MERCURY VAPOR IN WORKPLACE ATMOSPHERES

Method Number:	ID-140
Matrix:	Air
OSHA PEL:	0.1 mg/m^3 as total mercury (TWA)
Collection Device:	A passive or an active sampling device are available. Both devices use Hydrar or hopcalite as the solid sorbent.
Recommended Sampling Rate Passive Dosimeter:	0.020 L/min (@ 20 °C and 101 kPa)
Active Sampler:	0.20 L/min
Recommended Air Volume Range Passive Dosimeter:	9.6 L
Active Sampler:	3 to 100 L
Analytical Procedure:	The sorbent is digested using nitric acid and hydrochloric acid. The mercury in the sample is reduced to elemental mercury using stannous chloride and analyzed using a cold vapor-atomic absorption spectrophotometer.
Detection Limit Qualitative Passive Dosimeter:	0.002 mg/m^3 for a 240-min (4.8 L) sample
Active Sampler:	0.00067 mg/m^3 for a 75-min (15 L) sample
Quantitative Passive Dosimeter:	0.004 mg/m^3 for a 240-min (4.8 L) sample
Active Sampler:	0.0013 mg/m^3 for a 75-min (15 L) sample
Precision and Accuracy Passive Dosimeter Validation Range:	0.061 to 0.20 mg/m^3
CV_T(pooled)	0.039
Bias	+0.008
Overall Error	±8.6%
Method Classification:	Validated Method
Date (Date Revised):	1987 (June, 1991)

Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Similar products from other sources can be substituted.

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1. Introduction

This method describes the collection of airborne elemental mercury in a passive dosimeter or active sampling device and subsequent analysis using a cold vapor-atomic absorption spectrophotometer (CV-AAS).

1.1 Principle

The mercury dosimeter samples the workplace atmosphere by controlled diffusion into the badge while the active sampler uses a calibrated sampling pump. The mercury vapor entering either passive or active device is collected on a solid sorbent (Hydrar or hopcalite) which has an irreversible affinity for mercury (8.1, 8.2). After sample collection the sorbent is initially dissolved with concentrated nitric acid and then hydrochloric acid. Stannous chloride is added to an aliquot of the sample to generate mercury vapor. This vapor is then driven into an absorption cell of a flameless atomic absorption spectrophotometer for analysis.

1.2 History

Previously, mercury samples were collected on iodine-impregnated charcoal contained in glass tubes. The treated charcoal was analyzed for mercury by placing it in a tantalum sampling boat and then heating to drive the mercury vapor into the beam of an atomic absorption spectrophotometer (8.3). The amount of mercury was determined by absorbance at 253.7 nm. The detection limit was approximately 0.1 µg. Drawbacks with this method were:

a) The mercury vapor and hence the entire sample was immediately lost into the surrounding atmosphere
b) The method was imprecise at lower sample loadings (8.4)
c) The analytical technique was somewhat tedious Hopcalite solid sorbent (8.5) was substituted in place of the iodine-impregnated charcoal for mercury vapor sampling. Previously, hopcalite had been used in respirator cartridges for carbon monoxide and consisted of oxides of copper, manganese, cobalt, and silver (8.6). Analysis of recent batches of hopcalite used for mercury collection indicate the composition was mainly oxides of manganese and copper. Hydrar has been used as a substitute for collecting mercury vapor and is very similar in composition to hopcalite. A ceramic material, insoluble in nitric and hydrochloric acid, is present in the Hydrar but not in the hopcalite.

1.3 Advantages and Disadvantages

1.3.1 These sampling and analytical techniques have adequate sensitivity for measuring workplace atmospheric concentrations of elemental mercury.

1.3.2 The passive dosimeter used for collection of mercury vapor is small, lightweight, and requires no sampling pumps. Also, the dosimeter housing is reusable; therefore, cost per measurement is kept to a minimum.

1.3.3 The collected mercury sample is stable for at least 30 days.

1.3.4 Sample preparation for analysis involves simple procedures.

1.3.5 Either sampling device can be analyzed in any laboratory equipped with a CV-AAS.

1.3.6 A disadvantage with the passive dosimeter is particulate compounds cannot be collected with the device. A separate sampling pump and collection media should be used for particulate collection.

1.3.7 Another disadvantage with the dosimeter is sample rate dependence on face velocity. The dosimeter should not be used in areas where the air velocity is greater than 229 m/min (750 ft/min) since erratic increases in sampling rate may occur.

1.3.8 A disadvantage with the active device is the dependence on a calibrated pump to take the sample.

1.4   Toxic Effects (This section is for information only and should not be taken as a basis for OSHA policy.)

Exposure to elemental mercury vapor can occur via the respiratory tract and skin. Possible symptoms from an acute exposure include severe nausea, vomiting, abdominal pain, bloody diarrhea, kidney damage, and death. These symptoms usually present themselves within 10 days of exposure. Potential symptoms from a chronic exposure include inflammation of the mouth and gums, excessive salivation, loosening of the teeth, kidney damage, muscle tremors, jerky gait, spasms of the extremities, personality changes, depression, irritability, and nervousness (8.7, 8.8).

1.5   Workplace Exposure

Occupations with potential exposure to mercury and its compounds are listed (8.8):

amalgam makers	fur processors
bactericide makers	gold extractors
barometer makers	histology technicians
battery makers, mercury	ink makers
boiler makers	insectiside makers
bronzers	investment casting workers
calibration instrument makers	jewelers
cap loaders, percussion	laboratory workers, chemical
carbon brush makers	lampmakers, fluorescent
caustic soda makers	manometer makers
ceramic workers	mercury workers
chlorine makers	miners, mercury
dental amalgam makers	neon light makers
dentists	paint makers
direct current meter workers	paper makers
disinfectant makers	percussion cap makers
disinfectors	pesticide workers
drug makers	photographers
dye makers	pressure gage makers
electric apparatus makers	refiners, mercury
electroplaters	seed handlers
embalmers	silver extractors
explosive makers	switch makers, mercury
farmers	tannery workers
fingerprint detectors	taxidermists
fireworks makers	textile printers
fungicide makers	thermometer makers
fur preservers	wood preservative workers

1.6   Properties (8.7, 8.8)

Elemental mercury (CAS No. 7439-97-6) is a silver-white, heavy, mobile, liquid metal at room temperature. Some physical properties and data for mercury are:

Atomic Number	80
Atomic Symbol	Hg
Atomic Weight	200.61
Freezing Point	-38.87 °C
Boiling Point	356.90 °C
Density	13.546 g/mL (20 °C)
Synonyms	Quicksilver, Hydrargyrum

The high vapor pressure of mercury at normal temperatures combined with the potential toxicity makes good control measures necessary to avoid exposure. Also, the concentration of mercury vapor in the air rapidly increases as the temperature increases. To illustrate, listed below are vapor pressures of mercury, and mercury concentrations of air after saturation with mercury vapor at different temperatures:

Vapor Pressure-Saturation Concentration of Mercury at Various Temperatures			
Temperature		Vapor Pressure	Mercury Concentration
°C	°F	(torr)	(μg/m³)
0	32.0	0.000185	2,180
10	50.0	0.000490	5,880
20	68.0	0.001201	13,200
24	75.2	0.001691	18,300
28	82.4	0.002359	25,200
30	86.0	0.002777	29,500
32	89.6	0.003261	34,400
36	96.8	0.004471	46,600
40	104.0	0.006079	62,600

2. Range

2.1   The qualitative and quantitative detection limits for the analytical procedure are 0.01 μg and 0.02 μg mercury, respectively (8.9).

2.2   Working Range

The range of the analytical procedure has been determined to be 0.1 to 2 μg mercury. Using the analytical conditions specified, a nonlinear response was noted above 2 μg.

3. Method Performance

3.1   The SKC Hydrar gas monitoring dosimeter badge for mercury (SKC Inc., Eighty Four, PA) was evaluated at 80% RH and 25 °C over the range of 0.061 to 0.203 mg/m³ using a dynamic generation system (8.2).   The pooled coefficient of variation (CV_T) for badge samples taken in this concentration range was 0.039. The average recovery was 100.8% and the overall error was ±8.6%.

In a separate study, active samplers were spiked with mercury in the range of 1 to 2.5 μg. The mean recovery of these 125 quality control samples was 96.9% with a CV_1 of 0.106 (8.10).

3.2   In storage stability studies, the mean recoveries of Hydrar[R] samples analyzed 5, 14, and 30 days after collection were within ±10% of the known generated concentration (8.2).

3.3   The Hydrar active sampling device was compared using linear regression statistics to the dosimeter in a field study (8.11).   The dosimeter results agreed well with the active sampler and are summarized below (Note: A correlation coefficient and slope = 1 would indicate ideal agreement):

Number of paired samples   (N)   =   26
Concentration Range   =   0.01 to 0.7 mg/m³
Correlation coefficient   (r)   =   0.985
Intercept   (a)   =   0.017
Slope   (b)   =   0.960
Standard deviation of the slope   (Sb) =   0.038

4. Interferences

4.1   Sampling:

Particulate mercury compounds are a positive interference; however, the badge does not sample particulates and the glass wool of the active sampler prevents particulate from entering the sorbent. Chlorine in the sampled air does not interfere when using Hydrar or hopcalite sorbent. The chlorine does react with available mercury vapor in the air to presumably form mercuric chloride (8.12). Workplaces containing both chlorine and mercury should be sampled for both mercury vapor and particulate.

4.2   Analysis:

Organic-free deionized water should be used during sample and standard preparation. Any compound with the same absorbance wavelength as mercury (253.7 nm) can be a positive interference.   Some volatile organic compounds (i.e., benzene, toluene, acetone, carbon

tetrachloride) absorb at this wavelength and are considered analytical interferences. They occur as contaminants in the reagents used during sample preparation. These compounds are not expected to be retained on Hydrar or hopcalite during sample collection. Analytical interferences are rendered insignificant by using organic-free deionized water and at least reagent grade chemicals or by blank subtraction.

Increasing the concentration of nitric acid in the samples or standards appears to produce an elevated background signal. The nitric acid concentration in the samples and standards should not be greater than 10%.

5. Sampling

[Note: A prefilter assembly, consisting of a mixed-cellulose ester filter in a polystyrene cassette, can be used with the active samplers. Although a significant loss of mercury vapor, presumably due to the prefilter assembly, has been noted when using this type of sampling train (8.12), these results were not duplicated in a series of recent experiments (8.13).]

5.1 Equipment

Either tubes or dosimeters can be used to collect mercury vapor. The dosimeter should not be used when:

1) The air velocity of the sampling site is greater than 229 m/min (750 ft/min)

2) The operation being sampled is characterized by extremely poor hygienic practices and splashing of mercury on the badge may occur

3) Determination of total mercury is necessary and mercury particulate appears to be present in the workplace atmosphere

The tube can be used to determine **total mercury (vapor + particulate).** The badge can only collect mercury vapor. For short-term exposures to particulate mercury, or for wipe and bulk sampling and analysis consult reference 8.14 for further information.

5.1.1 PASSIVE DOSIMETER:

Gas monitoring dosimeter badge and pouch containing a Hydrar[R] capsule [badge - cat. no. 520-03, pouch - cat. no. 520-02 (SKC Inc., Eighty Four, PA)]. The capsule contains 800 mg of sorbent.

5.1.2 ACTIVE SAMPLER:

Hydrar[R] or hopcalite sampling tubes (cat. no. 226-17-1 or 226-17-IA, SKC, Inc., Eighty Four, PA). These are 6-mm o.d. x 70-mm long glass tubes which contain 200 mg of sorbent.

Note: Before use, the active sampling tubes must be examined for movement of the solid sorbent into the glass wool. See Section 5.3.1 for further details.

5.1.3 Sampling pumps capable of sampling at 0.2 liters per minute (L/min).

5.1.4 Assorted flexible tubing.

5.1.5 Stopwatch and bubble tube or meter for pump calibration.

5.2 Sampling Procedure - PASSIVE DOSIMETER

5.2.1 Assemble the components of the mercury monitoring badge according to manufacturer instructions (8.1).

Note: A foam insert must be placed in the Model 520-03 dosimeter to hold the capsule in place (8.13).

5.2.2 Record the sampling start time, sampling site temperature, and atmospheric pressure. Remove the protective cap and then place the dosimeter in the breathing zone of the employee. The suggested sampling time for the dosimeter is 8 h.

5.2.3   Immediately after sampling, carefully remove the sorbent capsule from the dosimeter and place it in the sorbent pouch. Fold the pouch top twice and press it flat to seal the capsule inside the pouch. Record the sampling stop time, final temperature, and atmospheric pressure. Calculate and record the total sampling time, average temperature, and pressure.

5.3   Sampling Procedure - <u>ACTIVE SAMPLER</u>

5.3.1   Calibrate each personal sampling pump with an active sampler in-line using a flow rate of about 0.2 L/min.

Note: A prefilter assembly consisting of a mixed-cellulose ester filter, polystyrene cassette, and a **minimum** amount of Tygon tubing can be used if:

a)   particulate mercury compounds may present a problem during sampling
or

b)   the hopcalite or Hydrar contained in the active sampling tube has migrated to the glass wool plug.

Before use, the active sampling tubes must be examined for movement of the solid sorbent into the glass wool. Certain lots of Hydrar or hopcalite have been noted as being very friable or having a sorbent particle-size range small enough as to allow migration. This movement can easily be noted - the glass wool in the sampling tube appears somewhat discolored (darkened) from the small sorbent particles. If sorbent migration has occurred, a prefilter assembly is recommended. The recommended sampling flow rate is also 0.2 L/min with the prefilter-sampling tube-pump assembly.

5.3.2   Connect a sampling tube (or sampling assembly) to a calibrated pump using flexible tubing. If a prefilter is used, connect it to the sampling tube with a minimum amount of Tygon tubing. Connect the other end of the sampling tube to the pump. Place the sampling tube (or assembly) in the breathing zone and the pump in an appropriate position on the employee.

5.3.3   Use an air volume in the range of 3 to 100 L to collect the mercury in the workplace air. Record the total volume.

5.3.4   Replace the plastic end caps on the active sampler after sampling is completed.

5.4   Sample Shipment

5.4.1   Securely wrap each sorbent pouch or active sampling tube end-to-end with an OSHA Form 21 sample seal. Also seal and prepare cassettes if a prefilter assembly was used.

5.4.2   Submit at least one blank sample with each set of samples. The blank sample should be handled in the same manner as the other samples except that an air sample is not taken.

5.4.3   Request the laboratory to analyze the samples for mercury. Submit any pertinent sampling information to the lab. <u>Record if a prefilter assembly was used</u>.

5.4.4   Ship the sealed pouches and used dosimeter housings, or active sampling tubes to the laboratory in appropriate containers as soon as possible. The filter/cassette assembly can also be submitted for mercury particulate analysis; however, sampling periods may be longer than reflected in exposure regulations.

6. Analysis

6.1   Safety Precautions

6.1.1   Wear safety glasses, labcoat, and gloves at all times.

6.1.2   Handle acid solutions with care. Avoid direct contact of acids with work area surfaces, eyes, skin, and clothes. Flush acid solutions which contact the skin or eyes with copious amounts of cold water.

6.1.3 Prepare solutions containing hydrochloric acid in an exhaust hood and store in narrow-mouthed bottles.

6.1.4 Keep B.O.D. bottles containing stannous chloride/hydrochloric acid solutions capped when not in use to prevent inhalation of noxious vapors.

6.1.5 Exercise care when using laboratory glassware. Do not use chipped pipets, volumetric flasks, beakers or any glassware with sharp edges exposed.

6.1.6 Never pipet by mouth.

6.1.7 When scoring the glass of active samplers to remove the sorbent before analysis, score with care. Apply only enough pressure to scratch a clean mark on the glass. Use a paper towel or cloth to support the opposite side while scoring. Moisten the mark with DI H_2O and wrap the tube in cloth before breaking. If the tube does not break easily, re-score. Dispose of glass in a waste receptacle specifically designed and designated for broken-glass.

6.1.8 Always purge the mercury from the CV-AAS into an exhaust vent.

6.1.9 Occasionally monitor the CV-AAS for mercury vapor leaks using an appropriate direct reading instrument.

6.2 Equipment - Cold Vapor Analysis

(Note: Specific equipment is listed for illustration only)

6.2.1 Atomic absorption spectrophotometer (model 503, Perkin-Elmer, Norwalk, CT).

6.2.2 Mercury hollow cathode lamp or electrodeless discharge lamp and power supply.

6.2.3 Biological Oxygen Demand (B.O.D.) bottles, borosilicate glass, 300 mL.

6.2.4 Peristaltic pump, 1.6 to 200 mL range, and controller, 1-100 rpm range (Masterflex model 7553-30 with model 7015 head, Cole-Parmer, Chicago, IL).

6.2.5 Quartz absorption cell, 22-mm (7/8 in) o.d. × 152-mm (6 in) long (part no. 303-3101, Perkin-Elmer).

6.2.6 Heating tape.

6.2.7 Variable transformer 50-60 Hz, 10 A, 120 V input, 0-140 V output, 1.4 kW (Superior Electric, Bristol, CT).

6.2.8 Tygon peristaltic pump tubing (part no. N06409-15, Cole-Parmer) and glass tubing.

6.2.9 Aerator (part no. 0303-3102, Perkin-Elmer).

6.2.10 Chart recorder.

6.2.11 Desiccant (Drierite, W.A. Hammond Drierite Co., Xenia, OH).

6.2.12 Volumetric flasks, volumetric pipets, beakers, and other laboratory glassware.

6.2.13 Automatic pipets, adjustable, 0.1 to 5.0 mL range (models P-1000 and P-5000, Rainin Instruments Co., Woburn, MA).

6.2.14 Glass tube scorer, or needle, 21 to 25 gauge - for removing metal screens in dosimeters or glass wool from tubes. A piece of bent wire can also be used.

6.2.15 Exhaust vent.

6.3 Reagents - All reagents should be at least reagent grade.

Stannous chloride, ($SnCl_2$)

6.3.1 Deionized water (DI H_2O), organic-free.

6.3.2 Hydrochloric acid (HCl), concentrated (36.5 to 38%), with a mercury concentration less than 0.005 ppm.

6.3.3 Mercury standard stock solution, 1,000 µg/mL: Use a commercially available certified standard or, alternatively, dissolve 1.0798 g of dry mercuric oxide (HgO) in 50 mL of 1:1 hydrochloric acid and then dilute to 1 L with DI H_2O. Store this reagent in a dark environment, preferably in an amber colored container.

6.3.4 Nitric acid (HNO_3), concentrated (69 to 71%), with a mercury concentration less than 0.005 ppm.

6.3.5 Nitric acid, 1:1: Carefully add equal portions of concentrated HNO_3 and DI H_2O.

6.3.6 Nitric acid, 10%: Carefully add 100 mL concentrated HNO_3 to 900 mL DI H_2O.

6.3.7 Stannous chloride ($SnCl_2$) solution, 10%: Dissolve 20 g $SnCl_2$ in 100 mL concentrated HCl. Slowly and carefully pour this solution into 100 mL DI H_2O and then mix well. Transfer and store the final solution in a capped B.O.D. bottle to prevent oxidation. Prepare this solution before each new analysis.

6.4 Glassware Preparation

6.4.1 Clean the B.O.D. bottles and stoppers with 1:1 HNO_3 and thoroughly rinse with DI H_2O prior to use.

6.4.2 Rinse all other glassware with 10% nitric acid and then with DI H_2O prior to use. Air dry all 50-mL volumetric flasks to be used in sample preparation.

6.5 Standard Preparation

6.5.1 Prepare a 1 µg/mL mercury standard by making appropriate ten-fold serial dilutions of the 1,000 µg/mL mercury standard stock solution with 10% HNO_3.

6.5.2 Prepare working mercury standards (ranging from 0.1 to 2.0 µg) and reagent blanks immediately prior to use. A few standards at each concentration should be made. Add an appropriate aliquot of the 1 µg/mL standard to a clean B.O.D. bottle containing enough 10% HNO_3 to bring the total volume to 100 mL. A suggested dilution scheme is given:

Mercury Standard (µg)	Aliquot (mL)*	Final Volume (mL)
Reagent Blank	0	100
0	0.1	100
0.2	0.2	100
0.5	0.5	100
1.0	1.0	100
1.5	1.5	100
2.0	2.0	100

* Aliquot taken from 1 µg/mL standard prepared in Section 6.5.1

6.6 Sample Preparation [Note: A hooked needle or piece of fine wire is useful to remove the dosimeter screen or glass wool (active sampler) and the sorbent particles.]

6.6.1 DOSIMETER

Open each sample pouch and remove the sorbent capsule. Carefully remove the screen from the top of the capsule without losing any sorbent. Carefully pour the sorbent into a clean, dry 50-mL flask without spilling any. Discard the screen and empty capsule.

6.6.2   ACTIVE SAMPLER

Score the tube with a glass tube cutter (also see Section 6.1.7) and then break open the front section of the tube above the glass wool. An alternative approach to scoring and breaking is to carefully remove the glass wool with a bent wire or needle.

a) If a prefilter was not used during sampling, place the glass wool and sorbent into separate 50-mL volumetric flasks.
b) If a prefilter was used and the glass wool appears to contain hopcalite or Hydrar, the glass wool can be analyzed along with the sorbent. Carefully transfer the glass   wool and sorbent to a 50-mL volumetric flask without losing any of the particles.

6.6.3   Prefilter

Prepare and analyze any prefilters according to reference 8.14.

6.6.4   Add 2.5 mL of concentrated HNO_3 followed by 2.5 mL concentrated HCl to each volumetric flask [Note: To minimize any loss of mercury through a change in oxidation state, the HNO_3 is added before the HCl (8.5)].

6.6.5   Gently swirl the sample occasionally for approximately 1 h. If Hydrar was used to collect the sample, the dark brown solution will also contain some undissolved clear to white-tan colored ceramic material.

6.6.6   Carefully dilute to a 50-mL total volume with DI H_2O. The final sorbent sample solution will be light blue or blue-green. This is a good place to stop if the analysis cannot be completed the same day.

6.7   Analysis - Instrument Parameters

6.7.1   Set up the CV-AAS as illustrated in Figure 1.

6.7.2   Wrap the heating tape around the quartz cell and then turn on the variable transformer. The heat setting on the tape should be sufficient to prevent water vapor condensation in the absorption cell.

6.7.3   Place the aerator in a B.O.D. bottle which contains approximately ½ to 1 inch of desiccant. Operate the peristaltic pump for approximately 30 min at full speed to remove any water vapor from the system.

6.7.4   Operate the hollow cathode or electrodeless discharge mercury lamp at the manufacturer's recommended current or power rating.

6.7.5   Use the following settings (Note: The mentioned instrument settings are for specific models used at the OSHA-SLCAL. If instrumentation other than what is specified in Section 6.2 is used, please consult the instrument manufacturer's recommendations.):

Atomic Absorption Spectrophotoineter:
Slit   0.7 nm
Signal   Repeat Mode
Function   ABS
Mode   ABS
Range   UV
Wavelength   253.7 nm
Filter   Out
EM Chopper   Off
Phase   Normal

Strip Chart Recorder:
Chart Speed   5 mm/min
Chart Range   10 mV

6.7.6   Optimize the ENERGY meter reading at 253.7 nm.

6.7.7 Align the beam of the mercury lamp so it passes directly through the center of the quartz cell windows. This can be accomplished by adjusting the burner height, depth, and angle knobs to give a minimum ABSORBANCE reading.

6.7.8 Operate the peristaltic pump at full speed. Rinse the aerator with DI H_2O and insert it into a holder in the exhaust vent.

6.7.9 Perform the following steps to obtain a baseline signal near an absorbance of zero:

1) start the chart recorder,
2) set the spectrophotometer absorbance reading to zero,
3) wait until the baseline stops drifting,
4) set the reading to zero again.

6.8 Analysis

6.8.1 Samples: <u>Immediately before analyzing</u>, transfer an appropriate aliquot of the sample solution to a clean B.O.D. bottle containing enough 10% HNO_3 solution to bring the total volume to 100 mL. The transfer must be done with a volumetric pipet.

6.8.2 Standards: <u>Immediately before analyzing</u>, prepare standards according to instructions listed in Section 6.5.2.

6.8.3 Deliver 5 mL of the 10% $SnCl_2$ solution with an automatic pipet to a B.O.D. bottle containing a standard, reagent blank, or sample to be analyzed. Immediately place the aerator into the solution with the peristaltic pump operating at full speed.

6.3.4 Record the maximum absorbance reading and label the signal produced on the strip chart.

6.8.5 Stop the pump, remove the B.O.D. bottle from the CV-AAS and stopper it. Rinse the aerator with DI H_2O and insert it into a holder in the exhaust vent. Turn the pump on at full speed until the CV-AAS system is purged of mercury and the baseline returns to zero.

6.8.6 If the absorbance reading of a sample is greater than the highest standard <u>at any time</u> during analysis, <u>immediately</u> remove the B.O.D. bottle from the CV-AAS. Purge the system following the procedure listed in Section 6.8.5. Take a smaller aliquot or dilute the high concentration sample and re-analyze. Make any necessary sample dilutions with 10% HNO_3 and use the appropriate dilution factor when calculating results.

6.8.7 Repeat Sections 6.8.3 through 6.8.5 for each prepared standard, reagent blank, or sample.

6.9 Analytical Recommendations

6.9.1 It is recommended to analyze the reagent blank, lowest, and highest standard two or three times each to check for contamination, reproducibility, and sensitivity before starting the sample analysis. A 2.0-µg mercury standard should give a three-quarter to full-scale deflection on the chart recorder and an absorbance unit reading of about 0.850 when using the equipment and conditions specified. The lowest and highest standard should provide a linear response and the lowest standard should be at least two to three times the blank signal.

6.9.2 It is also recommended to analyze an entire series of standards (including the reagent blank) at the beginning and end of the sample analysis to ensure standard readings are reproducible. As a general guideline, standard readings should be within ±10% throughout the analysis.

6.9.3 A standard near the concentration range of the samples should be analyzed after every four to five samples.

6.9.4 Quality control (QC) samples should be prepared and analyzed using the same matrix and analytical conditions as the samples. If possible, the QC samples should be generated from an independent source.

6.9.5 Approximately 10% of the samples should be reanalyzed.

7. Calculations

7.1 Use a least squares regression program to plot a concentration-response curve of peak absorbance versus the amount (µg) of mercury in each standard.

7.2 Determine the amount (µg) of mercury, A, corresponding to the peak absorbance in each analyzed sample aliquot from this curve.

7.3 Calculate the total amount (µg) of mercury, W, in each sorbent or glass wool sample:

$$W = \frac{(A)(Samplevol,mL)(DF)}{Aliquot,mL}$$

DF = Dilution Factor (if none, DF = 1)

7.4 A blank correction is made for each sample (Note: When using the reagents and conditions specified, previous blank results have been less than 1 µg). Calculate the concentration of mercury in each sorbent or glass wool sample:

$$Mercury \ mg/m^3 = \frac{W - Wb}{Air \ vol, L}$$

Where:
Wb = Total µg of mercury in the blank sample.
Air vol = Sampling time x flow rate (for <u>ACTIVE SAMPLERS)</u>

(Note: For <u>PASSIVE DOSIMETERS</u>, the sampling rate is affected by temperature and pressure. To correct for this, use:

$$Air \ vol = ST \times 0.020 \times (\frac{T_1}{T_2})^{1.5} \times \frac{P_2}{P_1}$$

Where:
ST = Sampling time (min)
0.020 = Sampling rate (L/min) at 20 °C and 760 torr
T_1 = Sampling site temperature (K)
T_2 = 293 K
P_1 = Sampling site pressure (torr)
P_2 = 760 torr

7.5 Reporting Results to the Industrial Hygienist

For PASSIVE DOSIMETER samples, report results to the industrial hygienist as mg/m^3 mercury vapor.

For ACTIVE SAMPLERS, report results as:

a) mg/m^3 mercury vapor
b) mg/m^3 total mercury

For mercury vapor result a): <u>If a prefilter was used</u> and the glass wool and sorbent were combined:

mercury vapor = glass wool + sorbent

The prefilter (if used) was present during sampling to assure that mercury particulate was not trapped in the glass wool.

For total mercury result (b): The sum of the mercury found in the sorbent (vapor), glass wool, and prefilter (if used) for each active sampler is considered. This result is used to determine total mercury.

Any mercury particulate anticipated on the prefilter can be analyzed for mercury. See Reference 8.14 for further details.

If sampling information has not been provided by field personnel, results are reported in total micrograms.

8. References

8.1 SKC Inc.: Gas Monitoring Dosimeter Badge for Mercury (Operating Instructions). Eighty Four, PA: SKC Inc., no publication date given.

8.2 Occupational Safety and Health Administration Technical Center: Evaluation of Mercury Solid Sorbent Passive Dosimeter by J. Ku (OSHA-SLTC Backup Report for Method No. ID-140). Salt Lake City, UT, Revised 1989.

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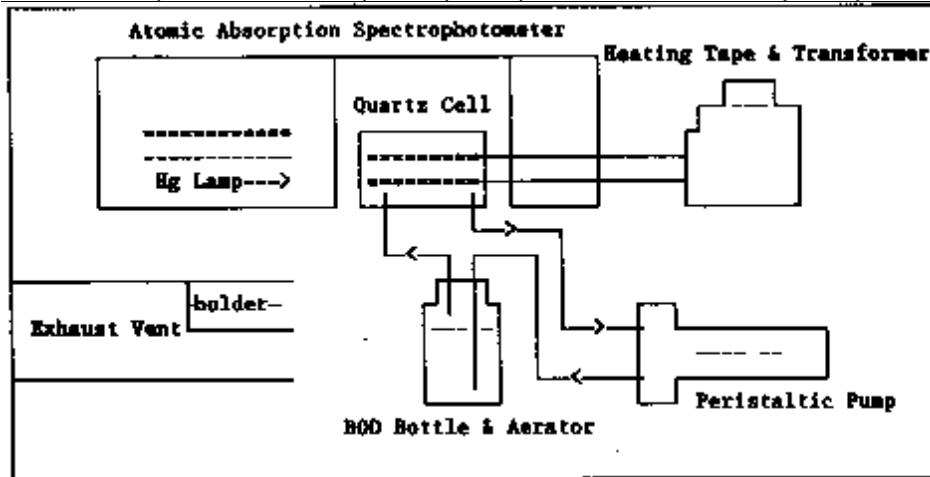Figure 1

Evaluation of a Solid Sorbent Passive Dosimeter for Collecting Mercury Vapor

OSHA Method ID-140 Backup (Revised December 1989)

Introduction

Several methods used to determine personal exposure to mercury vapor have been reported (13.1-13.7). A few of these methods employed passive monitors as the sample collection device. Passive monitors require no sampling pumps and usually are simpler to use than active samplers. Some passive mercury monitors must be analyzed by the manufacturer. A mercury dosimeter (SKC Inc., Eighty Four, PA) that can be analyzed in any laboratory equipped with a cold-vapor atomic absorption spectrophotometer (CV-AAS) is commercially available. This mercury dosimeter samples workplace air by diffusion of mercury vapor through polyethylene mesh discs which are located at the face of the badge. The mercury is then collected on a solid sorbent capsule containing approximately 800 mg of Hydrar® which resides in a plastic housing. The Hydrar® is analyzed by cold vapor, the capsule is discarded, and the plastic housing, after decontamination, is reusable.

According to the manufacturer, the sampling rate of the dosimeter badge at 20°C is 0.020 L/min when used in face velocities normally seen in industrial environments (13.7). This dosimeter has been extensively evaluated at the OSHA Salt Lake City Analytical Laboratory for use in compliance sampling.

(Note: The SKC dosimeter badge was modified by the manufacturer after this evaluation was performed. The dimensions of the badge housing were reduced and a metal O-ring replaced the Viton® O-ring previously used to hold the polyethylene discs in place. Extensive field studies were performed with the modified dosimeter badge after this evaluation. These studies compared this dosimeter to active samplers; results indicated good agreement. See reference 13.8 for more information.)

1. Evaluation Protocol

A laboratory evaluation was conducted over a broad range of mercury concentrations and variable sampling times for the Gas Monitoring Dosimeter Badges manufactured by SKC Inc., Eighty Four, PA. Mercury concentrations of about 0.05, 0.1, and 0.2 mg/m3 were used, which at to time of this study (1982) was equivalent to 0.5, 1, and 2 times the OSHA PEL (13.9) The evaluation consisted of the following experiments:

1. Analysis - desorption efficiency

2. Sampling rate

3. Sampling and analysis

4. Storage stability

5. Reverse diffusion

6. Sampling times

7. Sampling rate dependence on face velocity

8. Comparison of methods

All tests were performed at 80% RH and 25°C using a minimum of six dosimeters for each test. The tests were performed at atmospheric conditions of about 640 to 660 Torr and 20 to 25°C. All results for

the active sampling hopcalite sorbent have been pressure and temperature corrected to sampling site conditions.

Unless otherwise noted, a face velocity of about 15 m/min (50 ft/min) was used when exposing the dosimeters to mercury atmospheres.

2. **Laboratory Generation System**

A diagram of the generation system used for the evaluation is shown in Figure 1. The system consisted of five main components:

1. Humidity, temperature, and flow control system

2. Mercury vapor generating system (saturation unit)

3. Mixing manifold

4. Active sampling manifold

5. Dosimeter exposure chambers

This generation technique is based on the ability of mercury to readily evaporate at normal temperatures. The gas flow through the system and subsequent generation of mercury vapor is described: Diluent air was passed through a particulate filter, an indicating silica gel bed, and a charcoal bed to remove any impurities and water vapor. This purified air stream was split into two separate lines. One line passed through a humidity, temperature, and flow control system (Miller-Nelson Research, Model # HCS-301) for conditioning. The other line flowed through a low range flowmeter into a mercury vapor saturation unit as shown in Figure 2. This unit consisted of an enclosed glass flask containing a temperature-controlled pool of mercury. The mercury-ladened air leaving this unit then flowed through two 500-mL equilibrium vessels, which were immersed in a constant temperature (±0.02°C) water bath. The saturated mercury/air mixture was then mixed with the conditioned air to achieve the desired test concentration, temperature, and humidity (25°C, 80% RH). The final controlled concentration of mercury vapor flowed into a Teflon sampling manifold (for hopcalite sorbent sampling) and also into one of two different glass exposure chambers for exposing passive monitors. For a portion of the face velocity study, this mercury vapor flowed through an aluminum chamber instead of the glass chamber. The aluminum chamber, which contained an electric fan for producing different face velocities, was obtained from 3M (3M Co., St. Paul, MN). A similar chamber is described in reference 13.10.

3. **Sample Collection and Analysis**

The dosimeter and hopcalite sampling devices were exposed side-by-side following the step-by-step experimental procedure described in Appendix A. A Jerome Model 401 gold film mercury vapor analyzer (Arizona Instrument Corp., Jerome, AZ) was used as a direct reading device to periodically monitor the generation of mercury during the side-by-side sampling.

After sampling, the Hydrar® sorbent and hopcalite were separately dissolved in concentrated nitric acid (HNO3) and then hydrochloric acid (HCl). Each sample was diluted with deionized water to a specified volume. Aliquots of each sample were then analyzed for mercury by a cold vapor technique. Mercury vapor was swept from each sample by an air stream after an excess amount of stannous chloride was added. The mercury vapor was then analyzed by atomic absorption using a quartz cell as the absorption path. Detailed analytical procedures for the Hydrar® sorbent are described in references 13.7, or 13.11; reference 13.12 for hopcalite. Analytical procedures for either sorbent are essentially identical. This evaluation used procedures mentioned in reference 13.11 with one exception; the analyzed matrix for samples and standards was 5% HCl and 5% HNO3 instead of approximately 10% HNO3.

For all experiments except sampling and analysis (Section 6), known concentrations of mercury produced in the generation system were determined from the hopcalite results. In order to calculate overall error, the sampling and analysis experiment used theoretical values [based on the vapor pressure of mercury (13.13)] as known concentrations.

Results from the hopcalite samples were compared to theoretical calculations and also to results obtained using the Jerome Mercury Analyzer. The results of these comparisons are summarized in Table 1, which show close agreement for the three different types of measurement.

4. **Desorption Efficiency**

Procedure: A study was conducted in which three sets of spiked samples were prepared by adding appropriate volumes of a mercury stock solution into sorbent capsules. Each set contained six samples. The concentrations of the spiked capsules corresponded to 0.5, 1.0, and 2.0 µg. At the time of the study, these spikes were equivalent to 0.5, 1, and 2 times the PEL (if taking an 8-h sample at a sampling rate of 0.020 L/min). The spiked capsules were allowed to sit overnight before analyzing.

Results: Results in Table 2 indicate the average desorption efficiency (DE) is so close to 1.0 that a DE correction is not necessary.

5. **Sampling Rate**

Procedure: The dosimeter sampling rate was experimentally examined by measuring the mass of mercury collected by the sorbent when exposed to different concentrations of mercury. Side-by-side samples of hopcalite and dosimeters were taken from the generation system at three different concentration levels, 0.066, 0.108, and 0.203 mg/m^3 mercury. Exposure times ranged from 240 to 1,415 min. The sampling rate for each test was calculated using:

$$\text{sampling rate (L/min)} = \frac{\text{Hg found (µg)}}{\text{Hop Hg (mg/m}^3\text{)} \times \text{sampling time (min)}}$$

Where:

Hg found = amount of mercury found in the dosimeter sample

Hop Hg = air concentration of mercury in the generation system as determined by the hopcalite sampler

Results: Table 3 summarizes the sampling rate found when monitors were exposed to different mercury concentrations. The sampling rate was calculated assuming the dosimeter has 100% collection efficiency for mercury [Note: More detailed descriptions for the determination of sampling rate have been reported (13.14, 13.15)]. An average sampling rate of 0.01849 ± 0.00119 L/min was obtained which is very close to the manufacturer's stated value of 0.020 L/min at 20°C (13.7); however, the dosimeter sampling rate appeared to slightly decrease when sampling times were greater than 8 h.

6. **Sampling and Analysis**

Procedure: Six dosimeter samples at each of three different concentration levels were taken to determine the precision and accuracy of the passive monitor near the OSHA PEL. Overall error (OE) of the sampler at defined test levels was examined and calculated as:

$OE_i = \pm [|\text{mean bias}_i| + 2CV_i]] \times 100\%$

Where i is the respective sample pool being examined.

Results: Precision and accuracy data based on the NIOSH statistical protocol (13.16) is presented in Table 4. The pooled coefficients of variation for spiked (CV1) and generated (CV2) samples and overall

CVT were as follows:

CV1(pooled) = 2.7%

CV2(pooled) = 3.7%

CVT(pooled) = 3.9%

The bias found in generated sample results over the concentration range tested was -0.8% and OE was ±8.3%.

7. **Storage Stability**

Procedure: A study was conducted to assess the stability of the monitors when stored under normal laboratory conditions. Four sets, each containing six monitors, were exposed to 0.108 mg/m^3 mercury. The monitors were then stored on a laboratory bench. The first set of monitors was analyzed 1 day after exposure, the second set 5 days, the third set 14 days, and the last set 30 days.

Results: The results in Table 5 show that the collected sample is stable for at least 30 days. Average values were within ±10% of the known generated mercury concentration.

8. **Reverse Diffusion**

Procedure: A reverse diffusion test was used to determine if there is significant diffusion of mercury from the dosimeter sorbent back into the atmosphere after collection. Two sets of samples were used for this study. The first set of six monitors was exposed to 0.2 mg/m^3 mercury and 15.2 m/min (50 ft/min) face velocity for 4 h. The second set of six monitors was exposed using the same conditions, except these monitors were exposed continuously for another 4 h in purified air which contained no mercury vapor. A face velocity of 15.2 m/min was also used for the purified air.

Results: As shown in Table 6, the difference between the means of the two sets was less than 3%. These results indicate reverse diffusion should not be a significant problem during an 8-h sampling period.

9. **Face Velocity**

Procedure: To examine the SKC monitor sampling rate at various face velocities, a series of experiments were designed to test monitor uptake of mercury at selected face velocities in the range of 1.04 to 91.4 m/min (3.4 to 300 ft/min). Dosimeter and hopcalite samples were taken side-by-side. The collection of mercury with the hopcalite active sampling device is independent of face velocity at the levels tested.

As previously mentioned in Section 2, different exposure chambers were used for this experiment, two glass and one aluminum. Physical characteristics of the glass chambers are described in Table 7. The face velocity was altered by adjusting the contaminant flow rate through the glass chambers or by changing the speed of a fan located within the aluminum chamber. The first three tests (face velocities of 1.04 to 15.2 m/min) were performed using the glass chambers and a horizontal flow of contaminant at the badge faces. The final two tests were performed in the aluminum chamber, using the fan to circulate the controlled mercury atmosphere in the chamber and to provide two different face velocities. Average sampling rates were calculated using the equation mentioned in Section 5.

Results: Table 7 and Figure 3 summarize the response of the SKC mercury monitors to various levels of air movement. The results indicate the sampling rate does not significantly change above 15.2 m/min (50 ft/min). A problem were discovered after the aluminum chamber experiment was performed. The manufacturer-quoted face velocity for various fan speeds was also dependent on placement of the

monitors in the chamber. Placement geometry was not controlled during the experiment and actual velocities on the badge faces could have been lower than theoretical. This may explain the low sampling rate (0.01512 L/min) found at a theoretical velocity of 15.2 m/min. Using a hot wire anemometer after the experiments indicated the velocity during this experiment could have been as low as 7.6 m/min (25 ft/min). The sampling rate determined for this test was not used in Figure 3. Also, the actual velocity for the test conducted at 91.4 m/min could have been as low as 67 m/min (220 ft/min). Tests were not performed above this velocity due to design limitations of the chambers. Manufacturer statements indicate the dosimeter sampling rate is unaffected by face velocities from 7.6 to 228 m/min (25 to 750 ft/min) (13.7).

10. **Sampling Times**

Procedure: The ability of the dosimeter to sample mercury for extended periods was examined.

Twenty-one dosimeter samples were exposed to the same test concentration of 0.213 mg/m^3 using varied exposure times. The length of dosimeter exposure to mercury vapor ranged from 4 to 120 h.

Results: The length of sampling time at a fixed concentration was examined by plotting weight collected as a function of sampling time. This data, reported in Table 8 and illustrated in Figure 4, demonstrates linearity to at least 30 μg.

11. **Comparison of Methods**

Procedure: To compare the dosimeter results with a reference method, hopcalite solid sorbent was used. As mentioned in Section 2, dosimeters and hopcalite sorbent were simultaneously exposed during all tests. Three concentration levels were used. A methods comparison at a high concentration level (about 0.6 mg/m^3) was performed as an additional test to examine sample collection capacity.

Results: The two methods agree well with each other. Figure 5 shows a graphical comparison of the SKC mercury dosimeter and hopcalite results over the four concentrations tested. The solid line in the center portrays ideal agreement between the two methods (slope equal to 1). The solid and broken lines on either side of the center line are ±25% and ±10% confidence intervals, respectively. As can be seen, 95% of the measured values by these two methods lie within ±10% of the ideal response.

12. **Summary and Conclusions**

A small, lightweight, and reusable passive monitor was tested for the ability to accurately measure mercury vapor under various environmental conditions. The experiments described have led to the following observations concerning the performance of the SKC passive dosimeter badge for monitoring mercury vapor.

12.1 The SKC dosimeters showed excellent precision. The coefficient of variation of sample sets analyzed throughout the study was consistently less than 10%.

12.2 Storage stability was sufficient to compensate for typical delays in analysis seen in analytical lab settings. Reverse diffusion was not noted. Sampling efficiency was adequate for long-term sampling; however, a slight decrease in results was noted.

12.3 The monitor was affected by face velocities below 15.2 m/min (50 linear ft/min). At 6.1 linear m/min (20 linear ft/min), the dosimeter sampling rate was 22% lower than the experimentally determined rate at 15.2 m/min face velocity (Table 7). At 1.04 m/min, it was 30% lower.

12.4 Using either the Hydrar® dosimeter or hopcalite sampling tubes for determining mercury vapor should yield similar results in the concentration range tested.

In conclusion, the SKC dosimeter is a lightweight, reusable personal mercury monitor designed to be carried on the clothing of individuals, and can be analyzed in the lab by a simple analytical technique.

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Table 1
Determination of Generated Mercury Concentration Independent Methods

Set#	Method	Hg Concn mg/m^3	N (Samples)
I	JA	0.064	*
	HC	0.066	13
	TC	0.061	
II	JA	0.106	*
	HC	0.108	14
	TC	0.105	
III	JA	0.202	*
	HC	0.203	10
	TC	0.203	
IV	JA	0.597	*
	HC	0.605	4
	TC	0.573	

JA = Jerome Model 401 gold film mercury vapor analyzer

* These samples were taken periodically during each generation

HC = Hopcalite sorbent

TC = Theoretical concentration. The calculation is based on the following equation:

$$\text{Hg concentration (mg/m3)} = \frac{(q_{Hg})\,(P_{Hg} \times 3.22 \times 106)}{(q_{Hg} + q_{air})\,(T_m)}$$

Where:

q_{Hg} = flow rate of the mercury-saturated air (L/min)

q_{air} = flow rate of the dilution air (L/min)

P_{Hg} = vapor pressure of mercury (torr)

T_m = measured temperature of air saturated with mercury (K)

contains a more detailed explanation regarding theoretical calculations.

Table 2
Analysis - SKC Mercury Dosimeter

Level*	0.5 × PEL			1 × PEL			2 × PEL		
	µg Taken	µg Found	DE	µg Taken	µg Found	DE	µg Taken	µg Found	DE
	0.50	0.48	0.96	1.00	0.96	0.96	2.00	1.98	0.99
	0.50	0.48	0.96	1.00	1.02	1.02	2.00	2.14	1.07
	0.50	0.48	0.96	1.00	1.04	1.04	2.00	2.05	1.03
	0.50	0.49	0.98	1.00	1.01	1.01	2.00	2.01	1.01
	0.50	0.51	1.02	1.00	1.02	1.02	2.00	2.01	1.01
	0.50	0.49	0.98	1.00	1.00	1.00	2.00	1.97	0.99
N	6			6			6		
Average DE	0.98			1.01			1.02		
Std Dev	0.023			0.027			0.030		
CV1	0.024			0.027			0.03		
CV1(pooled) 0.027				DE = Desorption Efficiency					

* Transitional PEL of 0.100 mg/m^3

Table 3
Sampling Rate Evaluation - SKC Mercury Dosimeter
80% RH, 25°C and 15.2 m/min (50 ft/min)

Hg Concn** (mg/m^3)	Mass (µg)	Sampling Time (min)	Sampling Rate (L/min)
0.066	0.66	490	0.02041
0.066	0.89	780	0.01729
0.066	1.15	1,000	0.01742
0.066	1.67	1,415	0.01788
0.108	0.98	480	0.01890
0.203	0.93	240	0.01905
		N	6
		Mean	0.01849
		Std Dev	0.00119
		CV	0.065

** Determined from the hopcalite sampler results

Table 4
Sampling and Analysis
SKC Mercury Dosimeter
80% RH, 25°C and 15.2 m/min (50 ft/min)

(OSHA-PEL*) mg/m³ Taken	mg/m³ Found	F/T	N	Mean	Std Dev	CV2	OE
(0.5 × PEL)							
0.061	0.071	1.164					
0.061	0.067	1.098					
0.061	0.067	1.098					
0.061	0.067	1.098					
0.061	0.066	1.082					
0.061	0.065	1.066					
			6	1.101	0.033	0.030	16.2
(1 × PEL)							
0.105	0.108	1.029					
0.105	0.104	0.990					
0.105	0.096	0.914					
0.105	0.099	0.943					
0.105	0.102	0.971					
0.105	0.103	0.981					
			6	0.971	0.039	0.041	11.0
(2 × PEL)							
0.203	0.200	0.985					
0.203	0.202	0.995					
0.203	0.185	0.911					
0.203	0.183	0.901					
0.203	0.194	0.956					
0.203	0.196	0.966					
			6	0.952	0.038	0.040	12.8

*Transitional PEL of 0.100 mg/m³

F/T	=	Found/Taken
OE	=	Overall error (±%)
Bias	=	+0.008
CV2 (Pooled)	=	0.037
CVT	=	0.039
Overall Error (Total)	=	8.6%

Table 5
Summary of Storage Stability
SKC Mercury Dosimeter
80% RH, 25°C, and Known Concentration = 0.108 mg/m^3

Sample Age (days)	No. of Dosimeters (N)	Mean (mg/m^3)	Std Dev (mg/m^3)	CV
1	6	0.102	0.0041	0.041
5	6	0.111	0.0034	0.030
14	6	0.100	0.0067	0.067
30	6	0.111	0.0048	0.044

Table 6
Reverse Diffusion Test
SKC Mercury Dosimeters

Set (#)	Hg Found (µg)	Hg Concn (mg/m^3)	Statistical Analysis	
1	0.96	0.200	N	= 6
	0.97	0.200	Mean (mg/m3)	= 0.193
	0.89	0.185	Std Dev (mg/m3)	= 0.0078
	0.88	0.183	CV	= 0.04
	0.93	0.194		
	0.94	0.196		
2	0.86	0.179	N	= 6
	0.82	0.171	Mean (mg/m3)	= 0.189
	0.93	0.194	Std Dev (mg/m3)	= 0.011
	0.95	0.198	CV	= 0.06
	0.91	0.190		
	0.96	0.200		

Set 1 = Six samples exposed to 0.2 mg/m3 mercury for 4 h

Set 2 = Six samples exposed to 0.2 mg/m3 mercury for 4 h and then exposed an additional 4 h to purified air containing no mercury.

Table 7
Face Velocity Dependence for SKC Mercury Dosimeters
80% RH, 25°C, and a Concentration Range of 0.1 to 0.6 mg/m^3

Flow Rate (L/min)	Exposure Chamber Used	Face Velocity m/min (ft/min)		Samples (N)	Sampling Rate (L/min)
8.6	A	1.04	(3.4)	4	0.01294
12	B	6.1	(20.0)	6	0.01445
30	B	15.2	(50.0)	6	0.01849
10	C	15.2*	(50.0)	3	0.01512
10	C	91.4*	(300.0)	3	0.01915

Where:

A: Exposure chamber, obtained from Du Pont (E.I. Du Pont de Nemours & Co., Wilmington, DE). The chamber was constructed of glass and the dimensions were approximately 8 mm wide × 10 mm deep × 90 mm in length. The area section = 83.87 cm^2 (0.090 ft^2). A concentration of about 0.1 mg/m3 mercury was used.

B: A 1-L burette was used as an exposure chamber, area section = 19.63 cm2 (0.021 ft^2). A concentration of about 0.1 mg/m^3 mercury was used.

C: 3M chamber (3M Co., St. Paul, MN):
See reference 13.10 for a description of a similar exposure chamber. The chambers are virtually identical with two exceptions. The chamber used for this evaluation had an aluminum top cover and a honeycomb port design. The chamber described in reference 13.10 had a Plexiglas cover and a louvered port design.

In the aluminum chamber, face velocities were altered using different fan speeds instead of changing flow rates. The velocity/fan speed ratio had been previously determined by the manufacturer. A concentration of about 0.6 mg/m^3 mercury was used.

* Due to an unexpected dependence of monitor placement in the chamber, face velocities are approximate for these two experiments. For the two tests, the velocities could have been as low as 7.6 (15.2 m/min theoretical) and 67 m/min (91.4 m/min theoretical), respectively.

Table 8
Extended Sampling Times for the SKC Mercury Dosimeters
80% RH, 25°C and Known Concentration = 0.213 ± 0.011 mg/m^3

Sampling Time (h)	Mercury Weight Collected (µg)	Statistical Analysis	
4.0	0.96	N	6
	0.97	Mean (µg)	0.93
	0.89	Std Dev (µg)	0.03
	0.88	CV	0.039
	0.93		
	0.94		
24.0	4.56	N	3
	4.99	Mean (µg)	4.73
	4.65	Std Dev (µg)	0.23
		CV	0.048
48.0	9.40	N	3
	8.95	Mean (µg)	9.28
	9.49	Std Dev (µg)	0.29
		CV	0.031
72.0	16.23	N	3
	15.93	Mean (µg)	16.34
	16.87	Std Dev (µg)	0.48
		CV	0.029
96.0	21.95	N	3
	22.17	Mean (µg)	22.13
	22.28	Std Dev (µg)	0.17
		CV	0.0076
120.0	26.12	N	3
	25.83	Mean (µg)	26.51
	27.57	Std Dev (µg)	0.93
		CV	0.035

Appendix A

Sampling Procedure - Generation System

The following steps were performed when active and passive samples were taken for each experiment:

1. Adjust the flow rate of the dilution air and the flow rate of the mercury-saturated air to achieve a specified calculated Hg concentration.

2. Remove the complete dosimeter from the package. Keep the packaging material and pouch from potentially contaminated areas of mercury before sampling.

3. Record the sample number and the starting exposure time on the back of the monitor.

4. To start sampling, pry off the sealing cap.

5. * Attach the dosimeters onto a long piece of stiff Teflon tubing.

6. * Open the cap of the chamber and put the tubing into the chamber.

7 Close the chamber and assure a tight seal.

8. Attach the hopcalite samplers to the sampling manifold and to sampling pumps. Simultaneously expose hopcalite and Hydrar® sampling media.

9. Sample with hopcalite for 1 to 2 h at a flow rate of 0.2 L/min.

10. At the conclusion of the sampling period, immediately remove the dosimeter from the chamber and tubes from the manifold. Cap the tubes with plastic end caps.

11. As soon as possible after sampling, place the dosimeters in a clean area and remove the sorbent capsule by unscrewing the back cover. Remove the I.D. label and place on the pouch. Seal the capsule in the pouch by folding the top over twice and pressing flat.

12. Record the end of sampling time. Calculate the total exposure time.

* Steps 5 and 6 were used for the glass chamber exposures. When using aluminum chamber, dosimeters were fastened onto the built-in supports.

Appendix B

Theoretical Concentration Calculations for Generating Mercury Concentrations
(Note: Equations and Tables listed below were adapted from reference 13.13.)

Mercury concentrations in ppm (by volume) of the saturated stream of air can be calculated from:

$$C_{ppm} = \frac{P_{Hg} \times 10^6}{P_A} \qquad (1)$$

$$= \frac{W \times 22.4 \times T_m \times P_s}{V \times T_s \times M_{Hg}}$$

Where:

Cppm	=	concentration by volume (ppm)
PHg	=	vapor pressure of mercury (Torr)
PA	=	atmospheric pressure (Torr)
W/V	=	weight of mercury per unit volume of air (g/liter)
Tm	=	measured temperature of air saturated with mercury
Ps	=	standard pressure = 760 Torr
Ts	=	standard temperature = 273 K
MHg	=	molecular weight of mercury = 200.6 g/mole

Substituting in the known values and solving for the concentration in mg/m3, the above equation reduces to:

$$C_{mg/m^3} = \frac{PHg \times 200.6 \text{ g/mole} \times 10^6}{PA \times 22.4 \text{ liter/mole} \times (Tm/273 \text{ K} \times 760 \text{ mm}/PA)} \quad (2)$$

$$= \frac{PHg \times 3.22 \times 10^6}{Tm}$$

Some calculated values for PHg are shown:

Calculated concentrations of air saturated with mercury vapor

(18 to 28°C)

Temperature (°C)	Vapor Pressure of mercury (Torr)	Concentration of saturated air stream (mg/m³)
18	0.001009	11.2
20	0.001201	13.2
24	0.001691	18.3
26	0.002000	21.5
28	0.002359	25.2

When air is used to dilute the saturated mercury vapor, Equation 2 becomes:

$$C \text{ mg/m}^3 = \frac{q_{Hg} \times P_{Hg} \times 3.22 \times 10^6}{(q_{Hg} + q_{air}) \times T_m} \qquad (3)$$

Where:

qHg = flow rate of the mercury-saturated air (liters/min)

qair = flow rate of the dilution air (liters/min)

Some calculations using Equation 3 are shown:

Calculated concentrations of mercury vapor in air							
Flow Rate qair (L/min)	Flow Rate qHg (L/min)	mg/m³ Concentration of mercury vapor [Temperature (°C)]					
		18	20	22	24	26	28
18.0	0.018	0.011	0.013	0.016	0.018	0.021	0.025
18.0	0.036	0.022	0.026	0.031	0.037	0.043	0.050
14.0	0.050	0.040	0.047	0.056	0.065	0.077	0.090
9.95	0.050	0.056	0.066	0.078	0.091	0.11	0.13
9.9	0.10	0.11	0.13	0.16	0.18	0.22	0.25
9.8	0.20	0.22	0.26	0.31	0.37	0.43	0.50
9.7	0.30	0.34	0.40	0.47	0.55	0.65	0.76
9.6	0.40	0.45	0.53	0.62	0.73	0.86	1.01
12.0	0.90	0.78	0.92	1.09	1.28	1.50	1.76
6.0	0.60	1.02	1.20	1.42	1.66	1.95	2.29
6.0	0.67	1.12	1.32	1.56	1.83	2.15	2.52
None	All	11.2	13.3	15.7	18.4	21.5	25.3

Dynamic Generation System for Production of Mercury Atmospheres

Lab Air → Air Purifier → Flow-Temp-Humidity Control System ← Ion Exchange Column ← Lab Water

Flow-Temp-Humidity Control System ↓

Mercury Vapor Generator ----→ Mixing Chamber

Mixing Chamber ↓

Active Sampling Manifold ↓

Exposure Chamber → Exhaust
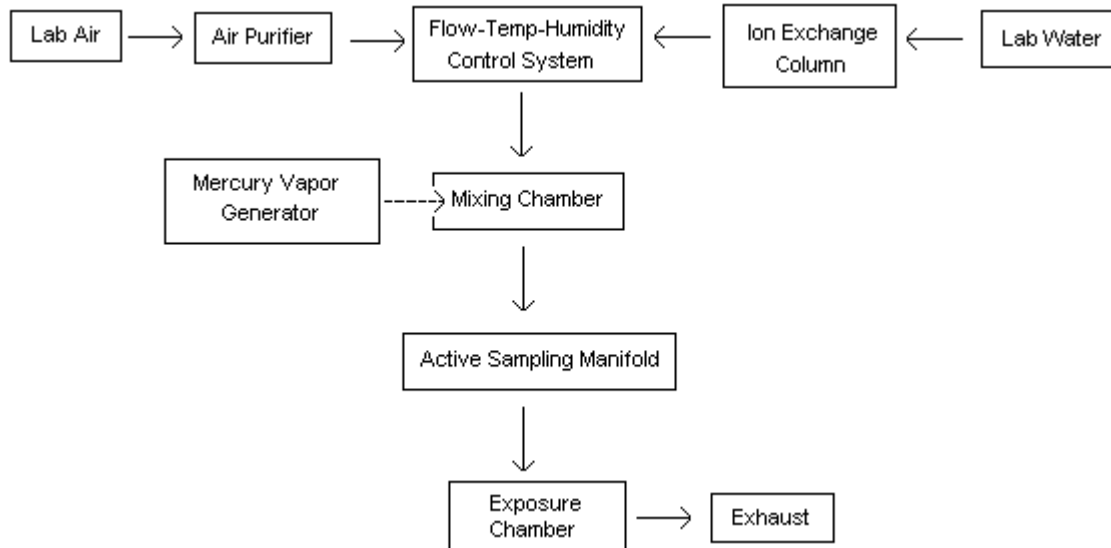
Figure 1 [Text Version]

Mercury Vapor Generating System - Saturation Unit

Flowmeter

Purified Air

Mercury

Mercury

Constant Water Bath

→ Mixing Chamber
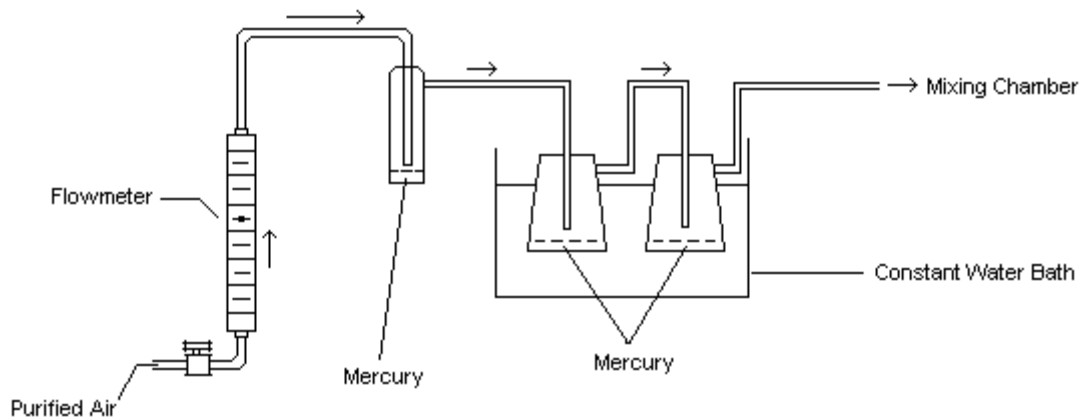
Figure 2

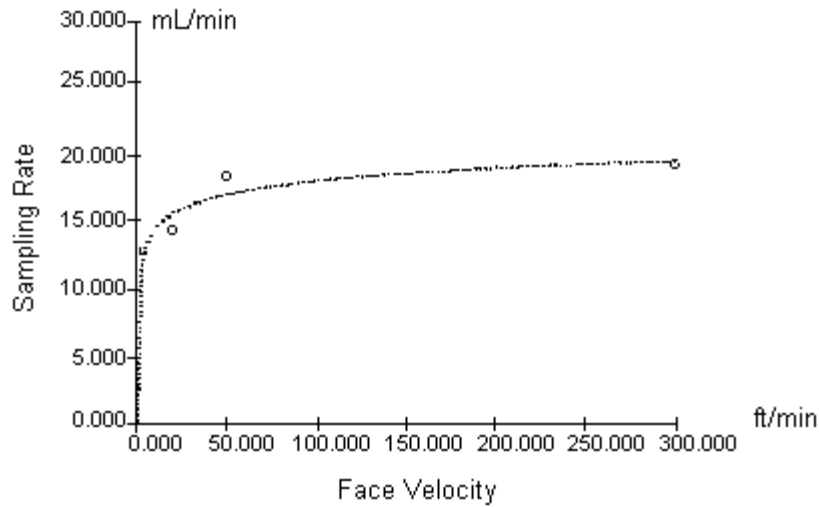## Sampling Rate Dependence on Face Velocity

Figure 3

Determination of Sampling Capacity - Extended Sampling Times
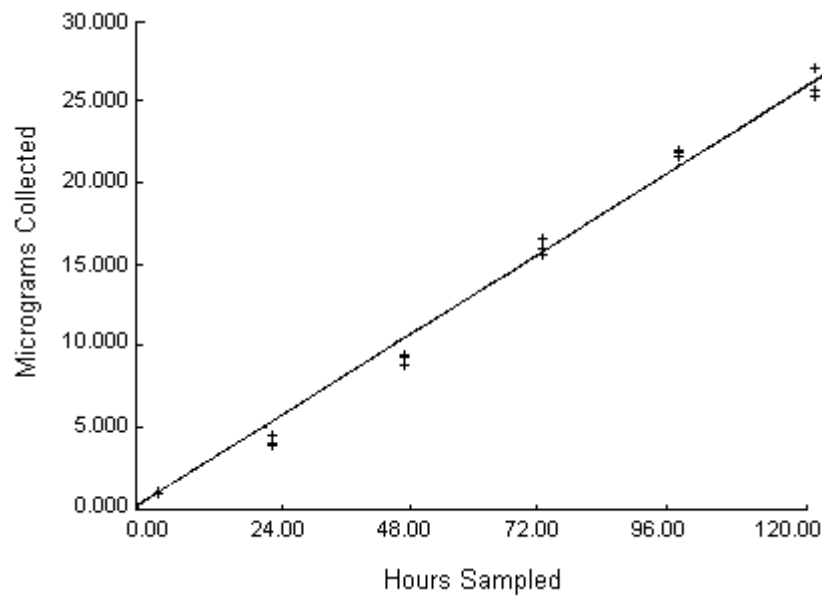## SKC Mercury Badge

Figure 4

Comparison of Methods
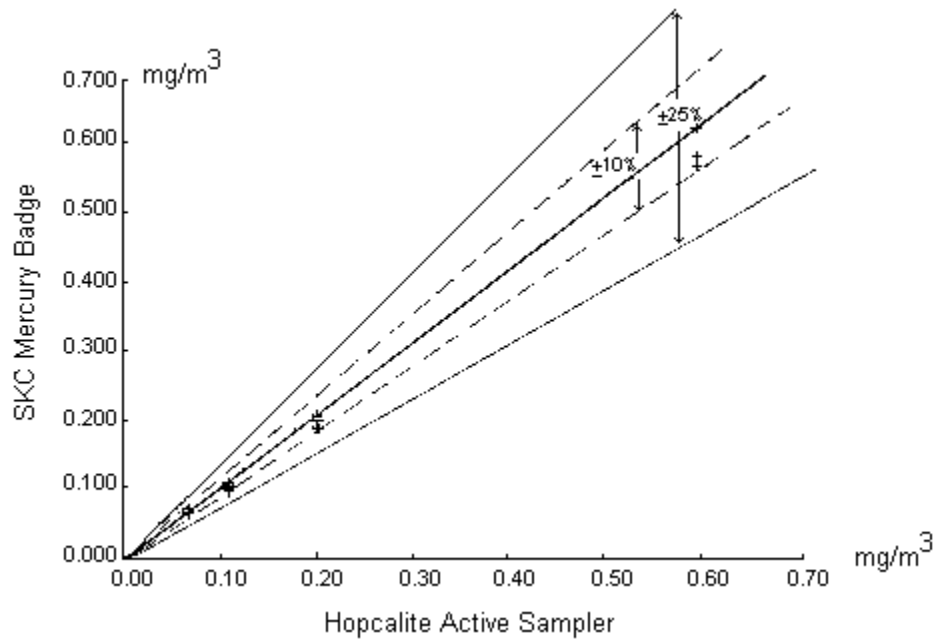SKC Mercury Badge Vs. Hopcalite Active Sampler

Figure 5