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This paper describes the construction and evaluation of a system capable of producing well-defined test mixtures of mercury in air, or other diluent gas, at mercury concentrations between zero and 16 mg/M³. The various parameters that affect the generation system and their interactions are discussed and data is given for the calibration of several different mercury monitors.

A calibration system for producing known concentrations of mercury vapor in air

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introduction

In recent years the use of portable, analytical instrumentation for measuring the concentration of various atmospheric contaminants has become increasingly important, especially for monitoring the presence and levels of specific contaminants in industrial plants. The Occupational Safety and Health Act of 1970 authorizes the Secretary of Health, Education and Welfare to prescribe regulations requiring employers to measure, record, and make reports concerning the exposure of employees to substances or physical agents which may endanger the safety or health of employees. When such measurements have legal implications, it is necessary to evaluate the performance of the analytical instrumentation periodically in order to insure proper instrument calibration.

Because the vapor pressure of mercury is well known and relatively low, saturation techniques may be readily adapted to the generation of accurately defined test atmospheres. Shepherd and Schuhmann first described such a system for use in the calibration of a flameless atomic absorption instrument for the measurement of mercury vapor.(1) This system was later improved upon by other workers.(1-3) The system described in this paper is a modification of the earlier work.

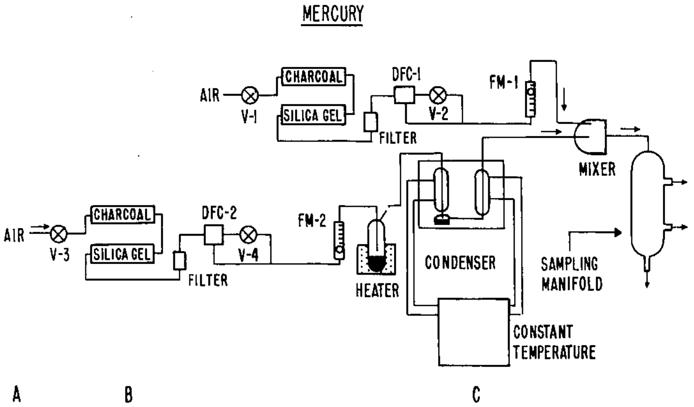

Figure 1 — Schematic diagram of generating system for mercury.

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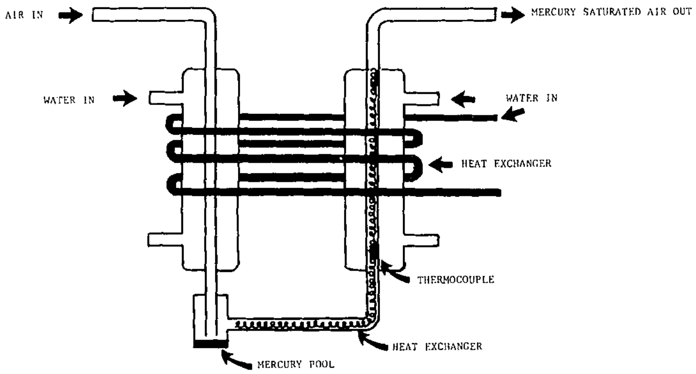

Figure 2 — Mercury condenser.

The evaporation method of generating test atmospheres of mercury vapor involves saturating air with mercury at an elevated temperature and then condensing the mercury vapor at a lower and accurately controlled temperature. The resulting mixture is further diluted with air to produce the desired concentration. By accurately controlling the two gas flows and the temperature at the condenser, mercury-in-air mixtures within ±2% of the calculated theoretical value can be obtained.

experimental

mercury generation system

A schematic of the mercury generation system is shown in Figure 1. Two streams of air pass through silica gel/charcoal driers and 60 micron filters to remove impurities. One stream goes through a differential flow controller (DFC-1), a regulating valve (V-2), and a high flow rotameter (FM-1), to the mixing chamber. This stream is subsequently used as the dilution air. The other stream flows through a differential flow controller (DFC-2), a regulating valve (V-4), through a low flow rotameter (FM-2) and into the saturation unit. The saturation unit is composed of two parts; a vaporizer and a condenser. The vaporizer is an electrically heated and thermostated container of mercury. the temperature of the vaporizer is generally kept 25° C higher than that of the condenser. The air stream passing through the vaporizer becomes saturated with mercury vapor. It then passes into a condenser where it is cooled rapidly and any excess mercury vapor condenses. The temperature of the condenser determines the concentration of the mercury in the first air stream. Figure 2 shows the condenser design. The condenser is imbedded in Styrofoam and placed in an aluminum box. The temperature of the condenser is controlled to at least ±0.1 °C by connecting it to a water source from a constant temperature bath containing methanol-water anti-freeze effective to -5° C. The water lines are well-insulated to minimize temperature changes that may occur between the bath and the condenser. After leaving the condenser, the air stream then passes into the chamber where it is diluted with the second air stream, and then passes into a manifold where samples can be withdrawn. Figure 3 is a picture of the mercury calibration unit. It is portable, and can be constructed from readily available components. NOTE: Since small amounts of mercury are

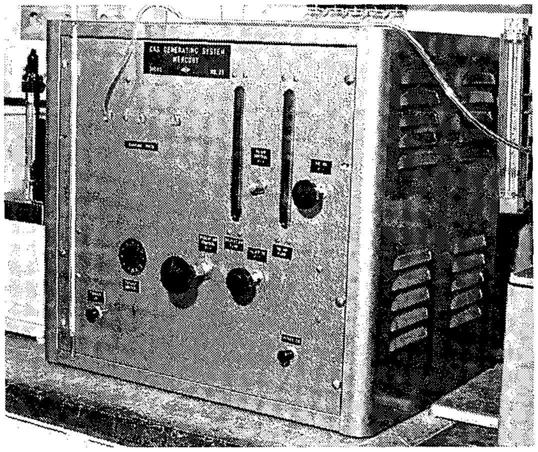

Figure 3 — Mercury calibration system.

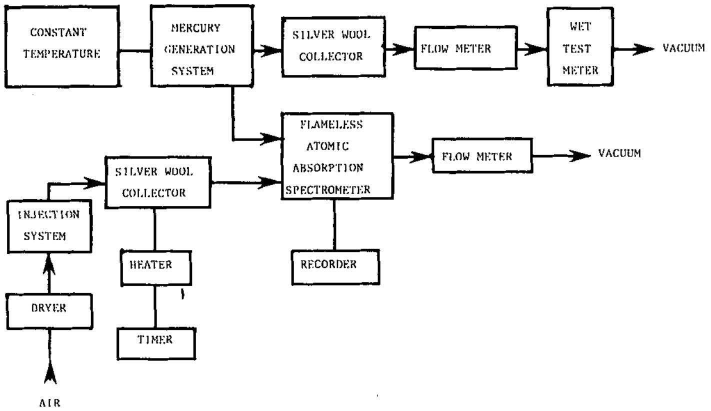

Figure 4 — Mercury generation and analysis system.

released into the atmosphere during the operation of this system, it should be properly ventilated during use.

analysis

The method used for analysis of the mercury concentrations was similar to that described previously.(4) Analyses were made by withdrawing samples from the manifold at 200 cc/min and collecting the mercury on silver wool. The mercury was then desorbed by controlled heating and was measured using a flameless atomic absorption spectrometer. The spectrometer was calibrated by injecting a known volume of saturated mercury vapor onto the silver wool, using a "head-space" technique from standards kept at a constant, accurately measured temperature. A block diagram of the mercury generation and analysis system is shown in Figure 4; the headspace calibration system as shown in Figure 5.

performance evaluation

calibration

As stated previously, the mercury generation system was calibrated by injection of known volumes of air saturated with mercury. A comparison of the atomic absorption signals given by these standards and samples taken from the generation system is shown in Figure 6.

sampling

When samples of mercury are adsorbed onto the silver wool collector which is then heated to

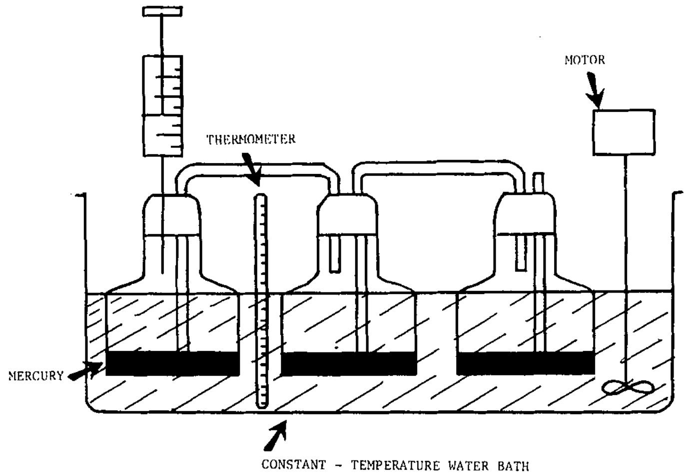

Figure 5 — Headspace calibration system.

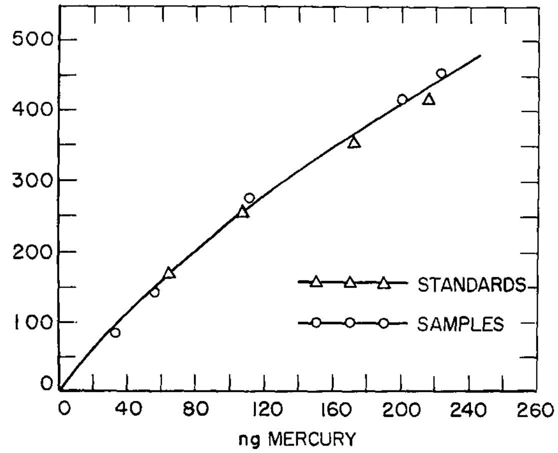

Figure 6 — Comparison of standards with generator output.

desorb the mercury for analysis, recorder traces similar to those shown in Curve A of Figure 7 are obtained. The peak shape, though not symmetrical, is very reproducible so that the peak height can be measured and compared with standards to determine the amount of mercury in the sample.

An alternative to collecting the mercury samples on silver wool and then heating to desorb them is to connect the atomic absorption instrument directly to a sampling port of the generation system and to monitor the mercury output directly. Curve B of Figure 7 shows the type of graph obtained. The sensitivity is not as great as in the first method, but this is not a serious limitation, since a mercury concentration of 0.005 mg/M^3 will still give a recorder deflection.

response time

As indicated in Curve B of Figure 7, the response time to produce a steady-state concentration of mercury vapor upon changing from one concentration to another is about 5 minutes at concentrations not different by more than 100 percent from each other, and about 10 minutes when larger concentration changes are made. The response time is about the same whether the concentration is being reduced or increased from some fixed value. A 10 minute equilibration period is recommended when changing concentrations.

temperature effects

Initially, upon comparing the calculated and observed mercury concentrations from the generation system, a difference of about 7 percent was noticed, with the output higher than that calculated. It was determined that the cause of this discrepancy was a temperature difference between the water bath and the condenser. To correct this problem, the condenser and the water lines were insulated and a copper-constantan thermocouple was installed at the condenser in order to accurately measure its temperature. The temperature difference using the modified arrangement is about 0.3°C at 0.0° C, which will cause results that are 3 percent higher without a temperature correction. If the temperature is measured and a correction factor applied, the calculated and observed values are the same. When the condenser is operated at room temperature, its temperature may be considered that of the bath assuming sufficient equilibration time.

The optimum condenser temperature for the concentration range of industrial hygiene interest was determined to be 0° C for concentrations between 0.005 and 0.100 mg/M^3, and 26° C for concentrations between 0.100 and 0.500 mg/M^3.

Experiments were also conducted to determine the effect of the saturator temperature upon the generator output. The optimum temperature difference between saturator and condenser is 25° C. At higher temperature differences, complete condensation

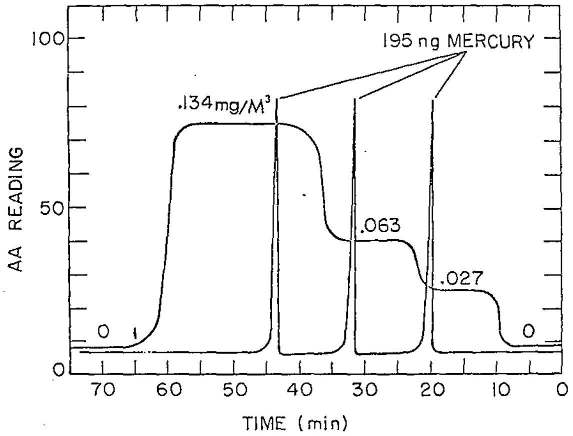

Figure 7 — Mercury sampling and analysis showing both continuous sampling and discrete samples.

TABLE I
Mercury Vapor Pressures and Corresponding Saturation Cencentrations in Air

T (°C)	Hg Vapor Pressure (mm)	Concentration* of Saturated Stream (mg/M³)
28	.002359	25.2
26	.002000	21.5
24	.001691	18.3
22	.001426	15.6
20	.001201	13.2
18	.001009	11.2
10	.000490	5.58
4	.000276	3.21
0	.000185	2.18

*This concentration must be corrected because of the change in volume which occurs when the saturated stream equilibrates to room temperature. (see example)

in the condenser does not occur and the output is higher than calculated, whereas, at lower temperature differences, complete saturation is not achieved and the output is lower than calculated. The temperature difference should be controlled at 25 ± 5°C.

calculations

The flow rates necessary to produce the desired mercury concentration, can be calculated using the following equation:

$$C_x = \frac{F_x \cdot C_b}{F_x + F_{air}} \tag{1}$$

where:

C_x = mercury concentration produced in the manifold (mg/M³),

F_x = measured flow rate of mercury stream (cc/min),

F_{air} = measured flow rate of diluent air stream (cc/min),

C_b = mercury concentration of the saturated mercury stream exiting the condenser (mg/M³).

Values for the vapor pressure of mercury at various temperatures can be found in most chemical data handbooks,[5] and this can be readily converted to the saturation concentration in mg/M³. The vapor pressure of mercury at

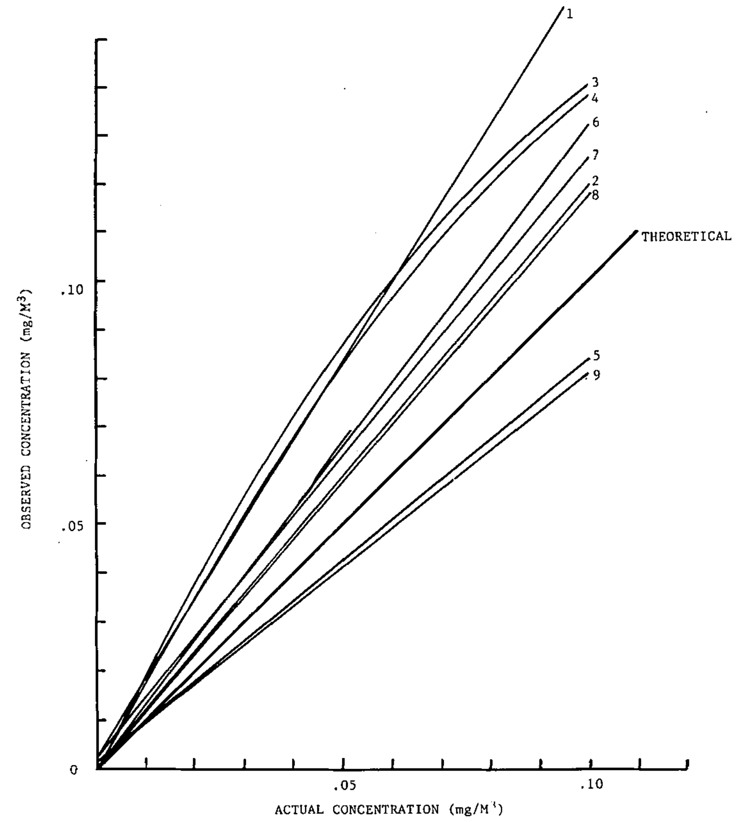

Figure 8 — Mercury monitor calibration curves.

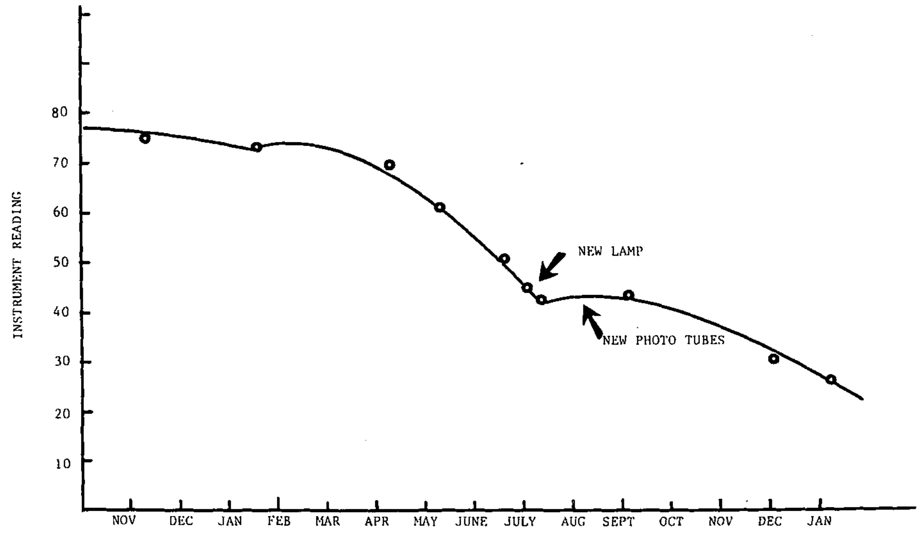

Figure 9 — Instrument response versus time.

various temperatures and the concentration resulting from this saturation of air with mercury vapor are shown in Table I. Because the concentration of gases or vapors expressed in terms of mass per unit volume varies with both temperature and pressure, C_b must be corrected if the condenser temperature is different from room temperature. The correction is simply the concentration at the temperature of generation of the vapor times the percentage change in the volume of air due to the difference in temperature, assuming ideality. For example, if the temperature of the condenser is 0° C and the temperature of the sampling manifold is 25° C, the correction will be:

$$C_{b\,\mathrm{corr}} = C_b \left(\frac{T_c}{T_m}\right) \qquad (2)$$

$$= 2.18\ \frac{\mathrm{mg}}{\mathrm{M}^3}\left(\frac{273.15}{297.15}\right) = 2.00\,\mathrm{mg/M}^3$$

where:

T_c = condenser temperature (°K),

T_m = sampling manifold temperature (°K).

This correction is 0.00366 percent per degree Centrigrade and may be expressed:

$$C_{B\,\mathrm{corr.}} = C_b\,[1\text{-}\Delta t\,(0.00366)] \qquad (3)$$

where:

Δt = the temperature difference between the condenser and the sampling manifold (°C).

Equation (1) then becomes:

$$C_x = \frac{F_x}{F_x + F_{air}}\ .\ C_b[1\text{-}\Delta t\,(0.00366)] \qquad (4)$$

results

In order to verify the usefulness of periodic recalibration of mercury monitoring instrumentation, several instruments were obtained and calibrated using the system described in this paper. These monitors were from several different manufacturers and had been in service varying lengths of time. Figure 8 shows the calibration curves obtained. The errors were considerable in some cases and were both positive and negative. Figure 9 shows the response of one of the instruments versus time when measuring mercury standards of the same concentration. There is general degradation of the instrument response which cannot be predicted beforehand. Assuming that the instrument is properly calibrated at the time indicated at the beginning of the graph (Figure 9), a year later the instrument response is one-third of what it should be. The change in sensitivity shown in this graph is due to the unique ageing characteristics of this particular instrument. Other instruments may or may not show similar behavior. This means that each instrument must be periodically recalibrated.

conclusions

The mercury vapor generation system described in this paper is capable of producing calibration mixtures of mercury vapor in air within ±2 percent of the theoretical value. This system provides a means of calibrating instruments for mercury analysis and may be useful in the evaluation of new and existing analytical methods. This study also shows the importance of periodic recalibration of mercury monitoring instrumentation. The system is relatively portable, and can be constructed from readily available components.

acknowledgements

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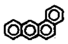
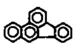
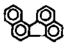
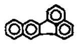
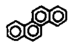
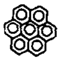
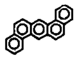
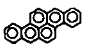
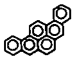
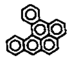
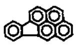
omission . . .

In the article *Coal gasification and occupational health* by Ronald J. Young *et al*, published in the December, 1978 issue of AIHAJ, Table I on page 987 was incomplete. The correct version of the table appears below.

TABLE I

Potential PAH Compounds Formed by Coal Gasification

Compound	Structure	Formula	Mol. Wt.
anthanthrene		$C_{22}H_{12}$	276.22
benz(a)anthracene		$C_{18}H_{12}$	228.28
benzo(b)fluoranthene		$C_{20}H_{12}$	252.32
benzo(j)fluoranthene		$C_{20}H_{12}$	252.32
benzo(k)fluoranthene		$C_{20}H_{12}$	252.32
benzo(g,h,i)fluoranthene		$C_{18}H_{10}$	226.26
benzo(g,h,i)perylene		$C_{22}H_{12}$	276.22
benzo(a)pyrene		$C_{20}H_{12}$	252.32
benzo(e)pyrene		$C_{20}H_{12}$	252.32
chrysene		$C_{18}H_{12}$	228.28
coronene		$C_{24}H_{12}$	300.34
dibenz(a,h)anthracene		$C_{22}H_{14}$	278.33
dibenzo(a,e)pyrene		$C_{24}H_{14}$	302.28
dibenzo(a,h)pyrene		$C_{24}H_{14}$	302.28
dibenzo(a,i)pyrene		$C_{24}H_{14}$	302.28
dibenzo(a,l)pyrene		$C_{24}H_{14}$	302.28
fluoranthene		$C_{16}H_{10}$	202.24
indeno(1,2,3-cd)pyrene		$C_{22}H_{12}$	276.22
perylene		$C_{20}H_{12}$	252.32
phenanthrene		$C_{14}H_{10}$	178.22
pyrene		$C_{16}H_{10}$	202.24