chronic exposures; the kidneys and the central nervous system (CNS). Of these two, CNS impairment is the better-documented effect in association with overexposure to elemental mercury in humans. The type and severity of CNS effects can vary depending on exposure level and other factors, but have commonly included tremors, gait impairment, decreased performance on a variety of neurobehavioral test parameters (e.g., finger tapping, motor coordination, memory, and ability to concentrate), and depression. These effects may dissipate somewhat following cessation of exposure, but damage is frequently irreversible. These types of impairment are obviously highly relevant to critical human performance situations, such as spaceflight, and earth-based occupational and spaceflight exposure limits for mercury are intentionally set to be protective of these CNS effects. Acceptable inhalation exposure limits for mercury in other settings vary somewhat depending on the particular populations that are being protected (see Tab 1).

<table>
<thead>
<tr>
<th>Guideline/Organization</th>
<th>Exposure Limit</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLV/ACGIH</td>
<td>0.025 mg/m³</td>
<td>40 hr work week (TWA)</td>
</tr>
<tr>
<td>REL/NIOSH</td>
<td>0.05 mg/m³</td>
<td>40 hr work week (TWA)</td>
</tr>
<tr>
<td></td>
<td>0.1 mg/m³</td>
<td>Ceiling value (max)</td>
</tr>
<tr>
<td>PEL/OSHA</td>
<td>0.1 mg/m³</td>
<td>Ceiling value (max)</td>
</tr>
<tr>
<td>RfC/USEPA</td>
<td>0.0003 mg/m³</td>
<td>Lifetime (70 yr)</td>
</tr>
<tr>
<td>MRL/ATSDR</td>
<td>0.0002 mg/m³</td>
<td>Lifetime (70 yr)</td>
</tr>
<tr>
<td>SMAC/NASA</td>
<td>0.01 mg/m³</td>
<td>7, 30, and 180 days</td>
</tr>
</tbody>
</table>

TLV=Threshold limit value
ACGIH=American Conference of Governmental Industrial Hygienists
TWA=Time-weighted average
REL=Recommended exposure limit
NIOSH=National Institute for Occupational Safety and Health
PEL=Permissible exposure limit
OSHA=Occupational Safety and Health Administration
RfC=Reference concentration
USEPA=United States Environmental Protection Agency
MRL=Minimal risk level
ATSDR=Agency for Toxic Substances and Disease Registry
SMAC=Spacecraft maximum allowable concentration
NASA=National Aeronautics and Space Administration

Table 1. Chronic exposure limits for mercury

6. SAFETY EVALUATION

6.1. Mercury Vapor Estimates
To estimate the amount of mercury vapor formed when an inactive lamp (stowed or 'off') is broken, we used a
study conducted by the New Jersey Department of Environmental Protection [30]. In this study fluorescent lamps containing 4.4-4.7 mg mercury were broken into a 32-gallon plastic barrel. The barrel was sealed, and samples of the air space were analyzed by a Jerome 411 Gold Film Mercury Vapor Analyzer. The amount of mercury vapor formed over a 2-week period was temperature-dependent, and ranged from approximately 17% to 40% for temperatures ranging from 40°F (5°C) to 85°F (30°C) [30]. Spacecraft cabin temperatures are typically maintained near 70°F (~20°C). The vapor pressure of mercury at 20°C is approximately 1/2 the vapor pressure at 30°C, so we would expect significantly less than 40% total mercury vapor formation over 2 weeks at typical cabin temperatures. In addition, the New Jersey study indicated a period of rapid volatilization (approximately 1/3 of the total vapor formed within the first 8 hours), followed by a decreasing rate of vaporization over the remaining days. Therefore, we assumed a maximum of 40% mercury vapor formation in crew vehicles for a period of 30 days or less.

In contrast, the percentage of mercury vapor formation may be greater for unmanned transport vehicles where internal temperatures might exceed 85°F. Also, when mercury-containing lamps are operating, essentially all of the mercury would be in the vapor form. Finally, any uncontained liquid mercury will continue to vaporize into the environment over time. Therefore, we assume 100% of the available mercury is in the vapor form if it escapes in an unmanned vehicle, while a lamp is operating, or when exposure may occur for more than 30 days (currently only on ISS).

6.2. Calculating Exposure Concentrations

The concentration of mercury vapor to which crew members may be exposed when an inactive lamp is broken can be calculated by dividing the amount of mercury vapor by the total habitable volume of that vehicle. For example, a lamp containing 10 mg mercury stowed (not operating) on the Space Shuttle (habitable volume = 65 m$^3$) would result in an average mercury vapor concentration (C) of 0.06 mg/m$^3$ (Eq. 1).

$$C = \frac{10 \text{ mg}}{65 \text{ m}^3} = 0.06 \text{ mg/m}^3$$

This estimate (Eq. 1) would apply to all elemental mercury sources that are not heated to temperatures above 85°F and when exposure is expected to occur for 30 days or less.

For mercury escaping in an unmanned vehicle, when a lamp is operating, or when exposure is expected to occur for more than 30 days, all of the mercury is assumed to be in the vapor form. For example, a lamp operating aboard the Space Shuttle would result in an average mercury vapor concentration (C) of 0.15 mg/m$^3$.

$$C = \frac{10 \text{ mg}}{65 \text{ m}^3} = 0.16 \text{ m}^3$$

7. FINAL RECOMMENDATIONS

Based on existing SMAC values for mercury vapors, the lack of continuous sources of vapor, and human absorption, distribution, metabolism, and excretion of mercury, we determined concentrations below which no adverse short- or long-term health effects would be expected to occur. We recommend stringent safety controls and verifications for any hardware containing elemental mercury that could yield airborne mercury vapor concentrations greater than 0.1 mg/m$^3$ in the total spacecraft atmosphere for exposures lasting 30 days or less. For exposures lasting more than 30 days, we recommend that safety controls and verifications be applied to any elemental mercury source that could yield concentrations greater than 0.01 mg/m$^3$.

8. REFERENCES

Final Recommendations

• Mercury vapor concentrations of 0.1 mg/m³ or less for 30 days or less will not result in a critical or catastrophic toxicity hazard.

• Mercury vapor concentrations of 0.01 mg/m³ or less for more than 30 days will not result in a critical or catastrophic toxicity hazard.
Got Mercury?

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Background

• Payloads and Systems components contain elemental mercury (Hg)
  – Lamps (metal halide, fluorescent)
  – Amounts range from \( \sim 2-30 \text{ mg Hg} \)

• Current environmental control systems cannot remove mercury from the cabin atmosphere
Properties of Mercury

- Occurs in three primary chemical forms
  - Divalent (compounds and ions)
  - Organic compounds (methylmercury, ethylmercury)
  - Elemental
Properties of Mercury

• Liquid at room temperature
• Slightly volatile at room temperature
  – Volatility (vapor pressure) increases steeply as temperature increases
  – Insoluble in water
Exposure to Mercury

• Vapors are the primary health hazard
  – Readily passed into the bloodstream from inspired air
  – Accumulates in the brain and kidneys
  – Oxidized to the divalent form and eliminated primarily through feces and urine
  • Average ½ life is ~60 days in the human body
Acute Health Effects

• Respiratory irritation and inflammation
  – Cough, chest pain/discomfort, impaired pulmonary function

• Neuropsychiatric symptoms
  – Tremor, irritability, hyperactivity
Chronic Health Effects

• Central nervous system (CNS)
  – Tremor, decreased coordination
  – Erethism (irritability, excitability, loss of memory, loss of self-confidence, insomnia, and depression)

• Kidneys
  – Renal dysfunction (proteinuria, etc.)

med.stanford.edu/nephrology/community/
Current Spacecraft Maximum Allowable Concentrations (SMACs)

- 1-hour: 0.1 mg/m³
- 24-hour: 0.02 mg/m³
- 7-day: 0.01 mg/m³
- 30-day: 0.01 mg/m³
- 180-day: 0.01 mg/m³
Safety Evaluation

- US Payload Safety Review Panel (PSRP) elected to consider release of elemental Hg a unique hazard
- Toxicology tasked with developing a non-hazardous limit
Considerations

• Single limit is insufficient
  – Different health endpoints for acute and chronic exposures
  – Chronic exposures possible since current ECLS systems cannot remove Hg

• Toxicology developed limits for exposures lasting 30 days or less and more than 30 days
Considerations

- Mercury Vapor Formation
  - Temperature dependent
    - Operating (heated) vs. stowed
    - Short-term vs. long-term exposure
17-40% of 4.5 mg Hg contained in fluorescent bulbs volatilized in a sealed environment over a period of 2 weeks at temperatures ranging from 40-85°F.
Calculating Exposure Concentration

- Stowed items on manned vehicles when exposure is expected to occur for 30 days or less (Shuttle, Soyuz)
  - Total Hg x 40% ÷ total vehicle volume
- Operational (heated) items on manned vehicles when exposure is expected to occur for 30 days or less
  - Total Hg x 100% ÷ total vehicle volume
Calculating Exposure Concentration

• For unmanned vehicles (Progress, HTV, ATV)
  – Total Hg x 100% ÷ total vehicle volume

• For manned vehicles when exposure is expected to occur for more than 30 days (ISS)
  – Total Hg x 100% ÷ total vehicle volume