

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 101.1

**DETERMINATION OF PARTICULATE AND GASEOUS MERCURY
EMISSIONS FROM STATIONARY SOURCES**

**OFFICE OF OPERATIONS
TECHNICAL SERVICES DIVISION
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METHOD 101.1

DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM STATIONARY SOURCES

TABLE OF CONTENTS

Section

1. Overview

- 1.1 Principle
- 1.2 Applicability
- 1.3 Range and Sensitivity
- 1.4 Interferences
- 1.5 Precision

2. Field Procedures

- 2.1 Apparatus
- 2.2 Reagents
- 2.3 Pretest Determination
- 2.4 Gas Volume Meter Checks
- 2.5 Leak Checks
- 2.6 Sampling Train Operation
- 2.7 Calculation of Percent Isokinetic
- 2.8 Sample Handling
- 2.9 Calibration

3. Laboratory Procedures

- 3.1 Apparatus

- 3.2 Reagents
- 3.3 Preparation of Sampling Train
- 3.4 Sample Recovery
- 3.5 Sample Preparation
- 3.6 Sample Analysis
- 3.7 Calibration
- 3.8 Calculations

4. **Engineering Calculations**

METHOD 101.1

DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM STATIONARY SOURCES

Section 1 of 4

1. Overview

1.1 Principle

Particulate and gaseous mercury (Hg) emissions are withdrawn isokinetically from the source and collected by a wet impingement train containing acidic potassium permanganate (KMnO_4) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

1.2 Applicability

This method applies to the determination of particulate and gaseous Hg emissions from stationary sources where oxidizable organic matter is less than 200 ppm in the effluent gases.

1.3 Range and Sensitivity

1.3.1 Range

After initial dilution, the range of this method is 20 to 800 µg Hg/ml. The upper limit can be extended by further dilution of the sample.

1.3.2 Sensitivity

The sensitivity of the method depends on the recorder/spectrophotometer combination selected.

1.4 Interferences

1.4.1 Sampling

Since excessive oxidizable organic matter in the stack gas prematurely depletes the KMnO_4 solution this method may not be used if oxidizable organic matter is present in excess of 200 ppm.

1.4.2 Analysis

Condensation of water vapor on the optical cell windows causes a positive interference.

1.5 Precision

Based on eight paired-train tests, the within-laboratory standard deviation was estimated to be 4.8 $\mu\text{g Hg/ml}$ in the concentration range of 50 to 130 $\mu\text{g Hg/m}^3$.

METHOD 101.1

DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM STATIONARY SOURCES

Section 2 of 4

2. Field Procedures

2.1 Apparatus

A schematic of the sampling train is shown in Figure 101.1-1. It is similar to the Method 5.1 train. The train consists of the following components:

- a. Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Temperature Sensor, Metering System, and Gas Density Determination Equipment. Same as Method 5.1.
- b. Probe and Probe Liner

Stainless steel probe with probe liner made of borosilicate or quartz glass.

c. Impingers

Five Greenburg-Smith impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first, second, and third impingers are of the standard Greenburg-Smith design with the standard tip. The fourth and fifth impingers are modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to about 1.3 cm (1/2 in.) from the bottom of the flask.

The first, second, and third impingers contain 100 ml of acidic KMnO_4 solution. The fourth is kept empty and the fifth contains a known weight of silica gel, or equivalent desiccant. A thermometer capable of measuring temperature to within 1°C (2°F) is placed at the outlet of the fourth impinger to monitor outlet gas temperature.

Instead of using silica gel, the moisture leaving the third impinger can be measured by monitoring the temperature and pressure at the exit of the impinger train and using

Dalton's law of partial pressures. However, the use of silica gel (or equivalent) between the impinger system and pump will prevent moisture condensation in the pump and metering device.

d. Filter Holder (Optional)

Borosilicate glass with a rigid stainless steel wire screen filter support (do not use glass frit support) and a silicone rubber or Teflon gasket, designed to provide a positive seal against leakage from outside or around the filter.

2.2 Reagents

Use ACS reagent grade chemicals or equivalent.

a. Water

Deionized, distilled water meeting ASTM D1193-77, Type 3 specifications. Reference to water throughout this method implies deionized, distilled water.

b. Sulfuric Acid 10 percent (v/v)

Add and mix 100 ml of concentrated H_2SO_4 with 900 ml of water.

c. Absorbing Solution

4 percent KMnO_4 (w/v). Prepare fresh daily. Dissolve 40 gm of KMnO_4 in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation.

d. Filter (Optional)

Glass fiber filter, without organic binder, exhibiting at least 99.95 percent efficiency on 0.3 μm dioctyl phthalate smoke particles.

e. Silica Gel

Indicating-type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. Silica gel may be used as received.

f. Crushed Ice or Dry Ice Pellets.

2.3 Pretest Determination

Select the sampling site and the minimum number of sampling points according to Method 1.1.

Determine the stack pressure, temperature, and the range of velocity heads using Method 2.1. A leak check of the Pitot lines should be performed (see Method 2.1).

With glass liners, install the selected nozzle using a Viton A, O-ring. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape to denote the proper distance into the stack for each sample point.

Assemble the train as shown in Figure 101.1-1 using a light coat of stopcock grease on ground glass joints, greasing only the outer portion to avoid possibility of contamination by the grease.

Place crushed ice or dry ice pellets around the impingers.

Determine the moisture content of the stack gas using Method 4.1 or its alternative to make sampling rate settings. Determine the stack gas dry molecular weight as described in Method 3.1.

Select a nozzle size for the range of velocity heads encountered, so that it is not necessary to change the nozzle to maintain isokinetic sampling rates. Do not change the nozzle during the run. Choose the differential pressure gauge for the range of velocity heads encountered.

Select a probe length suitable for sampling all traverse points. For large stacks, consider sampling from opposite sides of the stack (four sampling port holes) to reduce the length of the probe.

Collect sample over a minimum of 2 hours (minimum sample volume of 60 ft³). In some instances, high oxidizable organic content may make it impossible to sample for the minimum time. This problem is indicated by the complete bleaching of the purple color of the KMnO₄ solution. In these cases, the sample run may be divided into two or more subruns to ensure that the absorbing solution will not be depleted.

The sampling time must be an integer plus one-half minute and the same at each point.

2.4 Gas Volume Meter Checks

See Method 5.1, Section 2.4.

2.5 Leak Checks

Follow the procedure described in Method 5.1, Section 2.6.

2.6 Sampling Train Operation

Follow the procedure described in Method 5.1, Section 2.7.

2.7 Calculation of Percent Isokinetic

Calculate percent isokinetic to determine whether the run was valid or another test run should be made.

2.8 Sample Handling

Follow the procedure described in Method 5.1,
Section 2.9.

2.9 Calibration

See Chapter III.

METHOD 101.1

DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM STATIONARY SOURCES

Section 3 of 4

3. Laboratory Procedure

3.1 Apparatus

3.1.1 Sample Collection

A schematic of the sampling train is shown in Figure 101.1-1 and includes nozzle, probe, probe liner, impinger train, filter holder and filter. See Sections 2.1 and 2.2.

3.1.2 Sample Recovery

a. Glass Sample Bottles

Leakless, with Teflon-lined caps, 1000 and 100 ml.

b. Graduated Cylinders

250 ml.

c. Funnel and Rubber Policeman

3.1.3 Analysis

a. Volumetric Pipets

Class A: 1, 2, 3, 4, 5, 10 and 20 ml.

b. Graduated Cylinder

25 ml.

c. Steam Bath

d. Balance

Capable of weighing to ± 0.5 gm.

e. Atomic Absorption Spectrophotometer

Perkin-Elmer 303, or equivalent,
containing a hollow-cathode mercury
lamp and optical cell.

f. Optical Cell

Cylindrical shape with quartz windows
and having the dimensions shown in
Figure 101.1-2. Wind the cell with
approximately 2 meters of 24 gauge
nichrome heating wire, and wrap with
fiberglass insulation tape or
equivalent. Do not let the wires
touch each other.

g. Aeration Cell

Constructed according to the
specifications in Figure 101.1-3. Do
not use a glass frit as a substitute
for the blown glass bubbler tip.

h. Recorder

Matched to output of the
spectrophotometer.

i. Variable Transformer

To vary the voltage on the optical
cell.

j. Flowmetering Valve

k. Flowmeter

Rotameter or equivalent. Capable of
measuring a gas flow of 1.5
liters/minute.

l. Aeration Gas Cylinder

Nitrogen or dry, Hg-free air, equipped
with a single-stage regulator.

3.2 Reagents

3.2.1 Sample Collection and Recovery

a. Water, Absorbing Solution, Silica Gel

See Section 2.2.

b. Nitric Acid (HNO_3), 50 percent (v/v)

Mix equal volumes of concentrated HNO_3 and water. Add the acid to the water very slowly.

3.2.2 Analysis

a. Tin Solution

Dissolve 20 g of tin (II) chloride or 25 g of tin (II) sulfate crystals in 25 ml of concentrated hydrochloric acid (HCl) acid. Dilute to 250 ml with water. Prepare fresh daily and keep sealed when not being used. Do not substitute any other strong acid for HCl .

b. Sodium Chloride - Hydroxylamine
Solution

Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate (or 12 g of hydroxylamine hydrochloride) in water, and dilute to 100 ml.

c. Hydrochloric Acid (HCl), 8N

Dilute 67 ml of concentrated HCl₃ to 100 ml with water.

d. Nitric Acid (HNO₃), 15 percent (v/v)

Dilute 15 ml of concentrated HNO₃ to 100 ml with water.

e. Mercury Stock Solution, 1 mg Hg/ml

Prepare and store all mercury standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g mercury (II) chloride in 75 ml of water. Add 10 ml of concentrated HNO₃ and adjust the

volume to exactly 100 ml with water.
Mix thoroughly. This solution is
stable for at least one month.

f. Intermediate Mercury Standard

Solution, 10 μg Hg/ml

Pipet 5.0 ml of the "Mercury Stock
Solution" into a 500 ml volumetric
flask and add 20 ml of 15 percent HNO_3
solution. Adjust the volume to
exactly 500 ml with water. Thoroughly
mix the solution. Prepare fresh
weekly.

g. Working Mercury Standard Solution, 200

μg Hg/ml

Pipet 5.09 ml from the "Intermediate
Mercury Standard Solution" into a 250
ml volumetric flask. Add 5 ml of 4
percent KMnO_4 absorbing solution and 5
ml of 15 percent HNO_3 . Adjust the
volume to exactly 250 ml with water.
Mix thoroughly. Prepare fresh daily.

- h. Potassium Permanganate (KMnO_4), 5 percent (w/v).

Dissolve 5 μg of KMnO_4 in water and dilute to 100 ml.

- i. Filter

Whatman No. 40 or equivalent.

3.3 Preparation of Sampling Train

Clean all glassware by rinsing with 50 percent HNO_3 , tap water, 8N HCl , tap water, and finally water. Then place 100 ml of 4 percent KMnO_4 solution in each of the first three impingers. Place approximately 200 g of preweighed silica gel in the fifth impinger.

Install the selected nozzle using a Viton A O-ring when stock temperatures are less than 250°C (480°F). Use a fiberglass string gasket if temperatures are higher. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used.

If a filter is used, place the filter in the filter holder with a pair of tweezers. Be sure to center the filter and place the gasket in position to prevent the sample gas stream from bypassing the filter. Check the filter for tears after assembly is completed.

Leak check of the train in the laboratory is desirable.

3.4 Sample Recovery

Upon receipt inspect the train for general condition. Note if the silica gel is expended. Note any unusual conditions that may affect results. Recover the sample as follows:

3.4.1 Container No. 1. (Nozzle, Probe Liner and Impingers)

Using a graduated cylinder, measure the liquid in the first three impingers to within 1 ml. Record the volume of liquid present. This information is needed to calculate the moisture content of the effluent gas. (Use only graduated cylinders and

glass storage bottles that have been pre-cleaned as in Section 3.3.) Place the contents of the first three impingers into a 1000 ml glass sample bottle. (If a filter is used, remove the filter from its holder as outlined under "Container No. 3 in. below.)

Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner, and front half of the filter holder (if applicable) as follows: rinse these components with a total of 250 to 400 ml of fresh 4 percent KMnO_4 solution, add all washings to the 1000 ml glass sample bottle, remove any residual brown deposits on the glassware using the minimum amount of 8N HCl required, and add this HCl rinse to this sample container.

After all washings have been collected in the sample container, tighten the

lid on the container to prevent leakage. Label the container to clearly identify its contents.

3.4.2 Container No. 2. (Silica Gel)

Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container, and seal. As aids, the tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. Weigh the spent silica gel to the nearest 0.5 g and record this weight. Alternatively, weigh silica gel with the impinger.

3.4.3 Container No. 3. (Filter)

If a filter was used, carefully remove it from the filter holder, place it in a 100 ml glass sample bottle, and add 20 to 40 ml of 4 percent KMnO_4 . If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the sample bottle any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and a sharp-edged blade. Seal the container. Label the container to identify its contents.

3.4.4 Container No. 4, (Filter Blank)

If a filter was used, treat an unused filter from the same filter lot used for sampling in the same manner as Container No. 3.

3.4.5 Container No. 5 (Absorbing Solution Blank)

For a blank place 500 ml of 4 percent KMnO_4 , absorbing solution in a 1000 ml sample bottle. Seal the container.

3.5 Sample Preparation

Check level of the liquid in each container to ensure that no liquid was lost.

3.5.1 Containers No. 3 and 4

If a filter was used, place the contents, including the filter, of Containers No. 3 and No. 4 in separate 250 ml beakers, and heat the beakers on a steam bath until most of the liquid has evaporated. Do not take to dryness. Add 20 ml of concentrated HNO_3 to the beakers, cover them with a glass, and heat on a hot plate at 70°C for 2 hours. Remove from the hot plate and filter the solution through Whatman No. 40 filter paper. Save the

filtrates for Hg analysis. Discard the filters.

3.5.2 Container No. 1

Filter the contents of Container No. 1 through Whatman No. 40 filter paper to remove the brown MnO_2 precipitate.

Wash the filter with 50 ml of 4 percent KMnO_4 absorbing solution and add this wash to the filtrate.

Discard the filter. Combine the filtrates from Containers No. 1 and No. 3 (if applicable), and dilute to a known volume with water. Mix thoroughly.

3.5.3 Container No. 5

Treat this container as described in Section 3.5.2. Combine this filtrate with the filtrate of Container No. 4 and dilute to a known volume distilled water. Mix thoroughly.

3.6 Sample Analysis

Calibrate the spectrophotometer and recorder and prepare the calibration curve as described in Sections 3.7. Then repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 10 ml) of the samples until two consecutive peak heights agree within 3 percent of their average value. If the 10 ml sample is below the detectable limit, use a larger aliquot (up to 20 ml), but decrease the volume of water added to the aeration cell accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1.0 ml aliquot is off scale, further dilute the original sample to bring the Hg concentration into the calibration range of the spectrophotometer. If the Hg content of the absorbing solution and filter blank is below the working range of the analytical method, use zero for the blank.

Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary.

It is also recommended that at least one sample from each stack test be checked by the Method of Standard Additions to confirm that matrix effects have not interfered in the analysis. This method can be found in the Varian Manual, Introducing Atomic Absorption Analysis (1983), or in The Perkin Elmer Manual, Analytical Methods for Atomic Absorption Spectrophotometry (1976).

3.7 Calibration

Before use, clean all glassware, both new and used, as follows: brush with soap and tap water, liberally rinse with tap water, soak for 1 hour in 50 percent HNO₃, and then rinse with water.

3.7.1 Flow Calibration

Assemble the aeration system as shown in Figure 101.1-5. Set the outlet pressure on the aeration gas cylinder regulator to a minimum pressure of 500 mm Hg (10 psi). Use the flowmetering valve and a bubbler flowmeter or wet test meter to obtain a flow rate of 1.5 ± 0.1 liters/minute through the aeration cell. After the

flow calibration is complete, remove the bubbler flowmeter from the system.

3.7.2 Optical Cell Heating System Calibration

Using a 25 ml graduated cylinder, add 25 ml of water to the bottle section of the aeration cell. Attach the bottle section to the bubbler section of the cell and the aeration cell to the optical cell. While aerating at 1.5 liters/minute, determine the minimum variable transformer setting necessary to prevent condensation of moisture in the optical cell and in the connecting tubing. (This setting should not exceed 20 volts.)

3.7.3 Spectrophotometer and Recorder Calibration

The mercury response may be measured by either peak height or peak area.

The temperature of the solution affects the rate at which elemental Hg

is released from a solution, and consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). To obtain reproducible results, all solutions must be brought to room temperature before use.

Set the spectrophotometer wavelength at 253.7 nm and make certain that the optical cell is at the minimum temperature that will prevent water condensation. Set the recorder scale as follows: using a 25 ml graduated cylinder, add 25 ml of water to the aeration cell bottle and pipet 5.0 ml of the mercury standard solution into the aeration cell. Always add the Hg containing solution to the aeration cell after the 25 ml of water.

Place a Teflon-coated stirring bar in the bottle. Add 5 ml of 15 percent HNO_3 and 5 ml of 5 percent KMnO_4 to the aeration bottle and mix well. Attach the bottle section to the bubbler section of the aeration cell.

Before attaching, make certain that the aeration cell exit arm stopcock (Figure 101.1-3) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added), and there is no flow through the bubbler.

Add 5 ml of sodium chloride hydroxylamine in 1 ml increments until the solution is colorless. Now add 5 ml of tin (II) solution to the aeration bottle through the side arm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90 percent of the recorder full scale.

3.8 Calculations

For each source sample, apply a correction for the contribution of the field blank to the average maximum absorbance of the two consecutive

samples with peak heights that agree within 3 percent of their average. Use the calibration curve and this corrected average to determine the final weight of mercury in nanograms in the aeration cell for each source sample. Correct for dilutions made to bring the sample into the working range of the spectrophotometer. Calculate the Hg content in μg in the original solution as follows:

$$M_{\text{Hg}} = \frac{C_{\text{Hg}}(\text{AC}) (\text{DF}) V_f 10^{-3}}{S}$$

where:

M_{Hg} = Total Hg content in each sample, μg

$C_{\text{Hg}}(\text{AC})$ = Total nanograms of mercury in aliquot analyzed (reagent blank subtracted)

DF = Dilution factor for the Hg containing solution (before adding to the aeration cell)

V_f = Solution volume of original sample, ml

10^{-3} = Conversion factor, $\mu\text{g}/\text{ng}$

S = Aliquot volume added to
aeration cell, ml

METHOD 101.1

DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM STATIONARY SOURCES

Section 4 of 4

4. Engineering Calculations

Calculate the Hg emission rate using the following equation:

$$ER_{Hg} = \frac{M_{Hg}(A) (60 \times 10^{-6})}{V_m}$$

where:

ER_{Hg} = Emission rate of Hg, g/hr

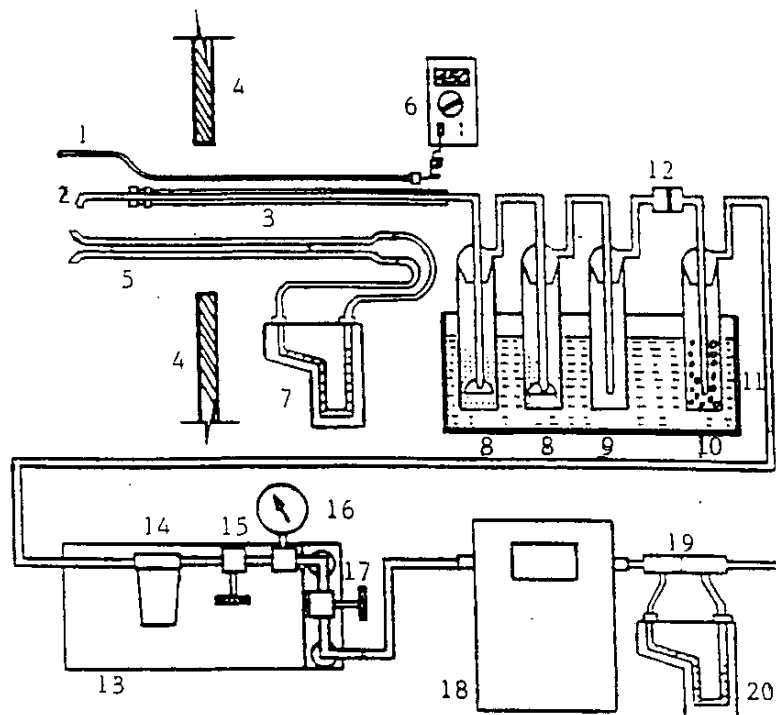
M_{Hg} = Total Hg in each sample, μg

A = Exhaust flow rate, dscmm (dscfm)

60 = Conversion factor, min/hr

10^{-6} = Conversion factor, g/ μg

V_m = Sample volume, dscmm (dscfm)



- | | |
|---|--|
| 1. Temperature Sensor | 11. Ice Bath |
| 2. Nozzle | 12. Filter (Optional) |
| 3. Glass Lined Stainless Steel Probe | 13. Sealed Pump (Leak Free) |
| 4. S-type Pitot Tube | 14. Filter for Pump |
| 5. Stack Wall | 15. Metering Valve |
| 6. Temperature Sensor Meter | 16. Vacuum Gauge |
| 7. Pitot Tube Inclined Manometer | 17. By-pass Valve |
| 8. Impinger with 100 ml
Acidic KMnO_4 | 18. Temperature Compensated
Dry Gas Meter |
| 9. Empty Bubbler | 19. Orifice |
| 10. Bubbler with Silica Gel | 20. Orifice Inclined Manometer |

Figure 101.1-1

Mercury Sampling Train Setup-Wet Impingement Method

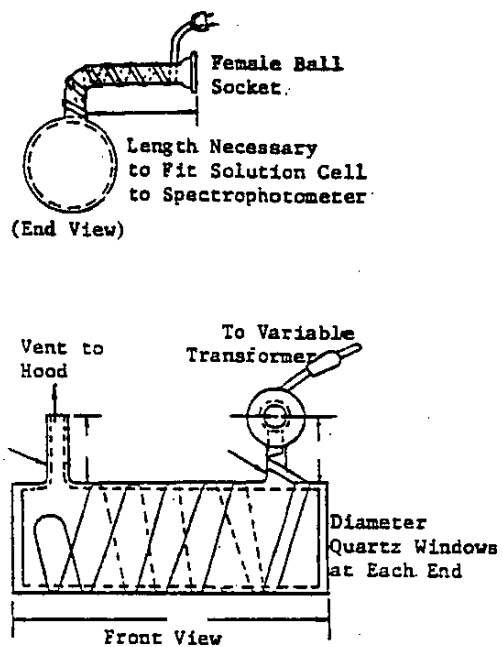


Figure 101.1-2
Optical Cell

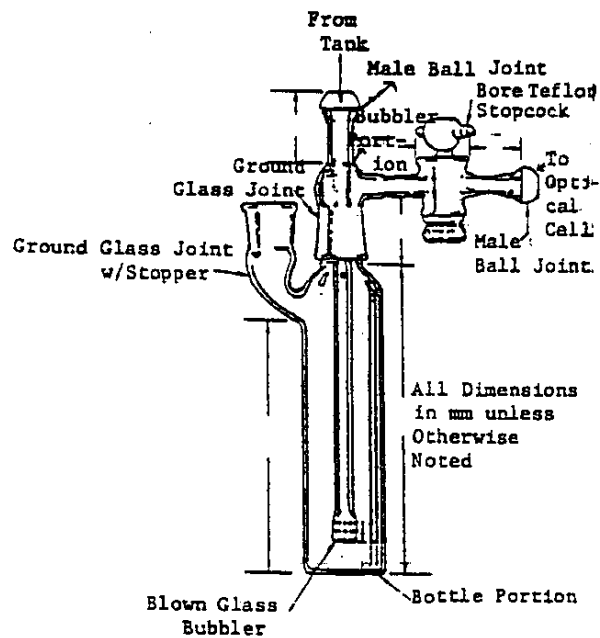
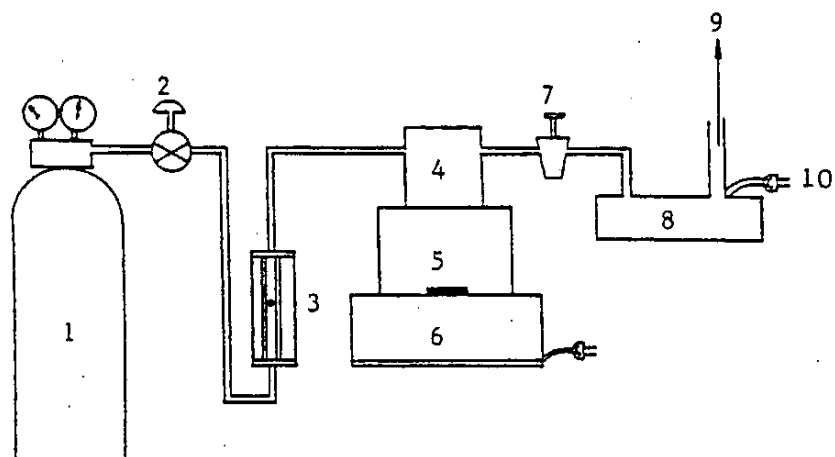


Figure 101.1-3
Aeration Cell



- | | |
|----------------------------------|-----------------------------|
| 1. N ₂ Cylinder | 6. Magnetic Stirrer |
| 2. Needle Valve for Flow Control | 7. Exit Arm Stopcock |
| 3. Flow Meter | 8. Optical Cell |
| 4. Aeration Cell | 9. To Hood |
| 5. Magnetic Stirring Bar | 10. To Variable Transformer |

Figure 101.1-4
Schematic of Aeration System