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AEROSPECT OPERATIONS CRITERIA FOR MERCURY THRESHOLDS

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FOREWORD

This study was conducted for the National Aeronautics and Space Administration, George C. Marshall Space Flight Center by IIT Research Institute under NASA Contract No. NAS8-31546. Dr. J. Briscoe Stephens was the NASA Project Officer and Dr. Sidney Katz was the IITRI Project Manager.

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Respectfully submitted,

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AEROSPACE OPERATIONS CRITERIA FOR MERCURY THRESHOLDS

Abstract

The hazards anticipated from a large-scale mercury spill during a possible failure in the pre-flight and early flight stages of the Space Shuttle have been studied. On the basis of existing data, toxicity thresholds were investigated as well as other consequences of mercury interacting with the environment.

Three sites of mercury spill were investigated: land, water, and atmosphere. The major problem arising from the release of mercury over land areas would be the presence of mercury vapor. Estimates of mercury vapor concentrations were made for ground and air spills with and without conflagration.

Spills in inland or coastal waterways may cause long-term contamination of the immediate environment by biological conversion of the mercury. These compounds can enter the food chain and affect both wildlife and humans. The present study focused on the early detection of a developing hazard.

A laboratory study of interactions between mercury vapor and ozone in a low pressure, high ultraviolet radiation environment approximated the conditions of a mercury vapor release in the ozone layer region of the stratosphere. Clear evidence of an interaction leading to the destruction of ozone by conversion to oxygen was obtained. This could, of course, lead to a serious impact on the earth's environment.

On the basis of published clinical information, environmental limits were proposed for human exposure to mercury vapor. Since inhaled mercury is retained with an efficiency approaching 100 percent, a time-concentration product was used to define safe levels for exposures of 10 minutes to 24 hours. It is

noted that since children have a greater susceptibility to mercury intoxication than adults a different set of standards should be applied to them. Mercury vapor tends to show fairly large concentration gradients with height, which may partly explain the greater sensitivity of children to this agent.

The recommended levels for human exposure to mercury vapor are shown in the following table:

MERCURY VAPOR EXPOSURE LIMITS, $\mu g/m^3$ (ppb)

Duration of Exposure	Adult	Child (<5 years)
10 min	300 (250)	2.5 (2)*
60 min	25 (20)	2.5 (2)
8 hrs	3 (2.5)	0.3 (0.25)
24 hrs	1 (0.8)	0.1 (0.08)

*Maximum recommended exposure level for all intervals less than 60 min.

The major hazard identified with the pollution of waterways by a mercury spill results from the consumption of contaminated fish. An assessment of the limited published data suggests that a combination of sediment analysis and pH assessment of the water can be used to indicate the existence of a potentially hazardous condition.

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PART I

Mercury Hazards in the Near Earth Environment

1. INTRODUCTION

This investigation is a phase of the hazards analysis of the NASA Space Shuttle Project. The Space Shuttle payload will include 1500 kg of elemental mercury to fuel the final stages of the vehicle's mission. The present study examines the consequences of an accidental release of the mercury during the initial flight stages from pre-launch to about 30 km in the atmosphere, the height of the ozone layer. Contingencies include the consequences of accidental spills and vehicle damage, with and without conflagration.

The report is presented in two parts. Part 1 analyzes the hazards of a spill in the near-earth environment over land or water, on the basis of available published data. Part 2 investigates the interaction of mercury with an ozone environment simulated in the laboratory.

1.1 Properties of Mercury

Mercury is widely distributed throughout the biosphere,(1) occurring in nature principally as the highly insoluble sulfide whose solubility product is 3×10^{-54} at 26°C. Mercury freezes at -39.9°C and boils at 357°C and has a specific gravity of 13.55 at 20°C. A mass of 1500 kg of liquid mercury occupies a volume of about 110 liters or 3.9 cu ft.

Mercury has a surface tension of 480 dynes/cm at 0°C. In free fall, liquid mercury will form droplets estimated to be about 1 mm in diameter.(2)

The vapor pressure of mercury has been reported in detail in the literature.[3] Some representative pressures and the corresponding vapor concentrations* are given in Table 1 and Figure 1.

Table 1

VAPOR PRESSURES OF MERCURY

Temperature, °C	Vapor Pressure, mm Hg	Saturated Vapor Concentration in Air mg/m^3	ppm
0	0.00019	2.15	1.57
10	0.00049	5.57	4.62
20	0.00120	13.2	10.9
30	0.00278	29.5	25.3
40	0.00608	62.5	55.5
50	0.01267	126.2	115.0
60	0.02524	243.8	237.0
100	0.2729	2350.0	2480.0

The mercury vapor diffusion rate in air can be estimated from Fick's Law:

$$N_{Hg} = - D \frac{dc}{ds}$$

*Concentrations are stated as follows in this report:

Mercury vapor in air

1 μg/m^3 (weight per volume) $\cong$ 0.8 ppb (weight per weight)

Mercury in water

1 mg/liter (weight per volume) $\cong$ 1 ppm (weight per weight)

1 μg/liter $\cong$ 1 ppb

Mercury in solids (food, fish, etc)

1 mg/kg = 1 μg/g (weight per weight) = 1 ppm

ppm = part per million; ppb = part per billion

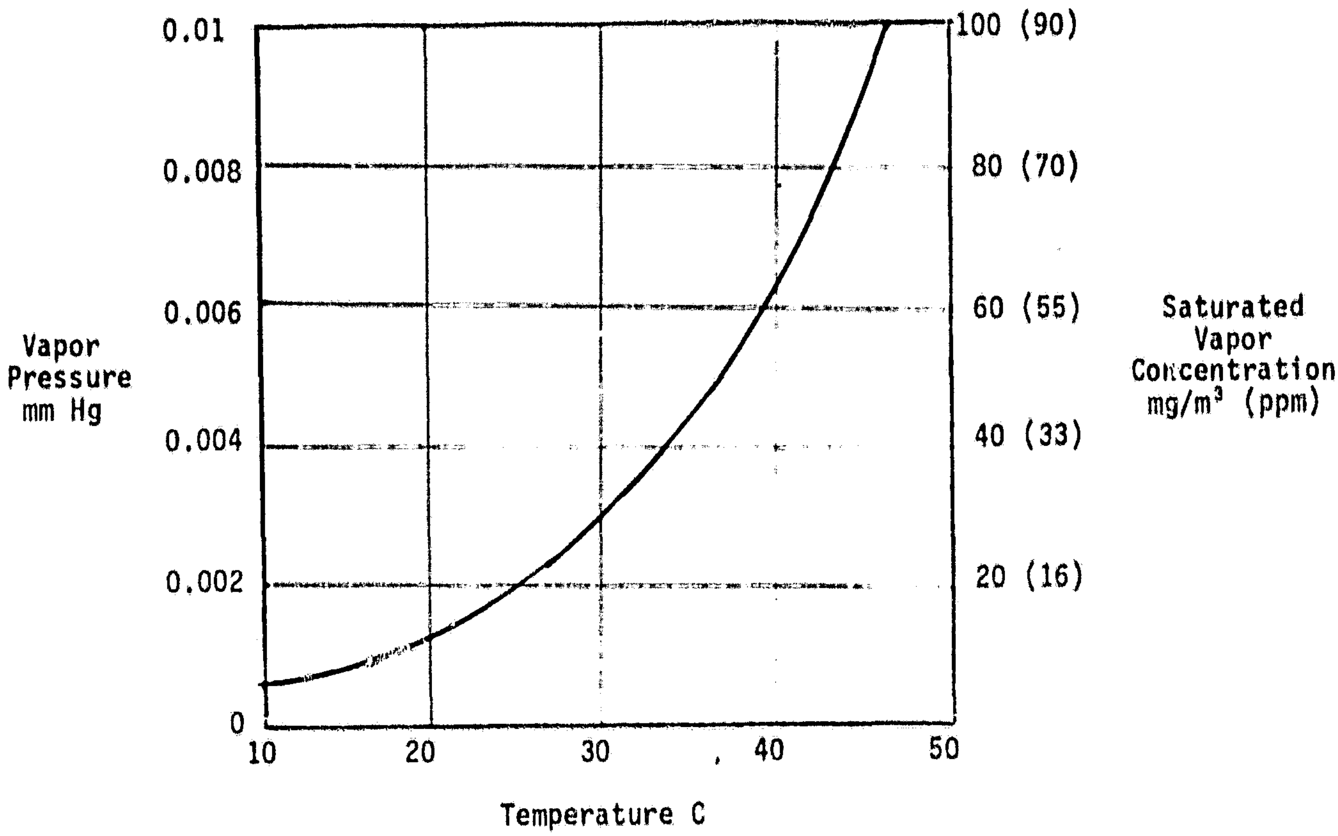

Figure 1. Mercury Vapor Pressure and Saturated Vapor Concentration in Air vs. Temperature.

N_{Hg} is the amount of mercury vapor diffusing per unit area per sec across a vapor concentration gradient of dc/ds. D is the diffusion coefficient for mercury vapor in air, estimated to be 0.299 cm^2/sec.[4]

The evaporation rate for mercury may be estimated from gas law kinetics using the relation:[5]

$$\mu = p \ (M/2\pi RT)^{1/2}$$

where μ is the evaporation rate per unit area in unit time. Calculated evaporation rates for mercury at selected temperatures are listed in Table 2.

Table 2

EVAPORATION RATES OF MERCURY AS A FUNCTION OF TEMPERATURE

Temperature, °C	Evaporation Rate, $g/cm^2/sec$
20	5.8×10^{-5}
30	1.31×10^{-4}
40	2.84×10^{-4}

1.2 Historical Background

The toxicity of mercury has been the subject of many reviews.[6,7,8,9,10,11] Mercury has been used in industry and medicine since antiquity and a qualitative awareness of its toxicity existed at least since Roman times.[12] Much of the current concern is related to a series of regional disasters in Guatemala,[13] Pakistan,[14] Iraq,[15] and on a lesser scale in the United States,[17] when animals fed contaminated grain were used for human consumption. Still another series of serious incidents occurred in Minimata and Niigata, Japan, in which seafood contaminated by industrial mercury effluents infected the neighboring human populations.[10]

In recent years, the release of mercury into inland waterways by agricultural and industrial electrochemical processes has been a subject of major concern. The evidence for the entry of elemental and inorganic as well as organic compounds of mercury into the food chain is well-established. Strong evidence points to its transfer with biological conversion to fish and subsequently to birds, animals, and ultimately to humans.[18,19]

This study is concerned specifically with the consequences of an isolated large-scale "point" release of elemental mercury. Two comparable incidents are reported in the literature involving the direct transfer of elemental mercury to a large human population.

In 1804 a fire in a mercury mine in Idria, Austria (now Yugoslavia), exposed the community to mercury vapor for several days. Nine hundred people developed characteristic mercury intoxication symptoms. No fatalities were reported. A report of the incident noted that domestic animals also showed mercury poisoning.[20] The second incident occurred at sea in 1810. A ship's leaking cargo of mercury affected "several hundred" sailors, ultimately causing three fatalities.[20] Other cases of acute elemental mercury intoxication described in the literature are comparatively recent, isolated events. They are listed in Appendix 2 of this report and discussed later in Section 3.1.

The toxicology of mercury has been reviewed in considerable detail by Friberg and Vostal,[21] d'Itri[18] and others. Inhaled mercury vapor is retained by the body with efficiencies reported to be as high as 100 percent.[22,23,24] It is rapidly transferred to the pulmonary and vascular systems. Very little absorption occurs along the alimentary canal,[25] and this form of exposure does not seem to be hazardous.[26] Exposure to mercury vapor during dental treatment has caused dermatitis in oral areas.[27] Mercury was formerly used in dermatological salves[28] and there is some evidence of cutaneous penetration.[29,30] A fatality has been reported, attributed to mercury penetrating an open cut.[31]

1.3 Exposure Levels

Mercury appears to have no useful function in metabolic processes[32] and its presence in an organism at any level constitutes a contamination. Because of its ubiquitous involvement in the environment, it is useful to distinguish between exposures which might be generated in the present operation and the more general problems of mercury toxicity.

The present problem is limited to a consideration of the toxic consequences of an inadvertent mercury spill. In the case of overland spills, the large class of hazards related to the misuse of toxic chemical materials and to persistent low-level chronic exposure are not relevant. Of present significance, is the inhalation of elemental mercury vapor, which is addressed in detail in this paper.

Where the spill is into a waterway, the hazard is caused by the introduction of the mercury into the biological food chain. This can occur over an extended period and may involve the conversion of mercury to highly toxic compounds, in particular the methyl derivatives.[32a]

The U. S. Environmental Protection Agency has reported background information on emission standards[33] and a number of tentative standards are listed below:

Recommended limits for exposure to airborne mercury:

- The U. S. Federal Register stated in 1972 that exposure in any 8-hour shift of a 40-hour week must not exceed the time-weighted average of 1 mg/10 m^3 (100 $\mu g/m^3$ or 80 ppb).[34]
- A proposed amendment in 1974 stated that the mercury levels should not exceed 1 $\mu g/m^3$ (0.8 ppb) averaged over a 30-day period.[35]
- The Rockwell SEPS Report[36] in 1974 cited the following limits for human exposure:

	10-min Average	24-hr Average
General Public	5 $\mu g/m^3$ (4 ppb)	0.5 $\mu g/m^3$ (0.4 ppb)
Industrial Worker	500 $\mu g/m^3$ (0.4 ppm)	50 $\mu g/m^3$ (40 ppb)

- The American Conference of Government and Industrial Hygienists recommended in 1971 a threshold limit value of 0.05 mg Hg/m^3 (40 ppb) for mercury, metal, inorganic mercury, and non-alkyl organomercury compounds.[37] The National Institute for Occupational Safety and Health (NIOSH) also cited 0.05 mg Hg/m^3 in 1973[38] for an 8-hour day and a 40-hour week.

Mercury levels in water and foods:

- The U. S. Public Health Service in 1970 proposed a standard of 5 ppb of mercury in water.[39] This level has official status in Russia.[40]
- In 1971, a Swedish committee applied a safety factor of 0.1 to an estimate of 300 μg of methyl mercury per day as the lowest toxic concentration for a 70 kg man. This led to a recommendation of 210 μg Hg per week.[41]

- In 1972, the Food and Agricultural Organization and the World Health Organization (WHO) established a provisional tolerable weekly intake of 300 μg of total mercury, of which not more than 200 μg may be methyl mercury. WHO also suggested a limit of 0.2 ppm of mercury in edible fish.[42]

2. ANALYSIS OF MERCURY SPILLS

2.1 Classes of Spills'

The mercury spills considered in this study could occur prior to or during launch, or after takeoff. The incidents could occur with or without heating. If the event occurs as a cold spill, the mercury may be released on the ground or in the air. In the latter case, fallout can lead to deposition on the land, in urban or rural areas, in water areas which may be inland, off-shore, or deep sea. If the event occurs with conflagration, a mercury vapor plume may form and diffuse away from its point of origin. The hazard can be correlated with the mercury concentration where the cloud intersects with the earth, or it may interact with the atmosphere. Each of these cases has been reviewed and hazardous limits estimated wherever possible. In doubtful cases, or where information is marginal, a pessimistic or "worst case" alternative has been used to develop the model. The interaction of mercury with ozone is discussed in a separate section.

2.2 Mercury Spills Without Conflagration

The following situations are discussed:

1. Ground-level spills
2. High-altitude spills
   - Deposition on land areas
   - Deposition in inland or coastal waterways
   - Off-shore deposition.

2.2.1 Ground Mercury Spills

The ground spill will deposit 1.5×10^6 g of mercury in a pool of 110 liters volume. Assuming a pool thickness of 0.1 cm, the pool will have an area of 1.1×10^6 cm^2, corresponding to a circular pool of about 11.8 m diameter.

In humid environments, mercury tends to form a thin oxide film which inhibits evaporation.[43] Under these conditions, the mercury can persist as a low level source of mercury vapor for a very long time. Dust, grease, some metals, and other contaminants can produce similar consequences.[44] Increases in temperature increase the saturation vapor pressure (Table 1) and evaporation can be accelerated by air flowing across the liquid mercury surface.[45,46]

In the following analysis, dry conditions and a clean mercury surface are assumed in order to define the highest mercury vapor concentration and, therefore, the most hazardous environmental consequences.

It is estimated (Table 2) that the evaporation rate of mercury at 20°C is 5.8×10^{-5} g/cm^2 sec. For a surface area of 1.1×10^6 cm^2, the total evaporation rate is 63.8 g/sec and therefore the time for total evaporation of the pool will be 6.5 hours. These data and the comparable figures for 30° and 40°C are listed in Table 3.

Table 3

EVAPORATION TIMES AND RATES FOR 1.5×10^6 g OF MERCURY IN A LIQUID POOL 1 mm THICK AT VARIOUS TEMPERATURES

	20°C	30°C	40°C
Evaporation rate, g/cm^2 sec	5.8×10^{-5}	1.31×10^{-4}	2.84×10^{-4}
Total Evaporation Rate, g/sec	63.3	144	313
Time for Total Evaporation, hr	6.5	2.9	1.3

The dispersal of the mercury vapor plume was calculated using Sutton's procedure [47] as modified by Turner,[48] assuming a daylight spill under strong solar irradiation with a surface wind of 2 m sec (~4.5 mi/hr). The mercury vapor concentration in the plume was assumed to have a Gaussian distribution in the horizontal and vertical planes normal to the wind, with total reflection (i.e., no deposition at the earth's surface). The calculations in Table 4 give the maximum centerline downwind vapor concentrations between 500 m and 3 km from the spill for the conditions stated in Table 3.

Table 4

DOWNWIND CENTERLINE CONCENTRATION OF MERCURY VAPOR (g/m^3) UNDER STRONG SOLAR IRRADIATION FOR CONDITIONS CITED IN TABLE 3

Temperature °C	20	30	40
Duration, hr	6.5	2.9	1.3
Concentrations:			
500 m downwind	9.2×10^{-4}	2.1×10^{-3}	4.5×10^{-3}
1 km downwind	1.0×10^{-4}	2.3×10^{-4}	5.0×10^{-4}
2 km downwind	1.3×10^{-5}	2.9×10^{-5}	6.4×10^{-5}
3 km downwind	5.3×10^{-6}	1.2×10^{-5}	2.6×10^{-5}

The data of Table 3 and 4 have been used to determine the contours of the vapor plume for the indicated conditions at ground level. Figure 2 shows isopleths at concentrations of 5×10^{-4} g/m^3 and 5×10^{-6} g/m^3 for ground level spills at 20°C and 40°C under bright, sunny conditions.

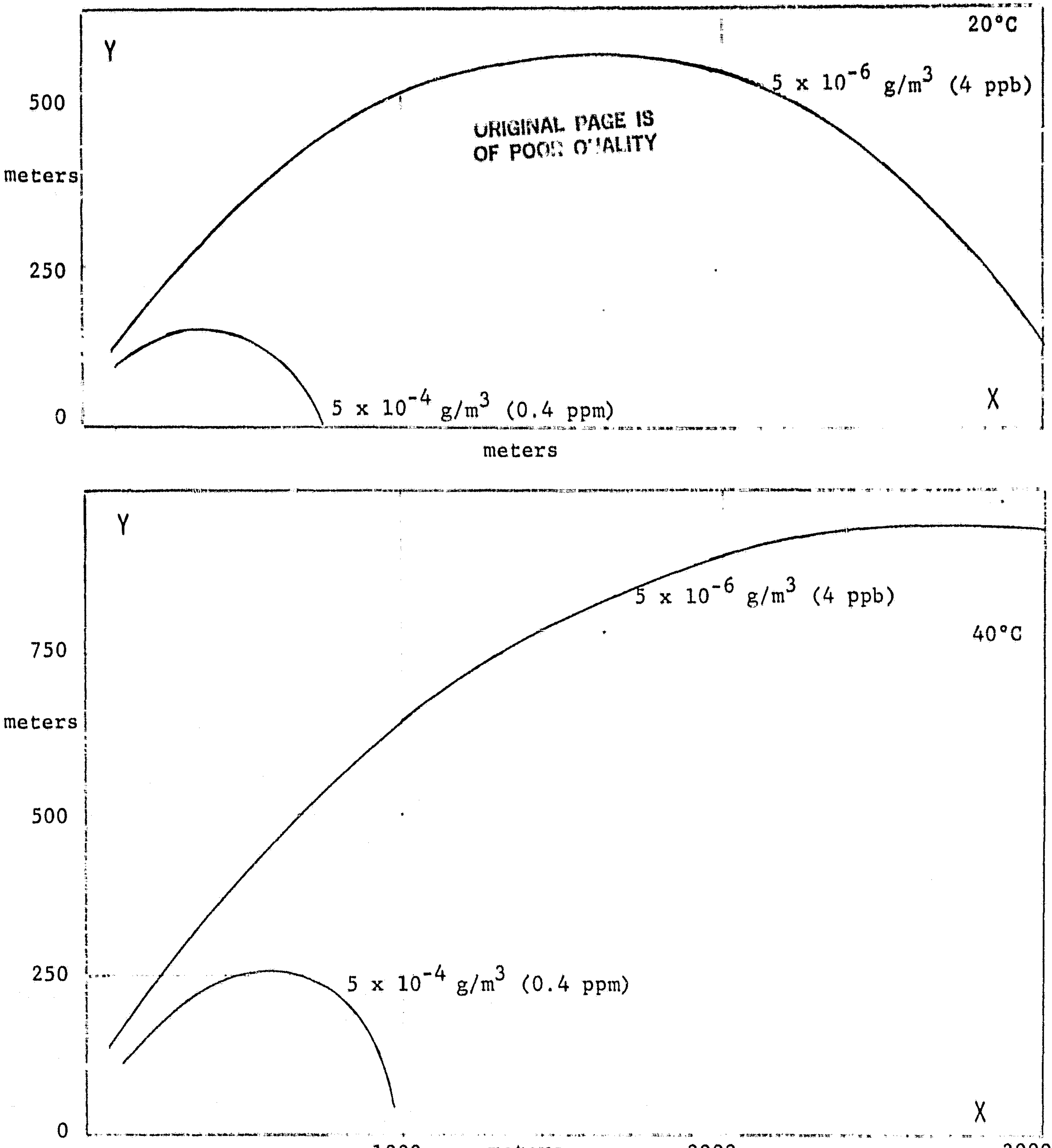

Figure 2. Isopleths for mercury vapor concentration at ground level from ground level cold spills of 1.5×10^6g of liquid mercury at 20°C and 40°C under bright sun and 2 m/sec wind in the "X" direction.

2.2.2 High Altitude Spills Without Conflagration

2.2.2.1 Deposition on Land Areas

A high altitude mercury release will lead to a breakup of the mass into droplets about 1 mm in diameter.(2) These particles will descend ballistically, with negligible response to brownian action. If the 1-mm spheres strike a small area, their initial total surface area will be 6.6×10^6 cm^2.

The evaporation rates* for the mercury at 20°, 30°, and 40°C are given in Table 5.

Table 5

EVAPORATION RATES AND TIMES OF 1.5×10^6 g OF MERCURY IN 1 mm DROPLETS AT VARIOUS TEMPERATURES

	20°C	30°C	40°C
Evaporation Rate, $g/cm^2/sec$	5.8×10^{-5}	1.3×10^{-4}	2.8×10^{-4}
Total Evaporation Rate, g/sec	383	864	1874
Approximate Time for Total Evaporation, hr	1.08	0.8	0.22

*These are initial evaporation rates. As the particles evaporate, their surface areas will decrease and there will be a reduction in evaporation rate and vapor concentration with an increase in total evaporation time. The figures in Table 5 are therefore conservative.

The possibility of the translocation of mercury deposited in rural land areas has been considered. Judging from mercury's low solubility and its relatively high vapor pressure, vapor-phase transport appears to be the most reasonable mechanism of transfer.

Among alternative mechanisms are ingestion by livestock, chemical conversion and transport, and evaporation followed by fallout.

Ingestion of metallic mercury does not appear to be physiologically hazardous. The oral use of mercury medicinally was formerly common, and in more recent observations elemental mercury did not appear to be absorbed in the gastrointestinal tract.[26]

Chemical conversion is conceivable via a route involving solution and oxidation. Mercury's low solubility in water, around 2×10^{-5} g/l (20 ppb),[49] indicates it is a low-efficiency operation, although dissolved oxygen may increase the solubilization of the mercury.[43] Mercury solution and transport also seems a low-efficiency process compared with evaporation. Nevertheless, the possibility of the mercury ultimately entering a waterway or a reservoir must be considered.[50]

2.2.2.2 <u>Deposition in Inland or Off-Shore Water Areas</u>

Mercury may be deposited either through fall-out[51] or aqueous run-off[52] in fresh-water lakes and ponds, swamp areas, off-shore salt-water regions, or the open sea. In the present state of our knowledge of the mechanisms of mercury accumulation, the hazards cannot be evaluated quantitatively because many of the links between cause and effect are speculative.

Exposure to methyl mercury, particularly via fish consumption, is among the more dangerous forms of exposure. The mercury content of the environment may be quite low, but correlations have been noted between the degree of contamination of the aqueous environment and the mercury content of the fish.[53] Mercury deposited in aqueous environments may undergo a biological conversion to methyl mercury during its entry into the food chain. Furthermore, certain species have shown a strong tendency to accumulate mercury, including salt-water swordfish and tuna and fresh-water perch, catfish, and suckers.[54,55]

Since the open sea is a region of nearly infinite dilution for mercury, fall-out from the present source would be without significant consequences.* A similar argument has been advanced in the case of off-shore tidal environments. It is presumed that particulate mercury fall-out will settle to the bottom and the dissolved mercury will be removed and diluted by the movement of the water.

Off-shore estuarine and land-enclosed waterways, however, as well as inland lakes, rivers, and swamp areas, must be considered since they may lack an efficient dilution mechanism to remove mercury.[56] Mercury deposited in bogs, lakes, and streams by industrial effluents and incorporated in bottom sediments can persist as sources of pollution of the overlying waters for 10-100 years.[19]

Studies of the mercury in the estuarine environment of the Gulf of Mexico, near the Mississippi River, Mobile Bay, and the Everglades, indicate a complexing interaction with high molecular weight organic material with insignificant loss of mercury to the aqueous environment. Slight releases of mercury to the surrounding water were observed following the dredging of coastal sediments.[57] No comparable studies have been made of the regions adjacent to the Cape Canaveral launch center. Therefore the toxic accumulations of mercury in

*This is discussed further in Section 3.2.

fresh-water and off-shore salt water areas adjacent to the launch site must be considered among the hazards of a vehicle failure.

2.3 Mercury Spills With Conflagration

A mercury spill with conflagration followed by rapid evaporation of the mercury can occur at any level. The following sections discuss ground and air-based conflagrations separately.

2.3.1 Ground-Based Spill With Conflagration

"Worst case" logic is used in the selection of the ground-based mercury vapor dispersal model. It is assumed that the spill involves conflagration leading to complete vaporization of the mercury. The combustion of 10 kg of a standard hydrocarbon fuel (n-octane) generates sufficient heat to evaporate 1500 kg of mercury completely. It is therefore reasonable to assume that evaporation during a conflagration could be rapid and total.

The mercury vapor cloud may be dispersed in several ways. Even if the somewhat extreme ambient temperature of 40°C is assumed, at which the mercury vapor pressure is 0.0061 mm Hg, the mercury content of the atmosphere will not exceed 60 mg/m^3 (55 ppm). The mercury cloud must therefore either expand or condense. If the cloud cools and condenses, mercury droplets will be deposited until the vapor saturation level is reached. If the cloud expands, two alternatives are possible: a high mercury vapor plume or a low hemispherical cloud. The hemispherical cloud at near ground level has been adopted as the case with the most hazardous potential. Assuming approximately uniform concentration, the radius and height of the cloud containing 1.5×10^6 g of mercury at a concentration of 60 mg/m^3 will be 228 m. This defines the dimensions and concentration of the extended source of the diffusion cloud. It should be emphasized that this is an idealized configuration both in symmetry and in the uniformity of the distribution of the mercury vapor.

Without undertaking a detailed calculation of the diffusion pattern, if the cloud expands uniformly to 6 miles* or 9.6 km from the center without vertical lift, the mercury vapor content will average about 34 $\mu m/m^3$ or 28 ppb. This is well below the limits suggested in the Federal Register and by the ACGIH for an 8-hour exposure (Section 1.3). It is, however, higher than the level of 5 $\mu g/m^3$ (4 ppb) recommended in the Rockwell report and the more conservative limit proposed in Section 3.1 of this report. It is therefore recommended that the current limits of the restricted area be replaced with an estimate based on a diffusion model using the available topography and meteorology of the region.

2.3.2 High Altitude Mercury Vapor Releases

The discussion here deals with approximate solutions to estimate the ranges and limits of the hazardous zones following a release of mercury vapor in flight. At moderate altitudes, one may use the standard procedures for near-ground analysis. The high altitude problem is less tractable because of the limited information on diffusion over long ranges.

The model described here assumes an instantaneous point release of mercury vapor, followed by radially uniform diffusion from the center. No assumptions of diffusion rate are made and therefore no time terms enter into the calculation. It is assumed arbitrarily that the cloud boundary is defined by the distance from the center, where the sphere contains 99 percent of the mercury. The detailed calculation, shown

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*The figure of 6 miles has been suggested as the limit of the restricted area during a Titan III launch.

in Appendix 1, defines the concentration of the expanding cloud where it intersects the earth (Figure 3). Where the cloud just touches the earth, the cloud center height is R, the cloud radius, and the concentration at the point of contact is ∿0. Where the intersection extends over an area, the concentration ranges from 0 at the edge of the contact zone A to a maximum at B, where the height of the cloud is h.

In the calculation, the origin in Figure 3 is the cloud center, and the entire system may drift with the wind.

Mercury concentrations were calculated over the entire altitude range. The data were plotted to establish representative isopleths as functions of cloud size and cloud height. Figure 4 indicates the boundary conditions for mercury concentrations of 500, 50, 10, and 5 $\mu g/m^3$ (400, 40, 8, and 4 ppb) as functions of cloud size and length.

The four isopleths in Figure 4 indicate mercury concentrations in the cloud at ground level, Point B of Figure 3, as a function of cloud radius and the height of the cloud center above B. Thus, for a total mercury spill of 1500 kg, when the cloud has expanded to, for example, 5 km radius, the chart indicates that the near earth maximum concentration will be 5 $\mu m/m^3$ (4 ppb) when the cloud center is 2500 m high.

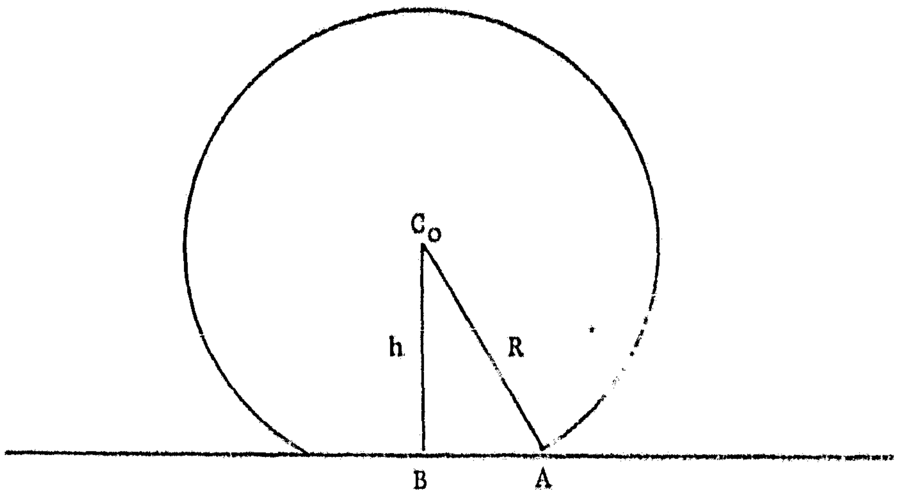

Figure 3. Mercury Vapor Cloud Geometry.

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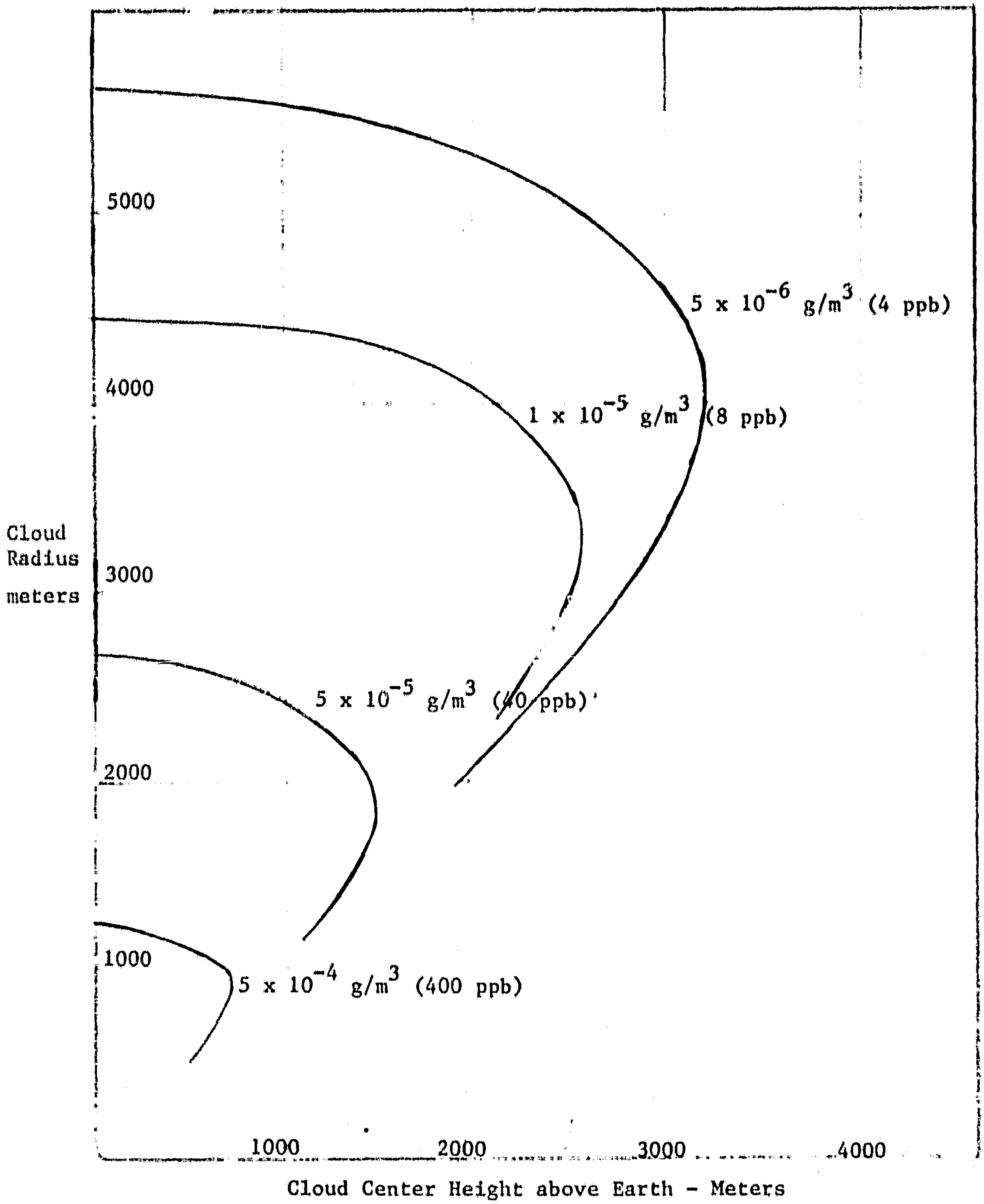

Figure 4. Mercury Vapor Concentrations at Ground Level of Clouds Generated at Various Altitudes.

3. ENVIRONMENTAL HAZARDS OF A MERCURY SPILL

Two major kinds of near-earth spill are possible: a release in the land or air environment or a deposition in an off-shore or inland waterway. The hazard levels of both spills are discussed separately below.

3.1 Mercury Released in a Land or Air Environment

The hazards identified with atmospheric mercury releases and the conclusions presented here are based on eleven published events described in Appendix 2 of this report and summarized in Tables 6 and 7. All these events involved acute intoxication following exposure to elemental mercury vapor. References cited earlier in this report[26] indicate that oral ingestion of elemental mercury is probably not a serious concern.

The published papers describe the environmental conditions surrounding these events poorly, using qualitative terms such as "elevated temperatures" and "several hours exposure." Event No. 11[58] was followed up by an attempt to reconstruct the conditions of the accident and make concentration measurements. These measurements are the best quantitative data available; indeed they appear to be the only published quantitative correlation between human exposure and its consequences.

There appeared to be two kinds of intoxication. One involved massive exposure by the inhalation of large amounts of rapidly generated hot vapor, as described in events No. 1,[59] 3,[60] 9,[61] 10,[62] and possibly 2.[63] The other class involved several hours of exposure at a relatively low concentration level. Massive exposure led to extreme illness or death to individuals who were close to the release. Adults in the general area of the release were only mildly affected and children slightly more so.

Table 6

SUMMARY OF PUBLISHED MERCURY VAPOR INHALATION INCIDENTS

Event	Exposure time (hr)	Site	Temperatures**	People Involved Adult Male	People Involved Adult Female	People Involved Children (age 0 to 5)	Fatalities Adult	Fatalities Children	Ref.
1	>½	home	e	1	1	1	-	1	59
2	16	home	e		1	3	-	3	63
3	1	home	e	1	1		-	-	60
4	*	industry	e	32			-	-	104
5	"several"	industry	e	8			1	-	105
6	3½-4½	industry	e	5			-	-	106
7	"a few"	laboratory	a***	2			-	-	45
8	-	hospital	a			6	-	2	107
9		home	e	1	1		-	-	61
10	8	home	e	1	1	3	-	-	62
11	2½-5	industry	u***	4			-	-	58
TOTALS				55	5	13	1	6	

*Three days intermittently.
**a = ambient; e = elevated; u = uncertain.
***air circulation in the chamber.

Table 7

COLLECTIVE SUMMARY OF MERCURY INHALATION INCIDENTS

Site	Number of Incidents	Number Included Adults	Number Included Children	Fatalities
Home	5	9	7	4
Hospital	1	--	6	2
Industrial or Laboratory	5	51	-	1

The greater susceptibility of small children is emphasized in Event No. 2. Under conditions of identical exposure time and place, the young adult survived, but the three children died. Again, in Event No. 10*, following an eight-hour exposure, the mother showed marginal symptoms of mercury poisoning, while three children were hospitalized for three days.

A significant aspect of Event No. 11 was the presence of a vertical concentration gradient in the environment in the absence of air circulation (Appendix B, Table B-1). This observation has been confirmed in a separate laboratory study in which the mercury concentration was found to vary from 2.5 mg/m^3 (2 ppm) at floor level to 0.02 mg/m^3 (16 ppb) at 2.5 m above floor level.[(64)] Calculations based on the barometric distributions law[(5)] indicate a decrease in mercury vapor concentration in quiet air at 20°C by a factor of about 0.45 per meter of height. A mercury vapor measurement of 1 mg/m^3 (0.8 ppm) at an adult's height, 2 meters, would indicate a concentration of 2.2 mg/m^3 (1.8 ppm) at the 1 meter height of a small child. Thus exposure to higher mercury vapor concentrations at a lower breathing level create an exceptional hazard for small children.

Air circulation appeared to be a significant factor in Events No. 7[(65)] and 11.[(58)] It is possible that air movement not only renewed the evaporation surfaces of the mercury pools but also transported the vapor throughout the chamber. The published data on Event No. 11 indicated that with air circulation, a uniform concentration of 1.1 mg/m^3 (0.9 ppm) was present.

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*Fick's Law,[(4)] indicates that the mercury distributions in a horizontal plane should be almost uniform after 3 hours.

Pertinent to the hazards analysis is the efficiency of inhaled mercury retention by the pulmonary system, estimated to approach 85 to 100 percent.[66,67] Over moderate time intervals, a time-concentration product should be used to define exposure levels. Thus if virtually all the inhaled mercury is retained, a 60-min exposure at a defined level would be as hazardous as a 120-min exposure at half that level*.

The Oak Ridge publication "Mercury in the Environment"[39] describes methods for the determination of allowable daily intakes (ADI) of mercury compounds. Two experiments are cited in which the minimum toxic dose is used as the base which is then reduced by a factor of 0.1 to establish a safe ADI level. A similar factor was used in the development of toxic levels for methyl mercury exposure.[41]

The exposure levels cited in Event No. 11 are hazardous rather than safe levels. In the absence of other guidelines, it is recommended that here, too, a factor of 0.1 be applied to define a probable safe limit and an additional safety factor of 0.1 be imposed. Thus a mercury vapor concentration of 0.01 mg or 10 $\mu g/m^3$ (8 ppb) for exposures of 150 min would be recommended for adult males.

The tenor of the data of Appendix 2 is that adult women are no more susceptible to mercury intoxication than men. This is not, however, true of children, where, as indicated in Events No. 1 and 2, exposure levels causing only illness in adults were fatal to children. The greater susceptibility of small animals compared to humans was noted in Event No. 7**.

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*Following prolonged exposure, the body begins to reject mercury leading to the establishment of equilibrium levels.[68,39]

**The similarity of animal to human retention of inhaled mercury has been noted in the literature.[69,70]

This suggests using a weight factor as a basis for an estimate. If we assume a tenfold weight ratio between an adult and a small child, the proposed exposure level for a small child would be 0.001 mg or 1.0 $\mu g/m^3$ (0.8 ppb) for 150 min.

3.1.1 Conclusions and Recommendations

We conclude that the efficacy of retention of inhaled mercury vapor mandates a control level defined by the product of concentration and exposure time. We also recommend that an additional factor, based on subject weight, be considered.

A baseline figure of 10 $\mu g/m^3$ (8 ppb) of mercury in the atmosphere for exposures of 150 min is recommended as an acceptable level for adult subjects, with a tenfold reduction for small children.

An added hazard for small children is the vertical concentration gradient of mercury in quiescent environments. Careful sampling of the environment at several levels is recommended. In addition, the exclusion of children from high-mercury concentration environments is recommended.

Table 8 presents these recommended exposure limits for adults and children for time intervals from 10 min to 24 hr. It includes the proposal that small children be limited to a maximum exposure level of 2.5 $\mu g/m^3$ (2 ppb) as an added safeguard against the vertical mercury concentration gradient problem.

3.2 Mercury Released into Aqueous Environments

The deposition of a large amount of mercury in an aqueous environment is considerably more complex than the cases discussed in Section 3.1. The impact on the environment may persist for many years or even centuries[19] and can involve translocation as well as chemical or biological conversion. The receptor environment may be aqueous off-shore marine regions or inland lakes and rivers.

Table 8

MERCURY VAPOR EXPOSURE LIMITS, $\mu g/m^3$ (ppb)

Duration of Exposure	Adult	Child (<5 years)
10 min	300 (250)	2.5 (2)*
60 min	25 (20)	2.5 (2)
8 hr	3 (2.5)	0.3 (0.25)
24 hr	1 (0.8)	0.1 (0.08)

*Maximum recommended exposure level for all intervals less than 60 min.

We exclude the open sea from present consideration by the following reasoning. The solubility of mercury in water is 40-60 ppb[49,71] and the actual mercury content of ocean waters is reported to be almost entirely elemental mercury, Hg^o,[72] ranging in concentration from 0.03 to almost 3 ppb.[73,74,75,76] The annual world discharge of about 10,000 tons from all anthropogenic sources may be compared with the estimated 25,000 to 150,000 tons from natural sources.[77] Considering these amounts and in view of the unsaturated condition of ocean water with respect to mercury, it is evident that the addition of 1.5 tons will not alter the deep sea environment significantly.

In coastal areas and inland waters, local conditions can be more serious and indeed clear correlations have been established between industrial discharges and mercury levels in fish.[78,78a] In particular, the catastrophes identified with the communities of Minimata and Niigata in Japan are instances of the drastic consequences of the transfer of industrial effluents through the food chain to human recipients.

The magnitude of these events has led government agencies to maintain close control of mercury release from industrial operations and of the mercury content of many foods, especially fish.[79] The Minimata plant effluents were originally said to have included the highly toxic methyl mercury. This fact has been questioned but is probably irrelevant because of the efficiency of the bio-transformation of mercury to the methyl form.[80] (also Ref. 10, p. 315 and Ref. 90, p. 18).

A perplexing aspect of the Minimata-Niigata incidents in the context of the present problem is their unique character. In spite of the evidence of extensive mercury contamination of waterways in many parts of the world, the number of clinically identified cases involving humans caused by the consumption of tainted fish is remarkably small. At the

Rochester University symposium on mercury in 1971,[10] only one suspected case of mercury poisoning caused by the consumption of fish was cited.[81] It was observed that this case, if real, "was the first recognized case in North America or Europe that was due to the ingestion of fish." (Ref. 10, p. 42)

More recently the government of Canada reported two instances of fish pollution in Indian communities near Dryden in Ontario and Quévillon in Quebec.[82] The Dryden incident has been investigated by American[77] and Japanese[83] specialists. The Japanese report deals in some detail with the episode against the background of the Minimata experience and concludes that conditions similar to the early stages of the Minimata epidemic appear to be developing in Dryden. The report observes that mercury levels in fish appear to be environmental indicators of hazardous conditions. Thus a representative set of measurements showed 16 ppm of mercury in the tissue of fish (pike) from a contaminated lake and about 1.5 ppm in an adjacent uncontaminated region.

In addition to the human problem numerous investigations show that many local fauna dependent on fish for their food supply are highly susceptible to injury from high mercury levels. Among the animals mentioned are cats, chicken, dogs, weasels, mink and otter,[83] turkey vultures, osprey, grebe, kingfisher, terns, herons, and wild ducks.[84,85]

Thus the presence of an unacceptably high mercury level in the fish is fairly clear evidence of contamination. Unfortunately, this is ex post facto evidence--the damage has been done and we are belatedly viewing the consequences of an event which called for correction at some time in the past. On the basis of published information on mercury levels in fish, this study has attempted to retrace the biological chain to determine the earliest point at which the development of a potential hazard can be identified.

The evidence appears to support the existence of a biological process for the conversion of mercury to a methyl mercury derivative during its travel along the food chain.(86) Even in the extreme case of the Minimata catastrophe the relevance of methyl mercury present in the factory effluent has been questioned and biotransformation of the mercury by the intermediate hosts has been advanced as the more likely mechanism of methyl mercury accumulation in the fish.(87) It is of some concern that a substantial time interval can exist between the inadvertent discharge of mercury into the aqueous environment and its transfer to its ultimate recipient.

3.2.1 Mercury Transfer in the Marine Environment

A short physical-biological chain of events describing the transfer of mercury in the marine environment is presented here. It should be emphasized that the interpretation of each event in the chain is a subject of current study with few completely satisfactory conclusions.

i. Initial deposition of the mercury in the waterway, followed by a rapid settling and accumulation of the mercury in the sediment of the bed.

ii. Absorption and conversion of the mercury by the biota of the sediment.

iii. Transfer and concentration of the mercury along the biological chain. Accumulation of the mercury by edible species, predominantly fish, crustaceans and shell-fish.

iv. Direct transfer of dissolved mercury to the organism.

i. Deposition of Mercury in the Waterway

Mercury is highly insoluble in water. Fairly good agreement exists in the measurement of the background mercury content of water. Stock & Cucuel[88] report 0.02 to 0.07 ppb, Dall' Aglio[49] gives values of 0.01 to 0.05 ppb, and Klein[89] gives a mean figure of 0.055 ppb with a standard deviation of 0.035. Higher levels can often be identified with the presence of a contaminant, which may be a mercury ion or compound either in solution or sorbed on suspended sedimentary particles.[90,91]

A mercury fall-out will accumulate rapidly in the bottom sediment of the waterway and considerable evidence indicates that the deposit will be localized. For example, a large mercury deposit was identified in the Wisconsin River below the site of a chlor-alkali plant at Port Edwards, Wisconsin.[92] Near the discharge point the bottom sediment contained 684 ppm of mercury, largely metallic. One mile downstream the level dropped to 12 ppm. A comparable condition was reported at Dryden, on the English River system in Western Ontario,[83] where bottom sediment showed a rapid and progressive decrease downstream from the site of the original deposit.

Kitamura[56] stated that near the drainage channel into Minimata Bay, probably from industrial sources, the sediment assayed 2010 ppm mercury, while 1.5 km from the discharge, at the entrance from the bay to the sea (Ariake Sea), the bottom mud assayed 12 ppm mercury. Other examples of the limited migration of mercury have been noted. The variation in the mercury content of fish in the St. Clair-Detroit River waterway also indicates a progressive decrease in the mercury content of the waterway downstream from the principal sources of contamination in Sarnia.[90] It is interesting to note that in this case the apparent region of maximum pollution was not at the point of discharge in the St. Clair River but in the "delta" region where the river entered Lake St. Clair.

ii. Absorption and Conversion of the Mercury

The residence time of the mercury in the waterway can be lengthy.[93] In a eutrophic environment, the mercury can be buried under the accumulating sediment and silt where it may persist almost indefinitely. Slow chemical conversions can involve complexing with very strong retention by the sediment. In an oxidizing environment, the mercury is converted to the mercuric ion where it can undergo conversion in the bottom mud to methyl mercury.[93,94] A large number of studies have attempted to identify these events as bio-transformation processes. While many of the proposed mechanisms appear plausible, their replication in nature has not been established.

iii. Transfer of Mercury Along the Biological Chain

This is a subject of considerable uncertainty. Copeland[95] has shown that Lake Michigan plankton and benthos contain appreciable levels of mercury, ranging from 0.9 to 2.2 ppm (dry weight, 80 percent moisture removed). Jernelov[96] adds algae to this list, and also describes a laboratory analysis of the stomach contents of fish. The subject fish, Northern pike from heavily contaminated waters, had a mercury content of ∿5.8 ppm. Fish residues in the pike stomachs averaged ∿3.1 ppm mercury, while bottom fauna in the stomachs of the fish residues contained 0.3 ppm mercury. In the course of his investigation, Jernelov was unable to correlate fully the methyl mercury content of the fish at the end of the food chain with the intermediate fish consumed. It was his conclusion that a substantial part of the methyl mercury in the pike is formed from mercury taken directly from the water.[97] Hartung[98] also believes that organisms in the water environment may accumulate mercury from a number of sources.

iv. Direct Transfer of Mercury to the Organism

The three previous sections of this report indicate the complexity of mercury transport through the aqueous biosphere. Most of the mercury present in fish is in the form of methyl derivatives. As noted in the previous paragraph, Jernelov[97] was unable to correlate the methyl mercury levels in the fish used in his investigation with the food sources. He therefore suggested that part of the methyl mercury was derived from dissolved mercury absorbed directly from the aqueous environment.

3.2.2 Data Evaluation and Conclusions

In reviewing the chain of circumstances leading to the contamination of fish, the accumulation of mercury in the bottom sediment appears to be the earliest identifiable factor. A multitude of secondary factors affect the retention and transfer of the mercury from the bottom sediment to the biological chain. Several of these have been cited, including water chemistry, eutrophication, degree of mercury complexing, and composition of sediment.

Laboratory tests indicate that the formation of methyl mercury in water is enhanced by slightly acid conditions.[99,100,101,102] Two series of field tests conducted by the Wisconsin Department of Natural Resources appear to support this observation. One series of tests assessed river water and river bottom sediment;[92] the other determined the mercury levels of fish in Wisconsin streams.[103] The data for 11 sites exhibiting industrial mercury pollution are given in Table 9. The tabulated data for each site include bottom sediment mercury, pH of the stream, and the mercury levels of fish in the area. Eight of the sites were pulp and paper plants where organic mercury slimicides were, or had been used. The two industrial sites were not identified, and the chlor-alkali plant deposit was mainly

Table 9

MERCURY DEPOSITS IN WISCONSIN RIVER SEDIMENTS
AND ACCUMULATION IN FISH

River	Plant*	Mercury in Sediment	pH	Mercury in Fish
		ppm		ppm
Chippewa	PM	1.2	7.1	0.60
Flambeau	PM	0.6	6.9	0.41
Flambeau	PM	1.4	7.2	1.07
Fox	PM	2.0	7.8	0.36
Fox	PM	1.5	7.2	0.21
Menominee	PM	1.2	7.6	0.45
Milwaukee	I	1.5	7.8	0.13
Rock	I	0.4	8.3	0.11
Wisconsin	PM	1.5	6.7	0.95
Wisconsin	PM	2.7	6.8	0.51
Wisconsin	CA	684.	6.8	1.24

*PM = Paper Mill; I = Industrial; CA = Chlor-Alkali Plant.
Plant locations are described in Ref. 16.

metallic mercury. Three of the four cases involving a pH below 7.0 (neutral) showed a mercury content in the fish in excess of the acceptable FDA level of 0.5 ppm. Of the seven samples showing a pH above 7.0, two had an unacceptable mercury level in the fish of the regions.

The data are limited but they indicate a degree of correlation between the mercury content of the bottom sediment of a waterway and the initiation of a hazardous condition to the biological food chain.

3.2.3 Recommendations

We recommend that the literature be reviewed for additional evidence of the correlation between the mercury content of bottom sediment, the pH of the water, and the mercury levels in the fish of the area. We also recommend that tentative standards be proposed, based on the evidence of Table 9, with modifications as additional data become available.

PART II

Spectroscopic Matrix Isolation Studies of the Hg + O_3 and HgO + O_3 Reactions

1. INTRODUCTION

In an earlier paper study for NASA* it was shown that the following reactions:

$$Hg(g) + O_3(g) \longrightarrow HgO(g) + O_2(g)$$

$$HgO(g) + O_3(g) \longrightarrow Hg(g) + 2O_2(g)$$

could result in the net catalytic destruction of ozone:

$$2O_3(g) \longrightarrow 3O_2(g)$$

These reactions could be important in stratospheric chemistry in the event of an inadvertent mercury release from a SEPS-type vehicle in the stratosphere.

When the earlier report was prepared there were no definitive data on the existence of gaseous mercury oxide (HgO_x) species, though their existence had been proposed by several workers to account for the known destruction of ozone in the presence of liquid mercury and for the mercury atom photosensitized ozone formation from oxygen. Central to the proposed ozone destruction cycle is the existence of gaseous mercury oxide or oxides, and although our experimental studies are not complete, we have definitive evidence that they do exist. These studies will now be described in some detail.

2. EXPERIMENTAL STUDIES

The vacuum line required for the experiments is shown schematically in Figure 5. This vacuum line serves three main purposes:

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*Criteria for Mercury in the Stratosphere, by A. Snelson. Prepared for NASA under Contract No. NAS8-31546, January 1977.

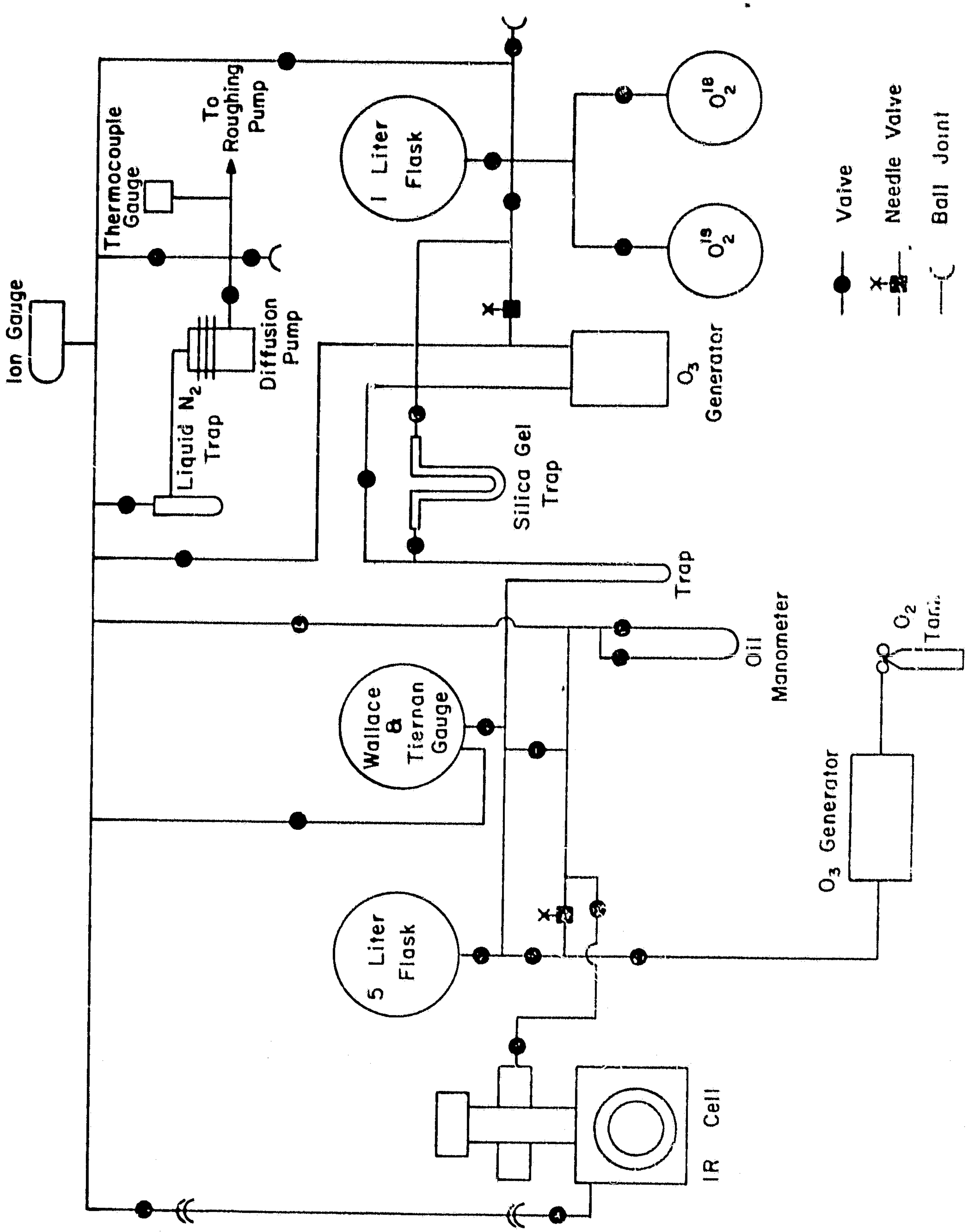

Figure 5. Vacuum and Gas Handling Line for Matrix Isolation Experiments.

(1) It is required for evacuating the matrix isolation cryostat and the molecular beam furnace shown in Figure 2. Pressures in the low 10^{-6} mm Hg are routinely obtained.

(2) It is used for preparing ozone from oxygen. There are two ozonizers. One unit, which operates at atmospheric pressure to give a ≈2 percent ozone in oxygen mixture, is used for preparing $^{16}O_3$. The ozone is either stored in blackened flasks of frozen at "dry ice" temperature on silica gel. The second ozonizer is a low pressure glow discharge unic which is cooled by liquid nitrogen during operation. This unit converts 50-75 percent of the oxygen to ozone and is used in preparing isotopically labelled ozone.

(3) It is used for preparing ozone-oxygen mixtures for use as the matrix gas, and for accurately metering these gases to the cryostat during the matrix isolation experiments.

All valves in the vacuum line which come in contact with ozone are constructed of glass and teflon to minimize decomposition of the ozone.

The matrix isolation cryostat and molecular beam furnace are of conventional design (Figure 6). An Air Products Displex Closed Cycle Refrigerator cools the cesium iodide window on which matrices are formed at routine temperatures of 10-12°K. The mercury is vaporized into the matrix from a suitable molecular beam effusion tube at a rate of ≈0.01 g/hr. The effusion rate is controlled by the temperature of the effusion tube. Matrix gas, usually a mixture of 5 percent ozone and 95 percent argon is fed into the cryostat at ≈100 cm^3 NTP/hr. This results in matrix dilution ratios of ≈1000:1.

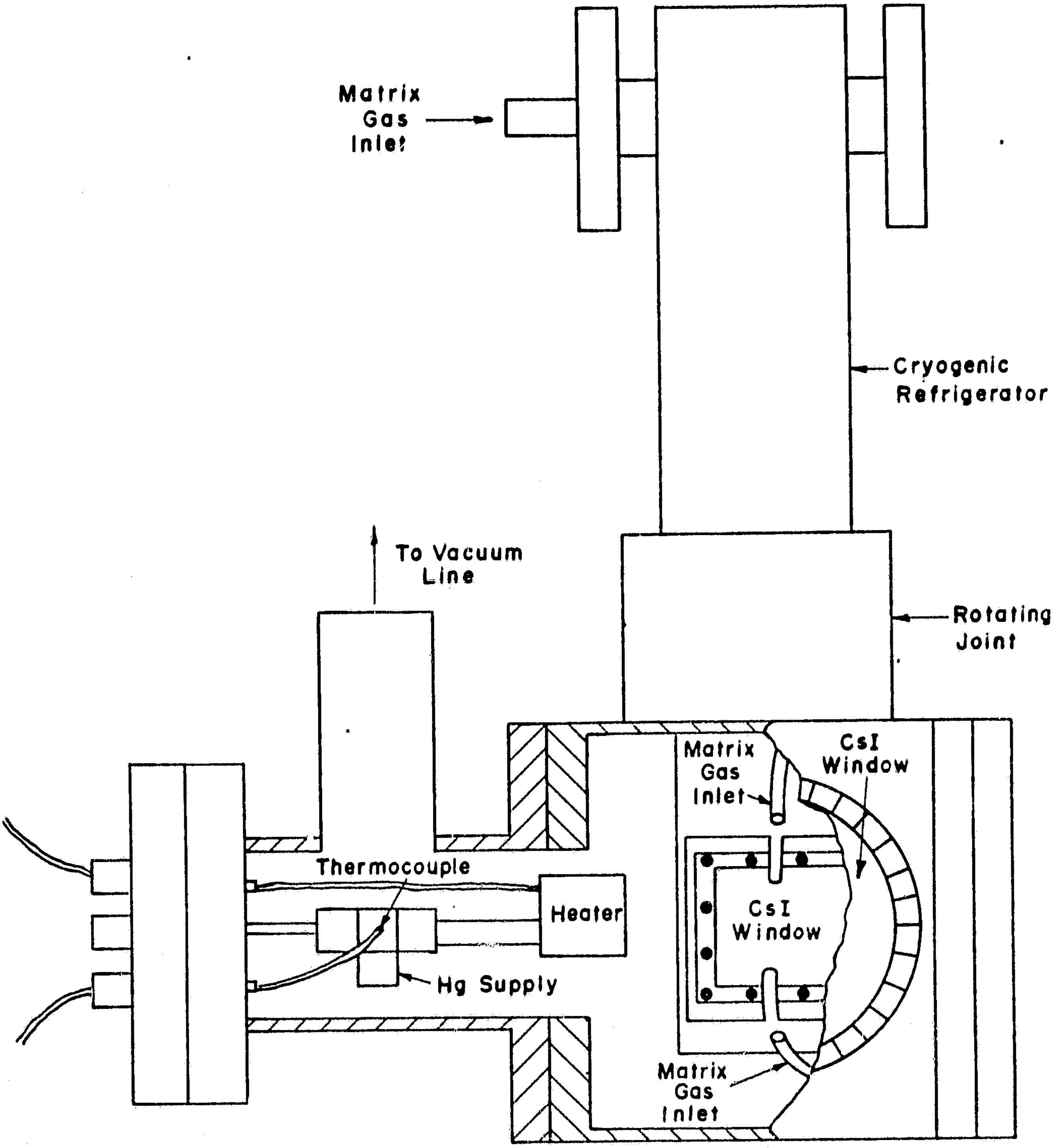

FIGURE 6. MATRIX ISOLATION CRYOSTAT AND FURNACE ASSEMBLY

During matrix deposition (1-3 hr), the cesium iodide window is irradiated with a medium pressure mercury arc.

Infrared spectra are recorded on a Perkin-Elmer 283 spectrophotometer, which covers the range 4000-200/cm with a frequency accuracy of $\pm$0.5/cm. Visible-UV absorption spectra are recorded on a Jarrell-Ash 1 meter Czerny Turner Scanning Spectrometer, using photomultiplier detection with tungsten lamp or xenon arc light sources.

3. RESULTS - DATA ANALYSIS

The infrared spectra that result from the interaction of mercury atoms with a matrix gas containing 5 percent ozone in argon irradiated with a mercury medium pressure discharge lamp during deposition are presented in Figures 7, 8, 9, and 10. These data are for ozone containing 99 percent ^{18}O. Similar experiments were also made for ozone containing the ^{16}O isotope. The absorption features which can definitely be assigned to ozone are indicated in these spectra. The remaining features can confidently be assigned to HgO_x species, largely on the basis of isotopic frequency shift-data and the fact that these bands only occurred when ozone and mercury were present in the system, and not when only one component was present.

The frequencies of the infrared absorption bands which can be assigned to HgO_x species containing either the pure ^{16}O or ^{18}O isotopes are presented in Table 10. A total of 14 bands are identified for each of the isotopic species, and in the majority of cases it is possible to tentatively assign isotopic counterparts in each of the ^{16}O and ^{18}O spectra. This large number of absorption bands at once implies that several mercury-oxygen species must be present. Obvious candidates are HgO, HgO_2 and HgO_3, none of which had been identified previously. Also shown in Table 10 are the ratios

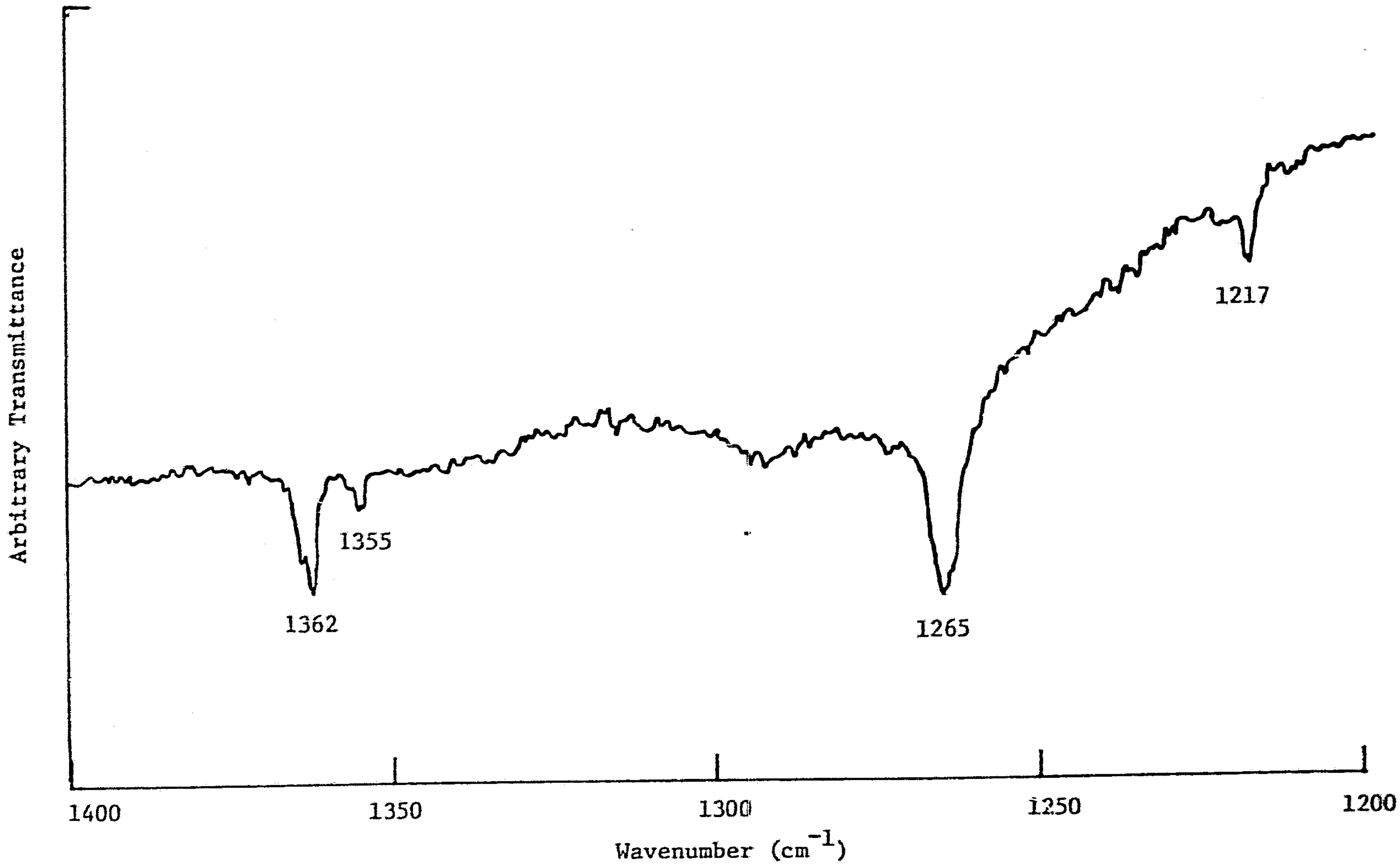

Figure 7. IR Matrix Isolation Spectrum of HgO_x Species Formed by the Interaction of Hg Atoms with a 5% $^{18}O_3$ Argon Matrix.

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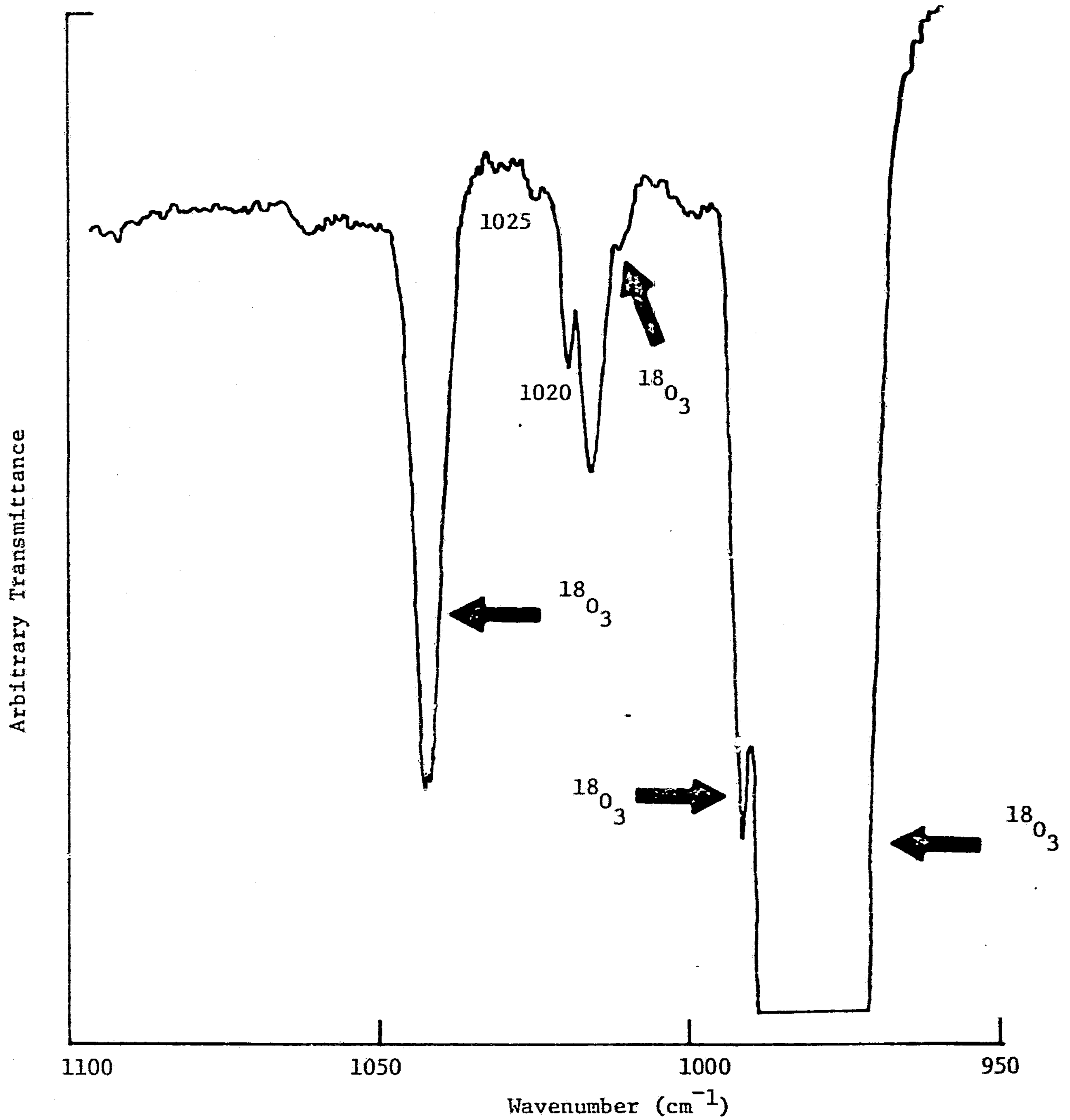

Figure 8. IR Matrix Isolation Spectrum of HgO_x Species Formed by the Interaction of Hg Atoms with a 5% $^{18}O_3$ Argon Matrix.

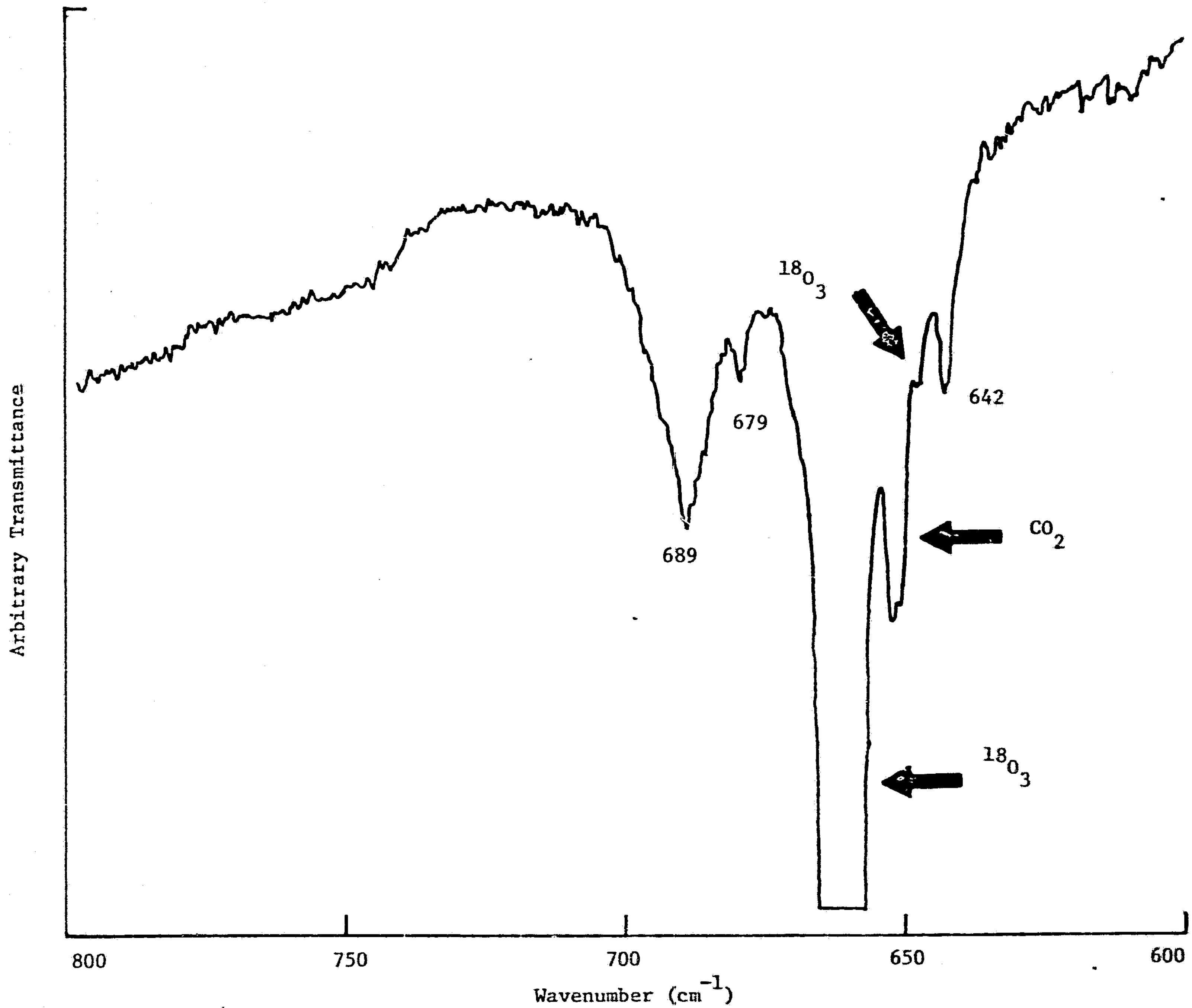

Figure 9. IR Matrix Isolation Spectrum of HgO_x Species Formed by the Interaction of Hg Atoms with a 5% $^{18}O_3$ Argon Matrix.

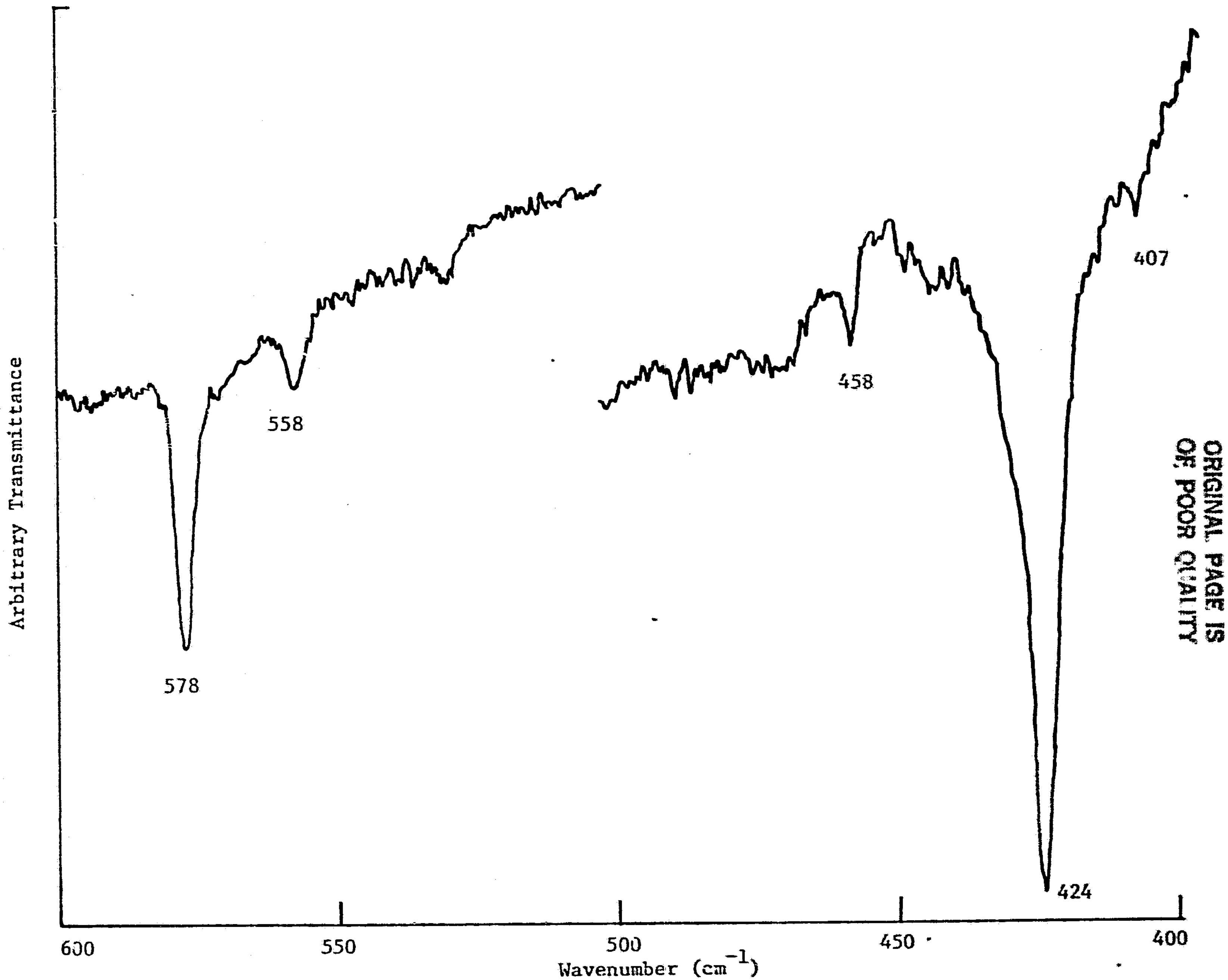

Figure 10. IR Matrix Isolation Spectrum of HgO_x Species Formed by the Interaction of Hg Atoms with a 5% $^{18}O_3$ Argon Matrix.

Table 10

INFRARED BANDS OF Hg/OXYGEN COMPOUNDS IN A O_3/Ar MATRIX

With $^{16}O_3$ (cm^{-1})	With $^{18}O_3$ (cm^{-1})	Ratio
----	1362	-----
----	1355	-----
1365*	----	-----
1341*	1265	1.06
----	1217	-----
1202*	----	-----
1198*	----	-----
----	1025 (weak)	-----
1081*	1020	1.060
730	689	1.060
----	679	-----
690	----	-----
676	642	1.053
645	----	-----
607	578	1.050
591	558	1.059
485	458	1.059
447	424	1.054
429	407	1.054

*low precision measurement

of the Hg $^{16}O_x$ to Hg$^{18}O_x$ frequencies where this can be calculated. For the species Hg^{16}O and Hg^{18}O, this ratio may be calculated theoretically at 1.056. From the ratios obtained experimentally, there are several candidate bands which have this ratio within the precision of the experimental measurements, $\approx \pm 0.3$ percent.

Figures 11 and 12 present the visible absorption spectra of Hg$^{16}O_x$ and Hg$^{18}O_x$ species, which were obtained at the same time as the IR spectra shown above. A total of five absorption features were obtained for each isotopic species. Due to a rapidly changing base line (single beam instrumentation) and the rather low intensity of the bands, it was not possible to locate the band centers very precisely. The wavelengths of the band centers are presented in Table 11.

These visible spectra can reasonably be interpreted in terms of a diatomic species - presumably HgO. The more intense bands at 6829, 6583, and 6355 Å, Figure 11, and the corresponding features in Figure 12, may be assigned to transitions from the v = 0, 1, and 2 levels of the first excited electronic state. The two weaker features at 6690 and 6456 Å may then be assigned to a similar transition for the HgO molecule trapped at a slightly different site in the matrix. The isotopic shift ratios for the ^{16}O and ^{18}O bands of the vibrational levels of the first excited state are given in Table 11. Within the precision of the measurements, these ratios are consistent with the calculated value of 1.056 for HgO. Assuming the validity of this assignment to a species HgO, the dissociation energy of the HgO ground state may be estimated at <42kcal. This compares with the value estimated in the JANNAF tables of ≈64kcal/mole.

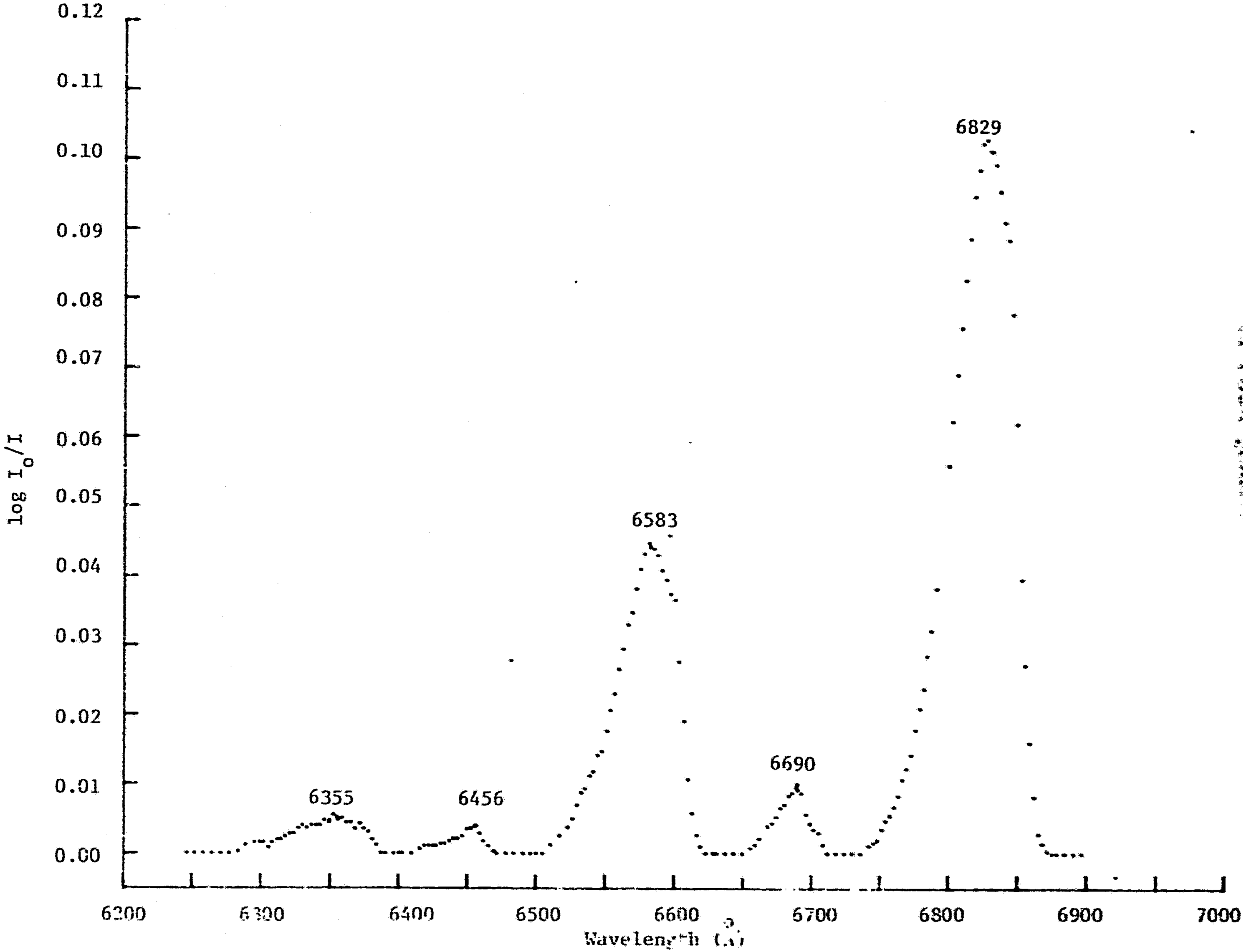

Figure 11. Visible Matrix Isolation Spectrum of HgO_x Species Formed by the Interaction of Hg Atoms with a 5% $^{18}O_3$ Argon Matrix.

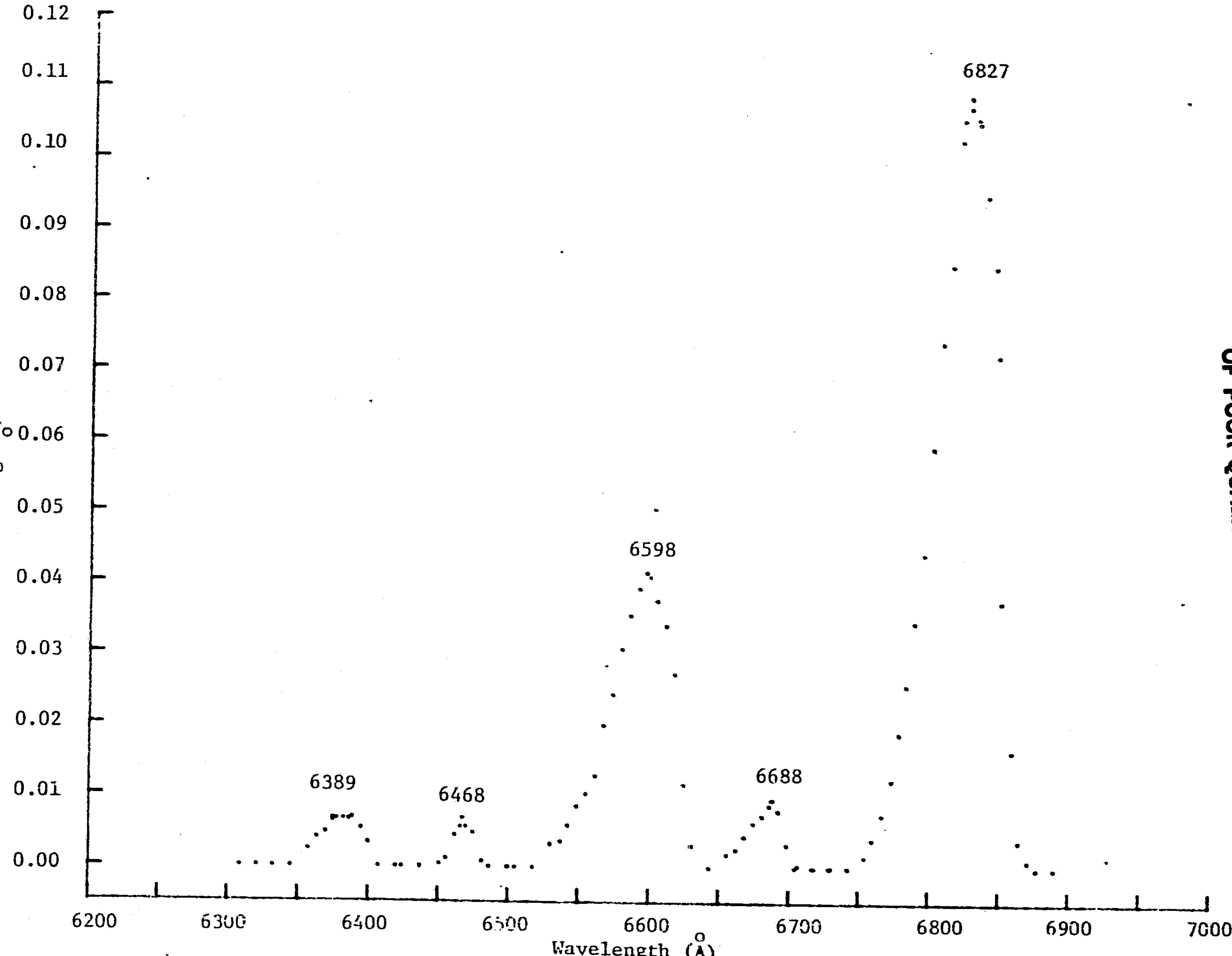

Figure 12. Visible Matrix Isolation Spectrum of HgO_x Species Formed by the Interaction of Hg Atoms with a 5% $^{18}O_3$ Argon Matrix.

Table 11

WAVELENGTH OF THE VISIBLE ABSORPTION BANDS OF HgO_x

With $^{16}O_3$

6829 ± 2 Å	= 14634 ± 4 cm^{-1}			
6690 ± 5 Å	= 14948 ± 12 cm^{-1}	548 ± 13 cm^{-1}		a
6583 ± 5 Å	= 15191 ± 12 cm^{-1}		541 ± 17 cm^{-1}	b
6456 ± 5 Å	= 15489 ± 12 cm^{-1}	545 ± 17 cm^{-1}		c
6355 ± 5 Å	= 15736 ± 12 cm^{-1}			

With $^{18}O_3$

6827 ± 2 Å	= 14648 ± 4 cm^{-1}			
6688 ± 5 Å	= 14952 ± 12 cm^{-1}	508 ± 6 cm^{-1}		a^1
6598 ± 2 Å	= 15156 ± 4 cm^{-1}		509 ± 17 cm^{-1}	b^1
6468 ± 5 Å	= 15461 ± 12 cm^{-1}	496 ± 13 cm^{-1}		c^1
6389 ± 5 Å	= 15652 ± 12 cm^{-1}			

Isotope Shift Ratios

$a/a^1 = 1.08 \pm 0.03$

$b/b^1 = 1.10 \pm 0.05$

$c/c^1 = 1.06 \pm 0.05$

The intensities of the visible and IR absorption bands have been compared and it appears tentatively that the IR band at 676/cm ($^{16}O_2$) spectra may be assigned to HgO. Progress has been made towards finding experimental conditions under which fairly good absorption band intensities may be obtained. Further work comparing absorption band intensities, together with isotopic studies, should undoubtedly allow a complete interpretation of the spectra to be made and the specific HgO_x species identified.

4. IMPLICATIONS WITH RESPECT TO THE OZONE DESTRUCTION PROBLEM

The results obtained thus far, although preliminary in nature, unequivocally demonstrate the existence of mercury oxide species, a fact which previously was in doubt. A tentative assignment of absorption bands to HgO has been made. Although further experimental work is required to clarify and interpret the data, the results obtained thus far indicate a catalytic ozone destruction process via mercury atoms as indicated previously appears a distinct possibility that cannot be ruled out. This entire area requires further study to define completely the possible stratospheric implications of the data thus far obtained.

Appendix 1

HIGH-ALTITUDE HIGH-TEMPERATURE MERCURY RELEASE MODEL

The high-altitude high-temperature mercury release model is described in Section 2.3.2 and illustrated in Figure 3.

Mercury vapor concentrations were determined as follows. If the mercury cloud boundary is defined as the envelope of the cloud containing 99 percent of the mercury vapor, then the cloud contains C_t grams of mercury vapor, where C_t equals 99 percent of 1.5×10^6g. As mercury diffuses from the center, the concentration at the center is a maximum, C_o. Intermediate concentrations are given by C, where

$$C = f\ (C_o;\ r) \quad (1)$$

where r is the radius at the intermediate point.

When r is 0, $C = C_o$ and

when r is R, $C \sim 0$

A number of functions can fit Equation 1 including the family

$$C = C_o\ [1 - (r/R)^n] \quad (2)$$

where n is the constant.

In the accompanying calculation, n = 2, and

$$C = C_o\ (1 - r^2/R^2)^* \quad (3)$$

At any radius, r, in the cloud, the mercury content of the spherical shell is

$$Hg_r = C(4\ \pi\ r^2\ dr) \quad (4)$$

where $C = C_o\ (1 - r^2/R^2)$ (2)

---

*Note that Equation 3 is equivalent to $C = C_o \exp\ (-r^2/R^2)$ when r^2/R^2 is small.

The mercury content of the entire cloud is

$$C_t = \int_o^R Hg_r \; dr$$

$$= 4 \pi C_o \int_o^R r^2 \; (1 - r^2/R^2) \; dr$$

$$= \frac{8}{15} \pi R^3 C_o \qquad (5)$$

Since $C_t \sim 1.485 \times 10^6$ g (99% of 1.5×10^6g)

$$C_o = \frac{8.863 \times 10^5}{R^3} \qquad (6)$$

and C is defined for all values of R by Equations 2 and 6.

Equations 2 and 6 were applied by determining C_o values for clouds of various radii and then determining the concentrations, C, as the cloud height, h, is varied. A typical situation is illustrated below where R is 1000 m.

From Equation 6, when R = 1000 meters,

$$C_o = 8.863 \times 10^{-4} \; g/m^3$$

Recalling that h = r, the concentrations for varying h, by Equation 3, are

h (meters)	C. g/m^3
200	8.50×10^{-4}
400	7.44×10^{-4}
600	5.67×10^{-4}
800	3.19×10^{-4}
1000	0

Appendix 2

A SUMMARY OF THE LITERATURE ON ACUTE MERCURY VAPOR INTOXICATION

This summary lists all events found in the medical literature relating to acute human exposure to elemental mercury vapor. The two large-scale events in Idria in 1804 and on the ship, the Triumph, in 1810[20], were described Section 1.2 and are not included here.

A total of 11 incidents involving a total of 73 people was identified in the medical literature.

Table 6 in Section 3.1 is a summary of each incident. Table 7 is a brief description of all the events.

A description of each event follows.

1. <u>Halifax, Canada, 1947[59]</u>

A four-month-old child and its parents were exposed to mercury vapor fumes in a small, warm, closed room (10 ft x 14 ft x 9 ft) for about one-half hour and with further exposure in an adjacent room for several hours more. The baby died three days later. The parents reported symptoms of "extreme fatigue, nausea, and abdominal cramps." Both survived.

It was estimated that 60 to 120 g of mercury may have been released. Assuming a room temperature of 30°C (86°F) the mercury vapor content at saturation would be 30 mg/m^3. With a room volume of 35.7 m^3, 1 g of mercury will establish saturation conditions at 30°C.

2. <u>Houston, Texas, 1947[63]</u>

Three children, aged 30, 20, and 4 months, and their 19-year-old mother were exposed to the fumes of a gas space heater which had been freshly painted with a mercury-containing paint.

The living space had a volume of 57 m^3. Exposure in the hot, tightly closed house was at least 16 hours. All three children died. The mother was acutely ill for two days, and was discharged after a month's hospitalization.

Again, assuming a room temperature of 30°C, saturated mercury conditions of 30 mg/m^3 would require only 1.7 g of mercury. It was estimated that the mercury content of the paint was 300 to 350 ml, corresponding to over 4 kg. While this figure seems improbably high, it indicated that saturated mercury vapor conditions existed throughout the exposure.

It was noted in the report that "the two children closest to the stove succombed first, the 4-month-old baby who was further removed survived longer, and the mother recovered". These distances are estimated roughly to have been 6, 8, 10, and 14 feet. The closest child was dead on arrival. The next died after two-and-one-half, while the youngest child survived for five days.

3. Tucson, Arizona, 1954[60]

This incident involved the exposure of a 29-year-old man and his wife to evaporating mercury fumes for about one hour. The man became acutely ill but recovered completely. The report contains no reference to the wife's condition.

The direct exposure to the evaporating fumes suggests a much higher mercury exposure than the levels dictated by saturated mercury at ambient temperatures.

4. Site not stated, 1937[104]

An incident was described involving workmen using torches in an enclosed area to modify industrial stills equipped with mercury seals. Work extended over a three-day period in an environment with apparently inadequate ventilation. Of the 32 people developing symptoms of mercury poisoning, three men were hospitalized, three others were ill but were not hospitalized, and the other 26 received medical and dental treatment. All recovered.

5. Site not stated, 1961[105]

A fatal incident was described, involving mercury inhalation for several hours following the rupture of a mercury vapor boiler. It is the only adult death recorded. A group of eight men were exposed "without precautionary measures" for about five hours while trying to retrieve a large amount of mercury spilled from a ruptured mercury boiler. The report stated that "the mercury was warm but not hot enough to burn the skin". All eight men exhibited symptoms of mercury poisoning and all but one recovered.

If the mercury was warm to the touch it probably exceeded body temperature, 37°C. It is therefore safe to estimate an atmospheric mercury vapor content in excess of 60 mg/m^3.

6. Germany, 1927 [106]

Three incidents occurred involving five workmen engaged in maintenance work on equipment formerly used for mercury storage. Cutting torches were used and exposure times were 3½ to 4½ hours. Respiratory symptoms ranging from "slight" to 14 days incapacitation were reported.

7. Denmark, 1937 [45]

A controlled investigation of exposure to mercury vapor was conducted. The chamber, 27 m^3 in volume, was used without ventilation but with the air in continuous circulation. Ambient temperature conditions existed. An extended experiment involving two subjects was terminated prematurely "after a few hours" when severe symptoms of mercury poisoning developed. Traces of mercury were observed on the floor. The subjects were ill for several days and complete recovery occurred after some months.

Experimental animals (guinea pigs, rats, and mice) died in 24 to 48 hours. In subsequent tests in which the air was not mixed, the test animals survived for several more days.

The authors note the hazards of working in poorly ventilated, mercury contaminated rooms with air circulation, especially at elevated temperatures.

Assuming an ambient temperature of 20°C, the equilibrium mercury vapor content of the chamber was 13 mg/m^3. This would correspond to 0.37 g of mercury in the vapor phase in the entire chamber.

8. Dresden, 1957 (107)

An incident in a children's clinic was initiated by the explosion of a mercury lamp. Six infants were in the room, four became ill and two died.

9. San Francisco, 1963 (61)

Two cases are cited in this incident in which a kitchen stove experiment on gold extraction led to the evaporation of mercury. The experimenter, a 25-year-old male, was hospitalized with acute symptoms of mercury poisoning. He was discharged after two weeks. His wife, age 19 who had been in an adjacent room, was also hospitalized. She was released after three days.

The diagnosis noted that while she had suffered some mercury vapor induced bronchial irritation, there was no severe bronchitis. It also stated that in mercury vapor inhalation "the irritative effect on the trachea-pulmonary tree constitutes the prime danger to life."

10. Tacoma, 1969[62]

This case also involved an amateur gold recovery experiment. An estimated 400 g of mercury was inadvertently evaporated on a hot kitchen stove. The incident occurred at midnight at one end of a single floor, 24 ft x 50 ft dwelling. An open central corridor ran the length of the house. Off the corridor were various family bedrooms and a furnace room with an air intake off the corridor. The family consisted of the experimenter, age 31, his wife, and three children, aged 4 and 3 years, and 14 months. The father continued to work in the kitchen for three hours. His wife was in an adjacent room. The two older children were in a bedroom about 20 ft from the kitchen and the 14-month old child was about 50 ft from the site of the mercury spill.

Eight hours after the initial incident, the family was removed and hospitalized. The father was extremely ill for two weeks. Four months later residual symptoms were still present. The mother was exposed intermittently when she went in and out of the kitchen after the spill. Her symptoms were minimal. The three children were mildly ill with coughing, vomiting, and in the case of the older two, slightly elevated temperatures. All three recovered completely in a few days.

11. Victoria, Australia, 1970[58]

Residual mercury has accumulated on the floor of a 600 m^3 storage tank. A small stream heating line ran across the floor. Four workmen were exposed in the tank for 5, 4, 2½ and 2½ hours, respectively. An air circulating system was on. All four men became ill for periods of a few days to a month.

A subsequent study of the tank's atmosphere was made. At the ambient temperature of 17°C, with no air circulating, the mercury content of the air showed a pronounced gradient, diminishing with height as shown in Table B-1. With a ventilating system removing air at 85 m^3/min, uniform mercury concentrations were observed, still at toxic levels, with both up draft and down draft ventilation.

Table B-1

MERCURY VAPOR LEVELS IN STORAGE TANK, mg/m^3

Conditions	At floor Level	At Breathing Level
No ventilation	2.1-2.9	1.7
No ventilation	4.0	2.9
Up draft ventilation*	1.1	1.1
Down draft ventilation*	1.5	1.5

*At 85 m^3 per min.

The equilibrium vapor pressure of mercury at 17°C corresponds to a vapor concentration of about 10 mg/m^3

Appendix 3

CORRECTIVE MEASURES FOLLOWING A MERCURY SPILL

C-1. Ground Spills

Where the area can be identified, mechanical methods are recommended, including covering with soil overlays or with plastic sheet, and when possible by collecting the spill and recovering the mercury. Stabilization by spraying with water tends to suppress vaporization and also to promote formation of an oxide film on the surface which tends further to inhibit evaporation.

When conditions are more severe, as in the case of a conflagration, chemical stabilizers will immobilize the mercury. For example, conversions to the chloride followed by hydrogen sulfide will form the extremely insoluble mercury sulfide.

C-2. Spills into Waterways

A spill into an aqueous environment can lead to long-term problems if the mercury accumulates in the bottom sediment.[57,19] The problem has been studied from a number of perspectives, involving direct mechanical removal, chemical and biological conversion, for either stabilization or removal. In addition, a degree of "natural" removal occurs as part of the bilogical cycle which may[93,94] or may not[7,1] involve the conversion of the metal to ionic form prior to conversion to organometallic mercury.

A number of processes for the removal or immobilization of mercury have been described, ranging from fairly detailed engineering studies to preliminary concepts.

A series of exploratory studies was made on sediments collected from streams and lakes, whose organic contents were said to vary over a considerable range. An overlay of iron from crushed automobile bodies was recommended to reduce methyl mercury and mercuric ions to elemental mercury. It was suggested that dredging and roasting to recover the reduced mercury from the sediment would be a relatively inexpensive procedure. Leaching with hypochlorite solution was useful in deposits with moderate or low organic contents.[108]

The treatment of sediments to increase their binding capacity for mercury ions was investigated as a means of reducing the mercury's availability either for methylation or for uptake by fish. It was found that long-chain alkyl thiols are effective and practical mercury-complexing agents. Polyethylene films were found to be ineffective barriers against methyl mercury ions, but with chemical sealants they might hold the complexing agent in place.[109]

Other polymer fiber systems have been found suitable for containment of mercury-contaminated sludges, including nylon, vinyl chloride, and ethylene-vinyl acetate copolymer.

A laboratory and plant-scale process was developed for the recovery of mercury from wastewater and sludge by precipitating with sodium sulfide, and then collecting and roasting the precipitate to recover the mercury.[110]

An imaginative concept of perhaps limited application involves increasing the pH of the aqueous environment to favor the formation of dimethyl rather than methyl mercury. The more volatile dimethyl form would then be lost by evaporation.[111]

The removal of inorganic mercury compounds from wastewater by a cell-reuse method using a mercury-resistant organism was investigated. It was shown that the mercury-resistant bacterium Pseudomonas was suitable for this purpose, among others. Related studies showed that the organisms were capable of tolerating high levels of mercury which they absorbed and subsequently released under biological stimulation.[112,70,113,114]

Other techniques have included covering the bottom sediments with sand and gravel,[16] silicate and clay,[39] either to isolate the deposit mechanically or to immobilize it by sorption of the mercury. Effective application of these chemical restraints with certain sludges may reduce significantly the mercury levels in fish in the environment.[115]

The addition of metals such as aluminum which can form amalgams with mercury has been proposed. The amalgam would presumably make the mercury unavailable for methylation.

A process termed "biological mining" involves the introduction of an organism with a high mercury tolerance, such as the clam, into the environment. Presumably the clams would accumulate large concentrations of mercury in their bodies, and would then be removed from the lake or stream.[39]

Mercury "getters" consisting of sulfur coated on cotton mesh and polyvinyl alcohol gel containing sulfur or phenyl thiourea have been investigated with indications of effectiveness. Elemental sulfur removes metallic and inorganic mercury. Phenyl thiourea retains inorganic mercury and methyl mercuric chloride.[116]

A procedure for the removal of mercury ions from water using rubber as the "getter" has been described.[117] The method attributed to M.E. Russell of the Atomic Energy Commission's Savannah River Ecological Laboratory, uses vulcanized rubber granules which tend to adsorb the Hg strongly.

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