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# HAZARD OF MERCURY VAPOR IN SCIENTIFIC LABORATORIES

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#### ABSTRACT

This paper is divided into two parts. The first part reports the determination of the amounts of mercury vapor found in the air of various ventilated and unventilated laboratories at the National Bureau of Standards and elsewhere. The new optical mercury-vapor detector devised by Woodson and produced by the General Electric Co. was used to secure this information. The concentrations found ranged up to 70 micrograms of mercury per cubic meter of air. Various sources of mercury vapor are described, as well as some measures taken to lower the concentration.

The second part, by members of the staff of the National Institute of Health, reports the results of extensive physiological and psychological examinations of 38 laboratory men who were exposed to the various concentrations of mercury vapor noted in part 1. The examinations of these men were made 3 months after the severest exposures had been terminated.

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#### Martin Shepherd and Shuford Schuhmann

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# Part 1. Mercury Vapor in Air

### By Martin Shepherd and Shuford Schuhmann

### I. INTRODUCTION

The danger of breathing mercury vapor has long been known. Considerable information concerning the physiological effects of this vapor is afforded by the researches of the United States Public Health Service and others.<sup>1</sup> The symptoms associated with mercury poisoning have caused many a moment's reflection on the part of imaginative laboratory workers. For instance, the long and interesting list of symptoms includes forgetfulness, a strong disinclination to work, mental fatigue, irritability, excitability, and other such matters associated with the daily history of normal people—both in and out of laboratories. Other symptoms such as headaches, digestive disturbances, and bad teeth are scarcely specific, but may furnish the excuse for a self-diagnosis which may cause unnecessary worry.

In real cases of chronic mercurialism such general symptoms as those mentioned are often present; but there are other more definite symptoms. However, no one wishes to observe these other symptoms in himself, and for this reason may be entitled to an occasional flurry of healthy concern over the condition of his laboratory with respect to the mercury hazard. There are then two direct questions to be answered:

1. What is the amount of mercury vapor in the air of various typical laboratories?

2. What is the permissible limit of mercury vapor in inspired air, especially for daily exposure over long periods?

Part 1 of this paper will confine itself entirely to the first of these two questions. Information concerning the second question is given in part 2.

While the two reports comprising this paper do not constitute a final answer to all cases, nevertheless they do give a general idea of what may be expected with regard to the hazard of mercury vapor in typical scientific laboratories. They are accordingly of interest to laboratory workers who have no clear idea of how much mercury vapor they may be dealing with, and what to expect from it.

The first question concerning the amount of mercury vapor to be expected is at least partially answered in this portion of the paper by the results of the examination of various typical laboratories, ventilated and unventilated, and containing different amounts of mercury (as liquid) of varying degrees of cleanliness. Among the laboratories examined were many devoted to typical as well as to special chemical and physical work. The laboratories were located at the National Bureau of Standards, the United States Department of Agriculture Experimental Station at Beltsville, Md., and the Geophysical Laboratory of the Carnegie Institution. Considerable concentrations of mercury vapor were found in some laboratories, although the general picture was not alarming. Remedial measures were taken where it was considered advisable.

<sup>&</sup>lt;sup>1</sup> An excellent bibliography of this subject is given by Clark Goodman, Rev. Sci. Instr. 9, 233 (1938). Of particular interest are U. S. Public Health Bulletin 234, A study of chronic mercurialism in the hatters' fur-cutting industry, by Neal, Jones, Bloomfield, Dallavalle and Edwards; and U. S. Public Health Bulletin 263, Mercurialism and its control in the felt-hat industry, by Neal, Flinn, Edwards, Reinhart, Hough, Dallavalle, Goldman, Armstrong, Gray, Coleman, and Postman.

## II. DETECTOR AND ITS OPERATION

### 1. DETECTOR AND THE SAMPLING MODIFICATION

Such a survey as that reported here could not have been successfully made without some such instrument as the GE optical detector. The various chemical methods that have been proposed are distinctly unsatisfactory. They are not only exacting and time-consuming, but are often inaccurate, usually because of the loss of mercury through volatility of its salts. One chemical method proposed by Nordlander,<sup>2</sup> based upon the reaction of mercury vapor with selenium sulfide, is successful for higher concentrations of this vapor in air. According to measurements made during the calibration of the optical detector, the lower limit of sensitivity of the Nordlander instrument is approxi-mately 150 micrograms ( $\mu g$ ) of mercury vapor per cubic meter of air. Since lesser amounts are of definite interest, the instrument was entirely unsuitable for a general survey of laboratories.

The new optical detector sponsored by the General Electric Co. was developed by Woodson.<sup>3</sup> Air to be examined is drawn by a motordriven pump through a section of iron pipe, at one end of which is an ultraviolet lamp, and at the opposite end a photoelectric tube sensitive to the radiation from this lamp (2537 A). According to Woodson, the response of the phototube decreases when mercury vapor is present and scatters the radiation. The phototube is connected to a triode amplifier whose plate current is indirectly measured as an indication of the amount of mercury vapor present.

The particular instrument used in this investigation was intended for permanent installation rather than for portable use, and it was accordingly mounted on the laboratory equivalent of a tea cart. Only one modification of the instrument was made-and this without changing a single part of the original apparatus. In order to be certain of the result obtained, the instrument must be used virtually as a differential device—that is, air containing no mercury must be compared with the air to be examined. Instead of making this comparison simultaneously, which would be desirable, but for which the instrument was not designed, it was made by repeatedly switching from the mercury-free air to the laboratory air. This was done with a two-way steel cock connected to the inlet of the apparatus. The large (10 mm) bores of this cock offered no appreciable restriction to air flow. One inlet of the cock admitted air to be tested; the other admitted air which must pass through Hopcalite,<sup>4</sup> which quantitatively removes mercury vapor from air, and so provides the reference air needed. To prevent the Hopcalite from offering significant restriction to air flow, a relatively thin layer (15 mm) of this material with comparatively large surface area (about 20 cm<sup>2</sup>) was supported on a screen within the glass tube acting as the absorbing vessel. The Hopcalite absorber has been tested from time to time by comparing air drawn through it with air taken directly from outdoors. No difference in composition was observed. The procedure used eliminated any effect of the rate of flow, to which the detector is somewhat sensitive.

 <sup>&</sup>lt;sup>2</sup> B. W. Nordlander, Ind. Eng. Chem. 19, 518 (1927).
 <sup>3</sup> T. T. Woodson, Rev. Sci. Instr. 10, 308 (1939).
 <sup>4</sup> Hopealite is a proprietary catalyst for the oxidation of carbon monoxide. Hopealite may now be obtained under the name Mercurysorb.

### 2. CALIBRATION OF THE DETECTOR

The detector was calibrated with air saturated with respect to mercury vapor at 0° C and known pressure. The amount of mercury in the air was calculated from the total pressure at the exit of the saturator and the known saturation pressure of mercury.<sup>5</sup> The calculated percentage by volume was reduced to milligrams of mercury per cubic meter of air, assuming the density of mercury vapor at 25°C to be 8.2 g/liter. Proper saturation with respect to mercury was shown to have been attained by approaching the desired equilibrium from opposite directions—that is, air containing no mercury was passed through a saturator at 0°C, and thereafter air containing more mercury than corresponded to saturation at 0°C was passed through the same saturator now acting as a condenser. Concordant results were obtained. The amount of mercury in the air used for calibration was varied by diluting the saturated air with air containing no mercury.

The apparatus used for this calibration is shown schematically in figure 1. Air containing no mercury entered the apparatus at the left under a pressure of  $8 \text{ lb/in.}^2$  The stream was divided and passed

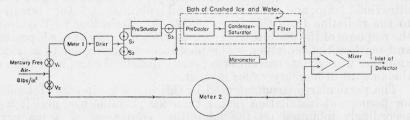


FIGURE 1.—Flow diagram of apparatus used for calibrating the detector.

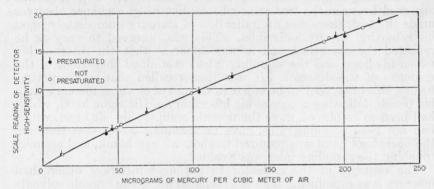
at controlled rates through the two special needle values, V1 and V2. The portion entering the apparatus through V1 was metered by a 1/20 ft.<sup>3</sup> wet test meter, and was then passed through a drier containing calcium chloride, which removed excess water that otherwise would have condensed in the saturator. After leaving the drier, one of two routes could be used. The air might be passed through a presaturator with stopcocks S1 and S3 opened and stopcock S2 closed; or the presaturator might be bypassed by reversing the setting of the stopcocks. This operation could be accomplished without changing the rate of flow through meter 1. The presaturator was a 500-ml glass flask with inlet leading to the bottom, its walls completely coated with freshly condensed mercury. Air leaving the presaturator contained enough mercury vapor to correspond to approximate saturation at temperatures ranging from 40° to 25°C. Depending upon the procedure selected, air containing such amounts of mercury vapor, or no mercury vapor at all, next passed through a cooling coil, a condensersaturator, and a filter. All three of these units were immersed in a bath of crushed ice and water held in a D'Arsonval tube. The condenser-saturator was a tall gas-washing bottle whose inlet terminated in a sintered glass disk which effectively subdivided the air stream. The disk was immersed in clean mercury, so that the air bubbled

<sup>&</sup>lt;sup>5</sup> Int. Crit. Tables 3, 205-206 (1928).

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through a 5-mm layer of this continually stirred liquid. The filter was a pack of glass wool about 3 cm thick. No mercury could condense beyond the filter, since there the temperature was above 0°C. A manometer registered the pressure at the inlet surface of the filter. When air entering the precooler contained more mercury than corresponded to saturation at 0°C, the condenser-saturator acted as a final condenser; and when air entering the precooler contained no mercury, the condenser-saturator acted as a final saturator.

The air which contained mercury vapor was finally passed to the mixer, where it joined a stream of air containing no mercury. The latter stream, entering through V2 and metered by a 1 ft<sup>3</sup> wet test meter (No. 2), formed by far the larger percentage of the total air entering the mixer. The system was thus designed to insure proper equilibrium, since only a small portion of the total air need be saturated, and this resulted in relatively small rates of flow through the





saturator. The mixer was a glass tube of about 6-cm diameter and 2 m long, provided with baffles. The inlet of the mercury-vapor detector projected about 20 cm into the mixer at the exit end. The total flow of air through the mixer always exceeded the amount drawn by the detector.

The two meters were compared under the actual experimental conditions which existed during the calibration of the detector. This was done by connecting meter 2 at the exit of the filter and making simultaneous observations of volume at different rates of flow. During the actual process of calibration, the detector was repeatedly

During the actual process of calibration, the detector was repeatedly adjusted to zero reading with reference air containing no mercury, and a series of readings were taken, both with and without the presaturator in the line, with each definite setting of V1 and V2. The two meters were read simultaneously. The data are plotted in figure 2. It will be seen that concordant results were obtained between the two methods of approaching equilibrium with respect to saturation with mercury. The sensitivity of the instrument may be varied, but the data given were all obtained with the detector adjusted to maximum sensitivity and a rate of flow of 0.5 ft<sup>3</sup>/min. At the lower concentrations, 1 scale division corresponds to approximately 9  $\mu$ g of mercury per cubic meter of air. The full range of the scale is 20 divisions, and tenths of a division may be estimated without difficulty.

The highest sensitivity claimed by Woodson is 10 micrograms per cubic meter ( $\mu$ g/m<sup>3</sup>), but our experience justifies the statement that an indication of half this amount can be relied upon under ordinary test conditions, and  $\pm 0.1$  of a scale division is usually significant under carefully controlled laboratory conditions.

### 3. GENERAL BEHAVIOR OF THE DETECTOR

During the entire progress of this work, the detector gave an excellent account of itself and repeatedly proved itself trustworthy. There were times when its indication was regarded with a moment's doubt. but in the end it always turned out that the operators and not the instrument had been fooled. A homely example will suffice to illus-trate. Before the sampling device was installed, outside air was being compared with air in a hallway by alternately connecting and disconnecting a glass sampling tube by hand. No difference was observed between the two atmospheres; but when a chance observer made the test, there was an indication of mercury immediately upon his removing the fresh-air inlet. This was observed to vary as he repeated the operation, and it was apparent that the distance be-tween his hand and the sampling inlet determined the extent of the response of the detector. It was then recalled that, a short time before, this observer had been left in the act of cleaning mercury from his bench, following a test of his laboratory. His right hand, which had been so employed, gave the upscale reading; his left hand, which had not been as industrious, gave no reading. From that time on, the operator's hand was required to show a clean blank, and actually touching the sampling inlet was avoided.

The response of the indicator to various substances other than mercury was examined. The list included all of the organic solvents to be found upon the shelf of the various well-equipped laboratories visited during the survey, as well as water vapor, carbon dioxide. illuminating gas, ozone, dust, tobacco smoke, and even some aqueous solutions of mercury salts. Marked responses to high concentrations of some organic solvents, ozone, and illuminating gas were noted. However, the use of the detector as specifically related to mercury vapor was in no way limited thereby, since the nose was always more sensitive than the detector. A room filled with a blue haze of tobacco smoke gave an indication of three times as much mercury vapor as was actually present; therefore, smoking was avoided in laboratories to be examined. The dust ordinarily present will not interfere. comparison of mercury-free air, taken from outside and from inside of a building whose air was cleaned with an electrostatic precipitator, showed no difference. Insofar as our extended experience goes, the detector can be trusted to indicate mercury vapor alone if the nose can detect no organic vapors, ozone, etc., and no dust or smoke can be seen.

The detector is somewhat sensitive to changes in temperature and to rate of flow. The two effects are associated, although a second factor, namely, the catalytic oxidation of mercury by the UV lamp, influences the response, particularly at the lower rates of flow. The detector is designed to operate at a fixed rate. However, calibrations were obtained at 0.25, 0.5, and 0.75 ft<sup>3</sup>/min, and were notably different. Changes in either temperature or rate of flow will cause a drift from the zero adjustment, and our greatest difficulty with the instrument arose from this fact. The difficulty was overcome by the sampling unit already described. This permitted such rapid intercomparison of the reference air with that to be tested that temperature equilibrium was no longer a primary consideration, and the effect of rate of flow was eliminated by making the sampling rate equal to the reference rate.

It was suspected that the possible accumulation of dust upon the glass walls of the UV lamp and photo tube might alter the calibration of the instrument, but no such change was measured after several months of use. However, it is possible that changes from this or other sources may sometimes occur; therefore, the instrument should be recalibrated periodically until its behavior is better established.

# III. LOCAL SOURCES OF MERCURY VAPOR FOUND IN LABORATORIES

The General Electric Optical Detector is admirably adapted to ferreting out local sources of mercury vapor, and many of these sources were explored during the survey of various laboratories. They will be noted now, since this will serve to give a general picture of laboratory conditions, which will later assist in understanding and interpreting the results reported for the average atmosphere of the same laboratories. It may be mentioned in this connection that many people seem to think that if mercury is exposed in a laboratory, the concentration of vapor within the entire room will be equivalent to saturation at the existing temperature. Fortunately, this is very far from true, since the mercury vapor from relatively small sources is quickly diluted by the air supplied by normal ventilation.

Mercury spilled upon a bench or floor is perhaps the commonest source of its vapor in most laboratories. The following example shows what happens after mercury is spilled. Nearly 100 ml of mercury was discharged from the top of a buret and fell about 1 meter to the bench below. Most of it collected as a pool upon the bench (designed to trap mercury), although some reached the floor and the side of an adjacent bench. The room was 20 by 18 by 11 ft., and was ventilated with eight complete changes of fresh air per hour. The room temperature was approximately 25° C. The air was examined at nose level 6 ft. from the bench. Fifteen minutes after the mercury was spilled, the air contained 120  $\mu$ g of mercury per cubic Twenty-four hours later the concentration had decreased to meter. 60  $\mu$ g/m<sup>3</sup>, and after another 28 hours to 35. The bench top was then shaken by blows of a mallet. Ten minutes thereafter the concentration in the air was again 120  $\mu$ g/m<sup>3</sup> cubic meter. This effect seems quite typical. Exposed mercury surfaces gradually collect a pro-tective film of oxide, sulfide, grease, dirt, etc., which diminishes the amount of mercury vapor escaping. When the surfaces are fresh-ened, the mercury again escapes in greater amounts. Another example of this effect was found in a small unventilated room, a portion of whose sheet metal (tinned) floor was amalgamated. The air of this room had repeatedly indicated 60  $\mu$ g of mercury per cubic The concentration had been so uniform and reproducible meter. over a period of several months that the room had been used for brief experiments associated with respiration and with a reagent for

removing mercury vapor. One day the air of this room indicated almost no mercury vapor. While the senior author was pacing the floor wondering what had gone wrong with the detector, he remembered that the room had not been used during the past month. The pacing was continued at an accelerated tempo, and soon fresh surfaces of mercury had been rubbed up, and the air of the room again contained 60  $\mu$ g of mercury per cubic meter. The higher concentration of mercury vapor usually found at floor level is reasonably explained by the fresh surfaces and elevated temperatures following the brisk massage applied by the sole of a shoe.

A bench top may hold mercury that cannot ordinarily be seen. For example, mercury was spilled upon a smoothly finished maple bench top. It was then brushed off, the bench top was carefully wiped off with a damp cloth, and no mercury could be seen. For months thereafter, the hand could first be held near the inlet of the detector to insure no response, then rubbed over the bench top and so made to give a high response. The microscope disclosed ample reason for the response of the detector; viewed so, the bench top was splattered with small globules of mercury.

Mercury kept in open containers is probably the second most common source of its vapor in most laboratories. If the mercury is left undisturbed over long periods and is visibly dirty, it may not yield much vapor. The air within a radius of 20 in. of open bottles containing such mercury indicated less than 10  $\mu$ g/m<sup>3</sup>; but when the mercury was disturbed by moving the container, the concentration increased immediately. The air at nose level near the mercury switch used with a resistance bridge and platinum resistance thermometer contained 20  $\mu$ g/m<sup>3</sup> for a moment after the position of the switch had been altered. The air at the atmospheric opening of a leveling bulb containing mercury showed 20 to 30  $\mu$ g/m<sup>3</sup> at nose level 20 in. from the bulb, when mercury was flowing into the bulb. These observations were made in ventilated laboratories.

Mercury may sometimes fall upon surfaces which are heated at times. Often its presence in such spots is not suspected. During the survey of various laboratories, cylindrical rheostats, thermal insulation of diffusion pumps, ovens and such devices, and even electric lamps were found to be sources of mercury vapor. Amounts varying from 30 to 200  $\mu$ g/m<sup>3</sup> were found at respiratory levels in the immediate vicinity of such apparatus. This concentration was greatly reduced at distances greater than 2 or 3 ft. from the source.

The exhaust of ordinary vacuum pumps of the oil-immersed type is often a source of mercury vapor. This happens if the pumps are drawing air across mercury surfaces, or acting as backing pumps for mercury-vapor pumps. The air within 10 in. of the exhaust of such pumps indicated mercury vapor in amounts varying from 60 to 200  $\mu g/m^3$ .

Some types of high-frequency electric furnaces are prolific sources of mercury vapor.<sup>6</sup> The present practice is to place the furnace under a hood and remove the vapor by strong suction. Of various units so equipped, all but one examined in this survey were satis-

<sup>&</sup>lt;sup>6</sup> Turner has reported a very serious case of this sort. The amounts of mercury vapor he found were much too low, because of the extremely large error inherent in the analytical method available at that time. U. S. Public Health Service Report 39, No. 8 (1924); and B. W. Nordlander, Ind. Eng. Chem. **19**, 522 (1927.)

factory; in the exceptional case, 30  $\mu g/m^3$  was found in the air immediately outside of the screen guard of the furnace.

In one laboratory, hot bituminous material was poured onto amalgamated brass plates. With the wind in the proper direction, 200  $\mu g/m^3$  was easily detected during the pouring process. The air immediately around a stack of the amalgamated plates, at room temperature, contained 20 µg/m<sup>3</sup>.

While the following source does not strictly contribute mercury vapor to the laboratory air, it certainly does to the inspired air. It may therefore be included as important. A cigarette was tapped upon the maple top of a bench upon which mercury had been spilled and brushed off. No mercury was apparent on the bench top except by careful scrutiny through a magnifying glass. The end of the cigarette was examined under a low-power microscope. The tobacco held many small globules of mercury. Since tapping the cigarette prior to lighting it is a habitual practice with smokers, and a laboratory bench is often used for the purpose, this hazard should be realized.

# IV. AMOUNT OF MERCURY VAPOR FOUND IN THE AIR OF VARIOUS LABORATORIES

In the report which follows, the amounts of mercury vapor noted are expressed in micrograms per cubic meter of air, and represent the average of three or more observations made at significant respiratory levels. Comparison with reference air was always made. When necessary, a glass tube with short rubber connection was placed so that its inlet was, as nearly as could be judged, in the space most frequently occupied by the laboratory worker's nose. The glassrubber sampling inlet was repeatedly tested with mercury-free air to insure its freedom from contamination. (Rubber tubing is not to be trusted without such tests. It may have picked up organic solvents or even mercury. For this purpose, it must be free from talc.)

The survey was made during the winter months, and the laboratory windows were always closed. The room temperatures were approximately 25° C. Mercury had been spilled at one time or another in all of the laboratories examined. In many cases, it had been cleaned up and was no longer apparent; in other cases, more or less spilled mercury was visible.

The observations are given in table 1. The laboratories are divided into four groups with respect to the amount of mercury vapor found. A rough appraisal of the amount of spilled mercury, and specific sources of the vapor, are given for each laboratory. Ventilation is specified in somewhat general terms. "Natural" refers to steam-heated rooms, with ordinary unsealed doors and windows, and without forced ventilation. "None" refers to rooms without windows or vents, or rooms which have been reasonably closed for the purpose of maintaining constant temperature and humidity, where the ventila-tion occurs by occasionally opening and closing a door, or by seepage through materials of construction. Room 0 C was actually the nearest approach to a sealed airtight compartment. When forced ventilation was used, the number of changes of fresh air per hour is noted. The amount of mercury vapor found is expressed in micrograms per cubic meter of air.

Ventilation-Numerals speci-Micrograms Appraisal of mercury fy changes of air of mercury Laboratory Type of laboratory per hour. "Na-Kind of work done spilled on benches and Other sources of mercury vapor vapor per number tural" means floor cubic meter natural building of air ventilation GROUP I LABORATORIES-The air in all of these laboratories contained less than 4 µg of mercury per cubic meter. Mercury had been spilled on benches or floor some time prior to test. In some cases none of this mercury was apparent at time of test 312 C ..... Chemical Inorganic analysis None apparent None 8 to 10\_\_\_\_\_ Several mercury seals 405 C do \_\_\_\_do\_\_\_\_\_ do 8 to 10\_\_\_\_\_ 221 I Organic analysis Very little\_\_\_\_\_ None Natural Metallurgical 208 M ..... Chem., phys., and metall. research ... Small amount Two ventilated induction furnaces \_\_\_\_do\_\_\_\_ 300 M ..... Physical\_\_\_\_\_ Barometry None apparent Barometers stored in sealed cabinet \_\_\_\_ do\_\_\_\_\_ 103 R\_\_\_\_\_do\_\_\_\_ Office\_\_\_\_\_ \_\_\_\_do\_\_\_\_ None..... 4\_\_\_\_\_ Radio wave meters\_\_\_\_\_ 111 R\_\_\_\_\_do\_\_\_\_\_ None\_\_\_\_\_ Amalgamated contacts 4\_\_\_\_\_ Shop\_\_\_\_\_ ob None 4 Electrolytic\_\_\_\_\_ 203 R\_\_\_\_\_do\_\_\_\_ ob \_\_\_\_do\_\_\_\_\_ 4 211 R do Radio frequency meters\_\_\_\_\_ do .....do\_\_\_\_\_ 4 Radio piezo-oscillators\_\_\_\_\_ 212 R\_\_\_\_\_do\_\_\_\_ None apparent\_\_\_\_\_ Open manometers\_\_\_\_\_ 4\_\_\_\_\_ Batteries\_\_\_\_\_ None\_\_\_\_\_ 12 E.\_\_\_\_do\_\_\_\_ None 4\_\_\_\_\_ 13 E\_\_\_\_\_do\_\_\_\_ Current balance ob \_\_\_\_do\_\_\_\_\_ 4\_\_\_\_\_ Very little\_\_\_\_\_ Amalgamated contacts 15 E.....do..... .....do..... 4\_\_\_\_\_ 16 E do Batteries\_\_\_\_\_ ob None 4\_\_\_\_\_ 18 E do .do..... ob \_\_\_\_\_do\_\_\_\_\_ 4\_\_\_\_\_ 211-12 M\_\_\_\_\_do\_\_\_\_ Metallurgical \_\_\_\_do\_\_\_\_ Ventilated furnace Natural\_\_\_\_\_ Aeronautical instruments 308-10 M ..... do...... Fair amount Open manometers do 212 E do Capacitance and inductance None\_\_\_\_\_ None\_\_\_\_\_ 4 214 E.....do..... Capacitance .....do..... Amalgamated contacts 4\_\_\_\_\_ 216 E\_\_\_\_\_do\_\_\_\_ Insulation\_\_\_\_\_ \_\_\_\_\_do\_\_\_\_\_ None 4\_\_\_\_\_ 305 E \_\_\_\_\_ do\_\_\_\_\_ Radioactivity .....do..... ....do\_\_\_\_\_ 4\_\_\_\_ 403 E\_\_\_\_\_do\_\_\_\_ Standard cells\_\_\_\_\_ \_\_\_\_\_do\_\_\_\_\_ One open manometer 4\_\_\_\_\_ 408 E \_\_\_\_\_do\_\_\_\_\_ do..... do None 4\_\_\_\_\_ ....do do G 3\_\_\_\_\_ Phys.-Chem\_\_\_\_ Microscopy\_\_\_\_\_ G 10\_\_\_\_\_do\_\_\_\_ Gases and rocks Considerable amount. Mercury in glass open to air Chemical..... Mercury in glass open to air G 12 Gas analysis Fair amount Physical\_\_\_\_\_ None None G 23.....

TABLE 1.—Survey of various typical laboratories with respect to mercury vapor in respiratory air

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GROUP II LABORATORIES—The air in all of these laboratories contained 4 to 12 µg of mercury per cubic meter. Mercury had been spilled on benches or floor in all of these laboratories some time prior to test. In all cases except one, some of this was apparent

| 3 I    | _ Engineering  | Mechanics                 |               | None   | Natural     | 4 to 8      |
|--------|--|---------------------------|---------------|--|-------------|-------------|
| 86 B-I | Physical   | Rubber                    |               | Dilatometer  | do          | 13 13 12 mm |
| 23 I   | do   | Leather                   | do            | Mercury in glass open  | do          |             |
| 26 I   | PhysChem   |                           |               |  | do          | 4           |
| 1 W    |  | Pyrometry                 | do            |  | 4           | 4 to 8      |
| 0 C    | _ Chemical   | Physical-Chemistry        | do            | Open manometers and vac. pumps                                       | 8 to 10     | 4 to 8      |
| E      |  | Dry cells                 | None apparent | None   | 4           | 4           |
| 7 E    | Physical   | Soil corrosion            | Small amount  | Mercury open to air  | 4           | 1           |
| 2 E    | do   | Photometry                | do            | Vacuum pumps   | 4           | 1           |
| )9 C   | Chemical   | Distillation of gases     |               | Mercury open to air, vacuum pumps and mercury in thermal insulation. | 8 to 10     | 8 to 12     |
| 3 E    | Physical   | Condensers and inductance | do            |  | 4           | 15          |
| 5 E    | do   |                           |               | Oven with broken thermometer   | 4           | 8           |
| 8 E    | do   | Photometry                | None apparent | Apparatus with small shaft revolving in                              | 4           | 8           |
|        | the second s |                           |               | mercury.   |             |             |
| 2 W    | Office   |                           | Very little   |  | Almost none | 8 to 1      |
| 6 I    | Physical   | Textiles                  | None apparent |  |             |             |
| 6 I    | _ Shop   | Mechanical                | Fair amount   | do   | Natural     |             |

GROUP III LABORATORIES—The air in all of these laboratories contained up to 20 µg of mercury per cubic meter. In addition to spilled mercury, some special apparatus or unusual condition contributed mercury vapor

| 108 C                  | Chemical                    | Preparing pure compounds—purify-<br>ing mercury.                         | Very little  | Hg switch on Mueller bridge. Hg stills in<br>special cabinet under hood. Hg switch<br>used with resistance bridge. Latter re-<br>sponsible for highest local concentration in<br>room. | 8 to 10                          | 4 to 20              |
|------------------------|-----------------------------|--|--------------|--|----------------------------------|----------------------|
| 208 C<br>406 C<br>23 B | Chemical<br>do<br>Shop      | Gas analysis<br>Bituminous<br>Mechanical                                 | Considerable | Gas analysis apparatus<br>Heated amalgamated brass plates  | 8 to 10                          | 12 to 20<br>16 to 20 |
| 139 I<br>336 I         | Ceramic<br>Physical<br>Shop | Porosity of ceramic bodies<br>Constant temperature room<br>Glass blowing | Fair amount  | Immersion pans.<br>Electrodes—contacts<br>Hg on warm thermal insulation inside special<br>oven of barometer-filling apparatus.   | Natural<br>12 ft³/min<br>Natural | 20<br>16<br>20       |

# GROUP IV LABORATORIES—The air in these laboratories contained up to 70 µg of mercury per cubic meter. Some of the rooms were unventilated. All contained mercury spilled on floors and benches, but in general the lack of ventilation was the predominant factor involved

| G 27  | Physical     |                                    | Small amount      | Some of spilled mercury on warm bench top             |         | 4 to 28  |
|-------|--------------|------------------------------------|-------------------|---|---------|----------|
| 209 W | do           | Pyrometry                          | do                | under heated furnace.<br>Induction furnace—ventilated | 4       | 6 to 24  |
| 244 I | Ceramic      | Porosity of ceramic bodies         | Large amount      | Immersion pans (covered)                              | Natural | 20 to 30 |
| 307 C | Photographic | Dark room                          | Small amount      |   | do      | 24 to 40 |
| 111 E | Physical     | Electrical resistance measurements | Considerable      |   | do      | 20 to 50 |
| 23 B  | do           | Gas analysis                       | Large amount      | Pools of mercury under cupboards                      | do      | 35 to 45 |
| 112 E | do           | Electrical resistance measurements | Considerable      | Mercury switches                                      | do      | 16 to 56 |
| 0 C   | do           | Polarograph                        | Very small amount | Amalgamated tinned floor                              | do      | 60       |
| 00 E  | do           | Electrical resistance measurements |                   |   | do      | 70       |
| 0 E   | do           | Gravity measurements               | Small amount      |   | do      | 60       |
|       |              |                                    |                   |   |         |          |

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A brief study of the table gives the following information. Of the 61 laboratories tested, 28 yielded less than 4  $\mu$ g of mercury per cubic meter of air, 16 yielded amounts varying from 4 to 12  $\mu$ g, 7 yielded up to 20 µg, and 10 yielded up to 70 µg. The amount of mercury vapor found depended primarily upon ventilation and thereafter upon the number and types of local sources, and the degree to which mercury surfaces were disturbed by mechanical means or mercury was vaporized by heating. The survey was not sufficiently extensive to justify any statistical correlation between the type of laboratory, in terms of physical or chemical, with the amount of mercury found, even though the largest amounts were found in physical laboratories. If such a correlation exists, it would probably find its natural explanation in the fact that chemical laboratories are generally very well ventilated, and special physical laboratories may not be. The total amount of mercury actually used is not the important factor. This is illustrated by comparing room 209 C, which yielded 8 to 12  $\mu$ g/m<sup>3</sup> of air, with room 0 C, which yielded 60  $\mu$ g. At least 500 lb of mercury is regularly used in room 209 C, and only a few grams in room 0 C. Although most of the mercury in the former laboratory is kept within closed glass vessels, the surface exposed to air far exceeds that exposed in the latter room, and in addition there are other local sources not present in the latter room. The difference lies in the ventilation.

In general, the survey should be comforting to those who work in well-ventilated laboratories and are not careless with their mercury. It may give a moment's pause to those who are too careless, and should cause some real reflection on the part of those who work with even small amounts of mercury in unventilated rooms. Whether such reflection is entirely justified is a problem for medical agencies. Until sufficient data have been collected to answer this question, the experiments outlined in the following two sections will be of interest.

# V. REDUCTION OF MERCURY VAPOR IN THE AIR OF SEVERAL LABORATORIES TESTED

### 1. EFFECT OF VENTILATION

By far the most effective means of reducing the mercury content of laboratory air is ventilation. The effect of ventilation is illustrated in the following experiments.

Room 209 C was examined under the same conditions of temperature and exposure to mercury, but with varying degrees of ventilation. With approximately 6 changes of air per minute, the air contained 12  $\mu$ g of mercury per cubic meter. With 8 to 10 changes of air per minute, 8  $\mu$ g/m<sup>3</sup> was found. With 2 windows open and a slight breeze blowing in, the concentration dropped to 3.

Room 0 C contained 60  $\mu$ g/m<sup>3</sup>; with a small blower forcing in fresh air, the concentration dropped to 32.

Room 23 B contained  $16^{\circ} \mu g/m^3$ ; with 2 windows open, the concentration dropped to 6.

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#### 2. REMOVAL OF LOCAL SOURCES

An example of what may be expected if local sources of mercury vapor are at least partially removed is afforded by the following experiment. The air of room 209 C contained 15  $\mu$ g of mercury per cubic meter under the following conditions: A few globules of mercury were trapped in the asbestos insulation surrounding a mercury-vapor pump, which was operating and therefore hot; three Hyvac pumps were operating, drawing air over mercury and discharging into the room; a few globules of mercury were on the surface of a lighted 60watt electric lamp; a few globules of mercury were visible on the floor and upon benches; the ventilation was 8 to 10 changes of air per hour; the laboratory temperature was 25° C. Then the exhaust from the Hyvax pumps was piped outside; the mercury was removed from the two heated surfaces, and partially (it can never be completely) removed from the floor and benches. Under these new conditions, and at the same temperature and degree of ventilation, the concentration was lowered from 15 to 4  $\mu$ g of mercury per cubic meter.

### 3. CLEANING AND REFLOORING

Room 112 E, an unventilated physical laboratory, contained a great deal of spilled mercury. Much of this had collected in cracks of the wooden floor, and had even run under baseboards. Walking across the floor would raise the concentration of mercury vapor considerably. The room was subjected to a thorough house-cleaning. The mercury was carefully cleaned up, the baseboards were removed and the hoarded supply removed, the floor was treated with sulfur, oiled, and thereafter a sealed linoleum floor was installed. Previous to this work, the concentration of mercury vapor in this room was 16 to 60  $\mu$ g/m<sup>3</sup> of air. After the cleanup, the concentration was lowered to 4 to 6  $\mu$ g.

In this connection, it is well to remember that when mercury is spilled upon the floor of an unventilated room, enough will remain in cracks and uneven places, even after cleaning up, to yield a considerable amount of vapor if the floor is walked upon. This suggests the advisability of a mercury-free duckboard. A rubber mat which can be discarded when contaminated is one means of avoiding difficulty.

### 4. REMOVAL OF MERCURY VAPOR BY IODIZED CHARCOAL

Room 0 C, the small unventilated room lined with tinned sheet metal, which was previously mentioned, consistently showed the presence of 60  $\mu$ g of mercury per cubic meter of air. A large ceiling fan circulated the air, and the concentration of mercury vapor was uniform throughout the room. A commercial device was installed which circulated air at the rate of approximately 250 ft<sup>3</sup>/min over (not through) iodized charcoal. The lowering of the amount of mercury vapor with time was as follows:

| Minutes of<br>operation of<br>the purifier | Concentration<br>of mercury<br>vapor in<br>micrograms<br>per cubic<br>meter of air |
|--|--|
| 10   | 64   |
| 10   | 32   |
| 20   | 10   |
| 30   | 5  |
| 40   | 4  |
| 60   | <4   |

# VI. RESPIRATORY EXPERIMENT—RETENTION OF INSPIRED MERCURY VAPOR

The following simple experiment was performed by the senior author and H. Matheson of this Bureau. As noted previously, room 0 C was a tightly sealed space in which known concentrations of mercury vapor could be uniformly distributed. With the ceiling fan operating and an open surface of clean mercury (approximately 4 in.<sup>2</sup> in area) placed within the room, it was possible to raise the concentration of mercury vapor to 200  $\mu$ g/m<sup>3</sup> of air within 5 minutes. When the source of mercury was removed, the concentration remained nearly constant for 20 to 30 minutes.

Using this well-suited environment for the experiment, air containing known amounts of mercury vapor was inhaled and then exhaled through the mercury-vapor detector. The rate of exhalation was measured by a flowmeter, so that the detector was supplied at its normal sampling rate. When air containing 60  $\mu$ g of mercury vapor per cubic meter was thus inhaled, the exhaled air contained no mercury vapor. When air containing 200  $\mu$ g was inhaled, the exhaled air contained 8 to 12  $\mu$ g in the case of one man and 0 to 8  $\mu$ g in the case of the other.

It is true that the conditions of the experiment do not represent normal respiration, since inspiration was deep and the respiratory rate was not normal. Nevertheless, the ability of the lung area to quickly and almost completely absorb these amounts of mercury vapor is startling. If absorption during normal respiration is of the same order of magnitude as indicated by these direct experiments, it would be entirely possible for a worker, occupied 8 hours per day, in a laboratory containing 15  $\mu$ g of mercury vapor per cubic meter of air, to absorb 72  $\mu$ g of mercury in the course of a day's work. (This assumes a respiratory volume of 10 liters/min, slightly in excess of the average for activity corresponding to "standing" and less than corresponds to the average for "walking 2 miles per hour.")

With the absorption of anything like this amount of mercury, one would expect to be able to detect it in the urine of workers so exposed. It is worthy of note that mercury was found in the urine of three men, whose exposures (before the laboratories were cleaned and reconditioned) were as follows:

Case 1.—Thirty-nine hours per week in room 208 C. About 30 hours per week working with gas analysis apparatus where the respiratory air contained 12 to 20  $\mu$ g of mercury per cubic meter. Total period involved about 10 years.

Case 2.—Approximately 2 hours per week with same exposure as case 1. About 37 hours per week in room 209 C at a concentration of 8 to 12  $\mu$ g/m<sup>3</sup>. Total period involved about 20 years. Case 3.—Exposure to 60  $\mu$ g/m<sup>3</sup> in room 0 C was intermittent, the

Case 3.—Exposure to 60  $\mu$ g/m<sup>3</sup> in room 0 C was intermittent, the maximum periods being approximately 2 hours, with a total of about 6 hours per week. Total period involved about 2 years. Urinary analyses in cases 1 and 2 were made by the Chemical

Urinary analyses in cases 1 and 2 were made by the Chemical Laboratory of the United States Army Medical Center, Walter Reed Hospital, in charge of Col. C. J. Gentzkow; tests in case 3 were made at this Bureau. The urinalyses were not quantitative, but in each case mercury was definitely isolated as the metal from the specimens. The physiological significance is not established, but it is suspected that such exposures had best be avoided if possible. These exposures were complicated, since in all three cases there was also opportunity for absorption through the skin, and in addition likelihood of contaminated cigarettes, particularly in the first two cases.

About 3 months after the concentration of mercury vapor had been reduced (as previously noted) in the worst of the laboratories reported in this survey, the National Institute of Health conducted a comprehensive series of physiological and psycological tests on 38 men from this Bureau who had previously been exposed to the various concentrations noted in table 1. The result of this investigation is given in part 2 which follows.

## Part 2. Medical Examination of Thirty-Eight Workers

By Robert H. Flinn,<sup>1</sup> J. Walter Hough,<sup>1</sup> and Paul A. Neal<sup>1</sup>

### I. INTRODUCTION

In recent years interest in industrial mercurialism has increased. This interest has been stimulated by United States Public Health Service studies of chronic mercurialism among workers engaged in the preparation of fur [1] and its fabrication into fur felt hats [2] and by a study by Markwith and his associates [3] in Ohio dealing with the problem of mercurialism among men engaged in the manufacture of copper amalgam. In connection with these investigations, attention has been attached naturally to the possibility of mercurialism occurring among workers in scientific laboratories, where often large quantities of mercury are used in such analytical procedures as gas analysis.

Turner [4] in 1924 made an investigation of mercurialism at the National Bureau of Standards. Nordlander [5] in 1927 showed the fallacy of earlier methods of measuring atmospheric mercury concentrations and presented a new method. Christensen [6] in 1937 warned of the danger of mercurialism in unventilated or poorly ventilated rooms. Goodman [7], Eltenton [8], and Giese [9] have dis-

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cussed methods of control of the mercury hazard in laboratories. McCarroll [10] in 1939 published the results of a United States Bureau of Mines investigation of the hazard of mercury vapor in analytical laboratories of the petroleum industry and presented detailed recommendations for the control of this hazard.

In the Public Health Service study of the hatting industry [2], 59 cases of chronic mercurialism were found on medical examination of 534 hatters employed in 5 representative felt hat factories. These workers were engaged in the fabrication of felt hats from fur that had been previously treated with a mercury carrot. Four of the 21 mixers and blowers, 8 of the 34 coners, 6 of the 29 hardeners, and 33 of the 179 starters and sizers were so diagnosed. These men were working at processes that offered an average mercury exposure of 500. 270, 250, and 210 µg of mercury per cubic meter of air, respectively [1], as measured by the Nordlander instrument. The incidence of mercurialism was found to increase with increasing intensity and duration of mercury exposure. From these data it was concluded that 100  $\mu g$  of mercury per cubic meter of air probably represents the upper limit of safe exposure. In the report of the hatting study, these values were stated in terms of *milligrams* per 10 m<sup>3</sup> of air.

Early in 1940 the Division of Industrial Hygiene, National Institute of Health, of the United States Public Health Service, received a request from the Medical Director of the United States Employees Compensation Commission to investigate the possibly harmful effects of working conditions on health in certain laboratories at the National Bureau of Standards, where large quantities of mercury were used as a confining fluid in gas analysis. A request was made for recommendations regarding any necessary steps to protect the employees who might be exposed to hazardous mercury concentrations.

In compliance with this request, the National Bureau of Standards was visited and it was found that mercury was being used in large quantities in the gas analysis laboratories, in laboratories for the testing of dental amalgams, and in certain other laboratories as described by Shephard and Schuhmann in the preceding part of this paper dealing with the environmental exposure of workers in these laboratories.

By means of a newly designed mercury detector [11], they were able to identify lower atmospheric concentrations of mercury in the workrooms than was possible with the Nordlander instrument, the range being from less than 4 to 70  $\mu$ g of mercury per cubic meter of air. As stated in part 1 of this report, about 3 months prior to this visit an attempt had been made to control the atmospheric mercury exposure of these workers. This had resulted in a material reduction of such exposure.

### **II. EXAMINATION OF EMPLOYEES**

In order to ascertain the possible effects of exposure to mercury, 38 employees of the National Bureau of Standards were examined, who had had varying degrees of exposure to mercury in the workrooms previously described. These examinations were made between June 28 and July 12, 1940. The duration of employment in such laboratories

varied from 1 year to 33 years and averaged 9.1 years. These medical examinations included a complete medical and occupational history and a physical examination with special attention to signs of mercurialism, such as intention tremor, abnormal psychic changes, vegetative changes such as abnormal blushing, sweating, and dermographia, and increased tendon reflexes. Intention tremor was also sought for by objective methods including a Porteus maze test, a handwriting test, and a psychologic test for hand steadiness. In addition to this, tests were given to determine reaction time, reactioncoordination time, and speed of tapping, as described in a recent study of the Public Health Service of fatigue among truck drivers [12]. Clinical laboratory examinations included hemoglobin determination (Newcomer), erythrocyte and leucocyte counts, differential white-cell counts, and determinations of stippled cells and reticulocytes. Routine urinalyses were made on all subjects. A chemical analysis was made for mercury in certain 24-hour urine specimens, using the method described by Goldman [2]. In addition, spectrographic determinations for mercury were made by the method described by Armstrong [2] on all 24-hour samples as well as on single specimens. A Kahn test was made on the blood of all persons examined, and the examination included an X-ray film of the chest.

Two previous studies of the Public Health Service in the fur-cutting and hatting industries had revealed 102 cases of chronic mercurialism among a group of 1,063 workers exposed. The average exposure of these workers varied from 20 to more than 700 µg of mercury per cubic meter of air. The symptoms observed in these examinations included complaints of tremor, psychic disturbances and nervous disorders, headache, drowsiness or insomnia, and weakness. The outstanding physical findings in this group of 102 cases included fine intention tremor; psychic disturbances, particularly irritability, excitability, timidity, apprehension, and restlessness; vaso-motor dis-orders as indicated by readiness to blush, excessive perspiration, and dermographism; increased tendon reflexes; gingivitis; and slight abnormalities of speech. The hatters with mercurialism tended to be underweight, to have increased systolic blood pressure, and to show albumin and red cells in the urine. At low atmospheric mercury exposures, the urinary mercury values were low and the range narrow. In successively higher atmospheric exposure groups, both the average value and the range of values increased, varying from 0 to 2.7 mg of mercury per liter. Many hatters with mercurialism were found to have measurable amounts of mercury in the urine, but these samples contained on the average slightly less mercury (0.297 mg of mercury per liter) than similarly exposed but nonaffected workers (0.413 mg of mercury per liter). No association was found between mercurialism and the hemoglobin content of the blood or reticulocyte and differential white-cell count.

It is known, of course, that any of the above symptoms and signs may occur in apparently healthy persons among the general population. Such was found to be the case in this study of 38 laboratory workers and in other studies of the Public Health Service among industrial populations not exposed to mercury. No individual was

found, however, in this study, with a sufficient combination of the above symptoms and signs of mercurialism to warrant a diagnosis of this disease, and those isolated symptoms observed were not of the degree of severity seen in hatters with mercurialism.

As a group, these 38 men were in good general health. The occurrence of tremor, psychic disturbances, abnormal reflexes, vegetative changes, and other abnormal physical findings was infrequent and was thought to be in about the same proportion as that for men of similar ages in industries with no mercury exposure. In no instance was more than a slight degree of tremor observed. This observation was substantiated by the results of the maze test, the hand steadiness test, and the handwriting test. As a group, they made good scores on the psychologic tests which measured manual steadiness, simple reaction time, reaction-coordination time, and speed of tapping. Spectrographic analysis of single and 24-hour specimens of urine revealed no measurable quantities of mercury (spectrographic threshold about 0.05 mg/liter). Spectrographic analysis of blood samples revealed no measurable mercury. Chemical analysis of fourteen 24hour samples of urine revealed no mercury. X-ray examinations of the chest revealed two cases of healed, minimal tuberculosis. Clinical examination of the blood and urine revealed no findings of interest.

One subject differed notably from the others in that on the first of three examinations, he showed evidence of intention tremor and psychic disturbances and had a history of excreting measurable amounts of mercury in the urine several months previously. He was suffering from a serious and painful vascular disease, however, that may have contributed to these symptoms as they were much improved on subsequent examinations. On the other hand, the possibility of a previous attack of mercurialism with a few intermittent residual symptoms could not be excluded. In this one case, previous exposure to mercury vapor had terminated 7 months before the physical examination.

### III. CONCLUSIONS

In conclusion, there was no medical evidence of mercurialism manifested by these 38 laboratory workers exposed to concentrations of from less than 4 to 70  $\mu$ g of mercury per cubic meter of air. These findings are in agreement with those made in other studies on mercurialism by the United States Public Health Service. Those studies showed that only with exposure to concentrations of more than 100  $\mu$ g of mercury per cubic meter, cases of mercurialism were found.

If working conditions in other laboratories are such that there is considerable doubt whether control measures for mercury exposure are adequate, it would be desirable to have an experienced industrial physician and industrial hygiene engineer evaluate the hazard and recommend suitable measures for its control. Shepherd, Schuhmann,] Flinn, Hough, Neal

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