SUMMARY SHEET 101
Mercury

Method (circle) 101 101A 102

			Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 5				
Job No.		FDS 5				
Sampling Location		FDS 5				
Run ID #		FDS 5				
Test Date		FDS 5				
Run Start Time		FDS 5				
Run Finish Time		FDS 5				
Net Traverse Points		FDS 1				
Traverse Matrix (Rectangular)		FDS 1				
Net Run Time, min	θ	FDS 5				
Nozzle Diameter, in.	D_n	FDS 5				
Dry Gas Meter Calibration Factor	Y	CDS 5				
Average ΔH (orifice meter), in. H_2O	ΔH	FDS 5				
Barometric Pressure, in. Hg	P_b	FDS 5				
Stack Static Pressure, in. H_2O	P_g	FDS 5				
Abs Stack Pressure ($P_b + P_g/13.6$), in. Hg	P_s	SS 5				
Average Stack Temperature, °F	t_s	FDS 5				
Avg Abs Stack Temperature ($460 + t_s$), R	T_s	SS 5				
Carbon Dioxide, % dry	$\%CO_2$	FDS 3				
Oxygen, % dry	$\%O_2$	FDS 3				
Carbon Monoxide + Nitrogen, % dry	$\%(CO+N_2)$	FDS 3				
Dry Molecular Weight, lb/lb-mole	M_d	FDS 3				
Average DGM Temperature, °F	t_m	FDS 5				
Volume of Metered Gas Sample, dcf	V_m	FDS 5				
Volume of Metered Gas Sample, dscf	$V_{m(std)}$	SS 5				
Volume Water Condensed, mL	V_{lc}	FDS 5				
Volume of Water Vapor, scf	$V_{w(std)}$	SS 5				
Moisture Content, fraction	B_{ws}	SS 5				
Pitot Tube Coefficient	C_p	CDS 2a				
Average Velocity Pressure, in. H_2O	Δp	FDS 5				
Average $[(t_{si} + 460)\ \Delta p]^{1/2}$	$[T_{si}\ \Delta p]^{1/2}$	FDS 5				
Velocity, ft/sec	v_s	SS 5				
Stack Area, ft^2	A	FDS 1				
Isokinetic Sampling Rate, %	%I	SS 5				
Mercury in original solution, μg	m_{Hg}	LDS 101				
Mercury Emission Rate, g/day	R	SS 101				
Audit Relative Error, %	RE	QA 1				
Matrix Check		LDS 12a				

Method (circle) 101 101A 102

		Run #1	Run #2	Run #3	Avg
Post-test Calibration Checks					
Temperature and Barometer	CDS 2d				
Differential Pressure Gauges	CDS 2d				
Metering System	CDS 5				

$$R = 17.64 \frac{m_{Hg} v_s A (86{,}400 \times 10^{-6})}{[V_{m(std)} + V_{w(std)}] \frac{T_s}{P_s}}$$

FIELD PROCEDURE 101
Particulate and Gaseous Mercury Emissions from Chlor-Alkali Plants

Note: This field procedure is the same as that in Method 5. Follow the general procedure given in FP 5, except for the items noted below. Use FDS 5.

A. Pretest Preparation

1. Omit the directions for the filter.
2. Clean all glassware (probe, impingers, and connectors, including sample recovery glassware) by rinsing with 50% HNO_3, tap water, 0.1 M ICl, tap water, and finally deionized distilled water.

B. Preliminary Determinations

1. Select a nozzle size to maintain isokinetic sampling rates below 1.0 cfm.
2. Select the sampling time (at least 2 hr) that accurately determines the maximum emissions that occur in a 24-hr period. For cyclic operations, run sufficient runs to accurately represent the emissions over the cycle.
3. When Hg or SO_2 concentrations are high, indicated by reddening (liberation of free iodine) in the first impinger, the sample run may be divided into two or more subruns to avoid depletion of absorbing solution.

C. Preparation of Sampling Train

1. Assemble the train as shown in Figure F101-1.
   a. Place 100 mL 0.1 M ICl in each of the first three impingers.
   b. Place about 200 g preweighed silica gel in the fourth impinger.
   c. An empty impinger may be inserted between the third impinger and the silica gel to remove excess moisture.
2. Use a Viton A O-ring for the nozzle when stack temperatures are $<500°F$ or a fiberglass string gasket when $>500°F$.

D. Sample Recovery

1. The cleanup area must be free of Hg contamination.
2. <u>Container No. 1</u> (Impinger/Probe)
   a. Measure the liquid in the first three impingers to within 1 mL. Place the contents into a 1000-mL glass sample bottle.
   b. Add any condensate and all washings to the 1000-mL glass sample bottle.
   c. Rinse probe nozzle, fitting, and liner with two 50-mL portions of 0.1 M ICl.
   d. Rinse the probe nozzle, fitting, and liner, and each piece of connecting glassware between the probe liner and the back half of the third impinger with ≤ 400 mL water.
   e. Tighten the lid on the container; mark the liquid level. Label the container.
3. <u>Container No. 2</u> (Silica Gel)

   See FP 5, step E5.
4. <u>Container No. 3</u> (Absorbing Solution Blank)

   Place 50 mL 0.1 M ICl absorbing solution in a 100-mL sample bottle. Seal and label the container.

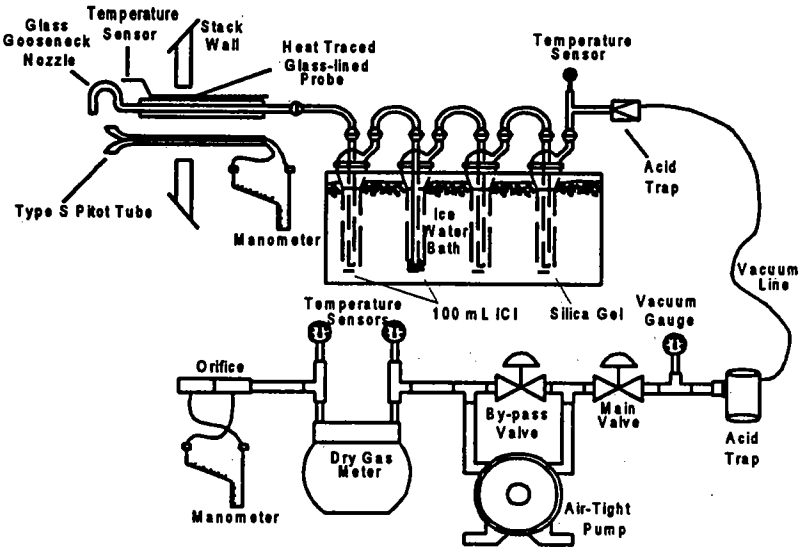

Figure F101-1. Mercury Sampling Train.

LABORATORY PROCEDURE 101
Particulate and Gaseous Mercury Emissions from Chlor-Alkali Plants

A. *Reagent Preparation*

1. Nitric Acid, 50%. Slowly adding the acid to the water, mix equal volumes of conc. HNO_3 and water.
2. Potassium Iodide, 25%. Dissolve 250 g KI in water, and dilute to 1 L.
3. Iodine Monochloride (ICl) Stock Solution, 1.0 M. Add 800 mL conc. HCl to 800 mL 25% KI. Cool. While stirring vigorously, slowly add 135 g potassium iodate (KIO_3), until a clear orange-red solution occurs. Cool, and dilute to 1800 mL with water. Keep the solution in amber glass bottles.
4. ICl Absorbing Solution, 0.1 M. Dilute 100 mL 1.0 M ICl stock solution to 1 L with water. Keep the solution in amber glass bottles and in darkness. Do not use after two months.
5. Tin (II) Solution. Prepare fresh daily, and keep sealed. Dissolve 20 g tin (II) chloride [or 25 g tin (II) sulfate] crystals in 25 mL conc. HCl. Dilute to 250 mL with water. Do not use other acids for HCl.
6. Hg Stock Solution, 1 mg/mL. Prepare and store all Hg standard solutions in glass containers. Dissolve 0.1354 g Hg (II) chloride in 75 mL water in a 100-mL glass volumetric flask. Add 10 mL conc. HNO_3, and adjust the volume to 100 mL with water. Mix thoroughly. Do not use after one month.
7. Sulfuric Acid, 5%. Dilute 25 mL conc. H_2SO_4 to 500 mL with water.
8. Intermediate Hg Standard Solution, 10 µg/mL. Prepare fresh weekly. Pipet 5.0 mL Hg stock solution into a 500-mL glass volumetric flask, and add 20 mL 5% H_2SO_4 solution. Dilute to 500 mL with water. Thoroughly mix the solution.
9. Working Hg Standard Solution, 200 ng/mL. Prepare fresh daily. Pipet 5.0 mL "Intermediate Hg Standard Solution" into a 250-mL volumetric glass flask. Add 10 mL 5% H_2SO_4 and 2 mL 0.1 M ICl absorbing solution that was taken as a blank and dilute to 250 mL with water. Mix thoroughly.

B. *Sample Preparation*

1. Note the level of liquid in the sample containers, and determine loss; note this loss, if any, on LDS 101.
2. Container No. 1 (Impinger/Probe)
   a. Transfer contents into a 1000-mL volumetric flask, and adjust volume to 1000 mL with water.
   b. Pipet 2 mL of diluted sample into a 250-mL volumetric flask. Add 10 mL 5% H_2SO_4, and adjust the volume to 250 mL with water. This solution is stable for 72 hr. (Note: The dilution factor will be 250/2 for this solution.)

C. *Equipment Preparation*

1. Clean all glassware, both new and used, as follows: Brush with soap and water, liberally rinse with tap water, soak for 1 hr in 50% HNO_3, and then rinse with deionized distilled water.
2. Set the ***flow rate through the aeration cell*** to 1.5 ± 0.1 L/min.
   a. Assemble the aeration system (see Figure L101-1).
   b. Set the outlet pressure on the aeration gas cylinder regulator to ≥10 psi.
   c. Use a flowmetering valve and bubble flowmeter to set the flow rate.
3. Calibrate the ***optical cell heating system*** as follows:
   a. Add 50 mL of water to the bottle section of the aeration cell, and attach to the bubbler section of the cell.
   b. Attach the aeration cell to the optical cell, aerate at 1.5 L/min, and determine the minimum variable transformer setting (not to exceed 20 volts) to prevent condensation in optical cell and connecting tubing.
4. Calibrate the ***spectrophotometer and recorder*** as follows:
   a. Set the spectrophotometer wavelength to 253.7 nm. Set the heating system on the optical cell at the minimum temperature to prevent condensation.
   b. First add 50 mL water to the aeration cell bottle, and then pipet 5.0 mL of the working Hg standard solution (or any Hg-containing solution) into the aeration cell. Never switch the order.

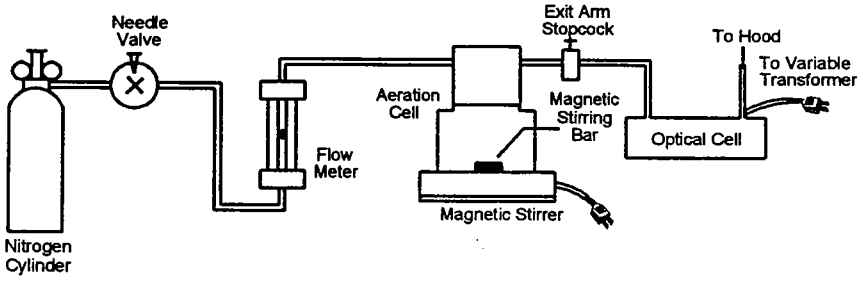

Figure L101-1. Schematic of Aeration System.

c. Place a Teflon-coated stirring bar in the bottle. **First** close the aeration cell exit arm stopcock and ensure that there is no flow through the bubbler. **Then**, attach the bottle section to the bubbler section of the aeration cell.

d. Pipet 5 mL stannous chloride solution into the aeration cell through the side arm, and immediately stopper the side arm. Stir for 15 sec, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring.

e. Determine maximum absorbance of the standard, and set this value to read 90% of the recorder full scale.

D. Calibration Curve

1. After setting the recorder scale, repeat steps C4a through C4d using 0.0-, 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-mL aliquots of the working standard solution (final amount of Hg in the aeration cell is 0, 200, 400, 600, 800, and 1000 ng, respectively).

2. Repeat until two consecutive peaks agree within 3% of their average value. [Note: Bring all solutions to room temperature to obtain reproducible results. Temperature affects the release rate of elemental Hg from a solution, the shape of the absorption curve, and the point of maximum absorbance.]

3. To prevent Hg carryover from one sample to another, do not close the aeration gas tank valve and do not disconnect the aeration cell from the optical cell until the recorder pen has returned to the baseline.

4. Between samples,

   a. It is unnecessary to disconnect the aeration gas inlet line from the aeration cell.

   b. After separating the bottle and bubbler sections of the aeration cell, place the bubbler section into a 600-mL beaker containing ~400 mL water.

   c. Rinse the bottle section of the aeration cell with water to remove all traces of the tin (II) reducing agent.

   d. Wash the aeration cell parts with conc. HCl if any of the following conditions occur:

      - A white film appears on any inside surface of the aeration cell
      - The calibration curve changes suddenly.
      - Replicate samples do not yield reproducible results.

5. Subtract the average peak height (or peak area) of the 0.0-mL aliquot blank from the averaged peak heights of the other aliquot standards. The blank absorbance should be ≤2% of full-scale; if greater, check for Hg contamination of a reagent or carry-over of Hg from a previous sample.

6. Plot the corrected peak height of each standard solution versus the corresponding final total Hg weight in the aeration cell (in ng), and draw the best-fit straight line. This line should either pass through the origin or pass through a point no further from the origin than ±2% of the recorder full scale. If not, check for nonlinearity of the curve and for incorrectly prepared standards.

E. Analysis

1. Container No. 1 (Impinger/Probe)

   a. Analyze an appropriately sized aliquot (1 to 5 mL) of the diluted sample until two consecutive peak heights agree within ±3% of their average. The peak maximum of an aliquot (except the 5 mL aliquot) must be >10% of the recorder full scale. If the 1.0 mL aliquot is off scale on the recorder, dilute the source sample.

   b. Run a blank and standard after every five samples; recalibrate as necessary.

   c. Check at least one sample from each test by the method of standard additions to confirm that matrix effects have not interfered in the analysis (see **LP 12, section D**).

2. Container No. 2 (Silica Gel)

   Weigh and record the spent silica gel to the nearest 0.5 g using a balance.

F. Alternative Analytical Apparatus

Alternative systems are allowable as long as they meet the following criteria:

1. A linear calibration curve is generated and two consecutive samples of the same aliquot size and concentration agree within ±3% of their average.

2. Spike recovery of Hg (II) is ≥95%.

3. Reducing agent is added after the aeration cell is closed.

4. The aeration bottle bubbler does not contain a frit.

5. Any Tygon tubing is as short as possible and conditioned until blanks and standards yield linear and reproducible results.
6. If manual stirring is done before aeration, it is done with the aeration cell closed.
7. A drying tube is conditioned as the Tygon tubing above.

LABORATORY DATA SHEET 101
Mercury

Client/Plant Name _____ Job # _____ Date _____

Spectrophotometer ID# _____ Date of Last Calibration _____ (≤6 months?)

Wavelength *(253.7 nm?)* _____ Temp. of optical cell _____ °F Analyst _____

Working Stds (mL)	Peak Height (H) 1	2	Avg.	H (Blk corr)	C_{Hg} (ng Hg)
0.0					0.0
1.0					200
2.0					400
3.0					600
4.0					800
5.0					1000

Note: Repeat each standard until two consecutive peaks agree within 3% of their average value.

Plot calibration curve [H_{avg} (corr) vs. C_{Hg}. Best fit straight line must pass through origin ±2% of F.S.

Sample ID#	Vol. Loss, (mL)	Sample Vol., V_f (mL)	Dilution Factor, D.F.	Aliquot Vol., S (mL)	Peak Height, H 1	2	Avg.	H Blk corr	C_{Hg} blk corr (ng)	m_{Hg} (μg)
Blank										
Standard										

m_{Hg} = µg in the original solution:

$$m_{Hg} = \frac{C_{Hg}\,(D.F.)\,V_f\,10^{-3}}{S}$$

____ All solutions at room temperature before analysis?

____ Peak maximum of an aliquot greater than 10% of the recorder full scale?

____ A blank and standard run after every 5 samples?

____ One sample checked by the method of standard additions? (Attach LDS).

QA/QC Check

Completeness ____ Legibility ____ Accuracy ____ Specifications ____ Reasonableness ____

Checked by: _____ _____

Personnel (Signature/Date) Team Leader (Signature/Date)

FIELD PROCEDURE 101A
Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators

Note: This method is similar to Method 101, except acidic potassium permanganate solution is used for sample collection and for the following variations: ***Use FDS 5.***

A. Preliminaries

1. Use fiberglass filters whenever particulate matter concentration is high. When the filter is ahead of the impingers, use the probe heating system to minimize the condensation of gaseous Hg.
2. Use a filter holder made of borosilicate glass with a rigid stainless steel wire-screen filter support (do not use glass frit supports), a silicone rubber or Teflon gasket, and a filter heating system.
3. If high oxidizable organic content completely bleaches the purple color of the $KMnO_4$ solution, divide the sample run into two or more subruns.
4. If there is excess water condensation, collect two runs to make one sample.

B. Preparation of Sampling Train and Sampling

1. Clean all glass sampling and sample recovery components by rinsing with 50% HNO_3, tap water, 8 N HCl, tap water, and finally DI water.
2. Place 50 mL of 4% $KMnO_4$ in the first impinger and 100 mL in each of the second and third impingers.
3. If a filter is used, see FP 5, step C4.
4. Maintain a temperature around the filter (if applicable) at 248 ± 25°F during sampling.

C. Sample Recovery

1. Container No. 1 (Impinger/Probe/Filter Holder)
   a. Measure the liquid volume in the first three impingers to within ±1 mL. Place in 1000-mL glass sample bottle.
   b. Rinse these components with a total of 250 to 400 mL of fresh 4% $KMnO_4$ solution; add all washings to the 1000-mL sample bottle.
   c. Remove any residual brown deposits on the glassware using the minimum amount of 8 N HCl required; add to the sample bottle.
2. Container No. 2 (Silica Gel)

   See FP 5, step E5.
3. Container No. 3 (Filter)
   a. Carefully remove the filter from the filter holder, place it in a 100-mL glass sample bottle, and add 20 to 40 mL 4% $KMnO_4$. If necessary, fold the filter such that the particulate cake is inside the fold.
   b. Transfer any particulate matter and filter fibers that adhere to the filter holder gasket to the sample bottle by using a dry Nylon bristle brush and a sharp-edged blade. Seal and label the container.
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.
5. Container No. 5 (Absorbing Solution Blank)

   Place 500 mL 4% $KMnO_4$ absorbing solution in a 1000-mL sample bottle. Seal and label the container.

LABORATORY PROCEDURE 101A
Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators

Note: *This laboratory procedure is similar to LP 101, except for the permanganate absorbing solution (used instead of iodine monochloride) and for the variations below. Use LDS 101.*

A. Reagent Preparation

1. Sulfuric Acid, 10%. Mix 100 mL conc. H_2SO_4 with 900 mL water.
2. $KMnO_4$ Absorbing Solution, 4%. Dissolve 40 g $KMnO_4$ in 10% H_2SO_4 to make 1 L. Prepare fresh daily and store in glass bottles.
3. Sodium Chloride-Hydroxylamine Solution. Dissolve 12 g NaCl and 12 g hydroxylamine sulfate (or 12 g hydroxylamine hydrochloride) in water; dilute to 100 mL.
4. Hydrochloric Acid, 8 N. Dilute 67 mL conc. HCl to 100 mL with water.
5. Nitric Acid, 15%. Dilute 15 mL conc. HNO_3 to 100 mL with water.
6. Potassium Permanganate, 5%. Dissolve 5 g $KMnO_4$ in water; dilute to 100 mL.

B. Sample Preparation

1. Container Nos. 3 and 4 (Filter and Filter Blank)
   a. Place contents, including the filter, 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.
   b. Add 20 mL conc. HNO_3 to the beakers, cover them with a watch glass, and heat on a hot plate at 70°C for 2 hr.
   c. Remove from the hot plate, and filter the solution through Whatman No. 40 filter paper. Save the filtrate for Hg analysis. Discard the filter.
2. Container No. 1 (Impinger/Probe/Filter Holder)
   a. Filter contents through Whatman 40 filter paper to remove the brown MnO_2 precipitate.
   b. Wash the filter with 50 mL 4% $KMnO_4$ absorbing solution, and add this wash to the filtrate. Discard the filter.
   c. Combine the filtrates from Container Nos. 1 and 3, dilute to a known volume with water. Mix thoroughly.
3. Container No. 5 (Absorbing Solution Blank).
   a. Treat this container as described in step B3.
   b. Combine this filtrate with the filtrate from Container No. 4, and dilute to a known volume with water. Mix thoroughly.

C. Equipment Preparation

1. Calibrate the ***optical cell heating system*** as in LP 101, step C3, except add 25 mL water to the bottle section of the aeration cell.
2. Calibrate the ***spectrophotometer and recorder*** as follows:
   a. Set the spectrophotometer wavelength at 253.7 nm. Set the optical cell heating system (see step C1).
   b. **First** add 25 mL water to the aeration cell bottle, and **then** pipet 5.0 mL working Hg standard solution (or any Hg-containing solution) into the aeration cell. Never switch the order.
   c. Place a Teflon-coated stirring bar in the bottle. Close the stopcock on the aeration cell exit arm, and ensure that there is no flow through the bubbler.
   d. Add 5 mL 4% $KMnO_4$, 5 mL 15% HNO_3, and 5 mL 5% $KMnO_4$ to the aeration bottle, and mix well. Now, attach the bottle section to the bubbler section of the aeration cell.
   e. Add 5 mL sodium chloride hydroxylamine in 1-mL increments until the solution is colorless.
   f. Add 5 mL tin (II) solution to the aeration bottle through the side arm, and immediately stopper the side arm. Stir the solution for 15 sec, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring.
   g. Determine the maximum absorbance of the standard, and set this value to read 90% of the recorder full scale.

D. Analysis

1. Follow the procedure to establish the calibration curve (see **LP 101, section D**) with appropriately sized aliquots (1 to 10 mL) of the samples until two consecutive peak heights agree within ±3% of their average value. See LP 101, section E for additional steps.

2. 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.

3. 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.