Standard Operating Procedure for Sampling of Vapor Phase Mercury

Gerald J. Keeler and Matthew S. Landis
University of Michigan
Air Quality Laboratory
109 South Observatory Street
Ann Arbor, MI 48109-2029

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1.0 Introduction to Principals of Vapor Phase Mercury Sampling and Analysis

Mercury in the atmosphere exists predominantly in the gas phase in the form of elemental mercury (Schroeder, 1982). Other species of mercury found in the gas phase include methyl and dimethylmercury, and mercuric chloride, mercuric hydroxide and free divalent mercury. Vapor phase mercury is quantitatively removed from an air stream by amalgamation onto gold. While the amalgamation process is believed to remove most vapor phase mercury species with >99% efficiency, the analytical procedure employed determines whether or not 'total mercury' or predominantly elemental mercury is quantified. At the University of Michigan Air Quality Laboratory (UMAQL) vapor phase mercury is collected onto gold-coated borosilicate glass bead traps by drawing air at a low flow rate through a baked glass fiber pre-filter followed by the gold-coated borosilicate glass bead trap. The air is prefiltered to eliminate particles from the gas phase collection traps. After sampling, vapor phase mercury is quantified by cold vapor atomic florescence spectrometry (CVAFS).

In the past, methods for collection of vapor phase mercury have dictated long sampling duration, often from 24 hours up to a week. The collection method employed for the Lake Michigan Loading Study and described in this protocol uses gold-coated borosilicate glass bead traps, which UMAQL has determined to be >99% efficient at collection of vapor phase mercury (at a flow rate <1 lpm). Dual-amalgamation and subsequent analysis by cold-vapor atomic florescence, allows detection of mercury at picogram levels. After thermal desorption, gold-coated bead traps are re-used since they do not exhibit memory effects. Due to the collection efficiency of gold-coated beads and the ability to detect picogram amounts of mercury, sampling strategies using gold-coated bead traps can employ much shorter duration samples than have previously been possible. Short sampling duration provides the resolution necessary to use receptor models in determining sources and source contributions of measured vapor phase mercury.

Preparation and collection of accurate and reliable data on mercury concentrations in environmental samples requires that ultra clean procedures are used. All sampling supplies with which a sample will come into contact must be acid cleaned in a Class 100 Clean Room. At the sampling site, precautions taken to avoid contamination of the sample include storing samples at an outdoor staging area and special operator handling. These and other techniques employed to minimize contamination of the samples are described in detail in this protocol.

2.0 Sample Preparation

2.1 Acid Cleaning Procedure

All Teflon filter packs, Teflon jars, Teflon tubing, gold trap fittings and end plugs (referred to below as 'supplies') are cleaned using an 11-day procedure described by Rossmann and Barres (1991).

Supplies to be acid cleaned are first rinsed in reagent grade acetone under a fume hood, then washed in hot tap water and diluted Alconox. Supplies are rinsed five times in cold tap water then rinsed three times in DI water. The supplies are then heated in 3M hydrochloric acid (EM Science Tracepur HCl in Milli-Q water (18.2 MÙ/cm)) for six hours at 80°C. One liter of 3M HCl is prepared by adding 750 mL of Milli-Q water to 250 mL of concentrated EM Science Tracepur HCl. The 3M HCl can be used several times and is stored for reuse in a polyethylene carboy dedicated for this purpose. The supplies are placed into clean polyethylene tubs which are then filled with the 3M HCl, making sure that all of the surfaces are submersed in the HCl. The tubs are covered and placed in a water bath which is heated to 80°C in a fume hood. The water in the bath is maintained at the level of the acid inside the tubs. After the water in the bath reaches 80°C, the supplies in the tubs are allowed to soak for six hours.

After the six hours, 80°C soak, the tubs are removed from the water bath and allowed to cool in the fume hood. When cool, the 3M HCl is poured back into its polyethylene carboy. The supplies are rinsed in the tubs three times with Milli-Q water. The supplies are then soaked in a 0.56M nitric acid solution (Baker Instra-Analyzed HNO_3 in Milli-Q water) for 72 hours at room temperature in the same polyethylene tubs in which they were heated with HCl. The nitric acid solution is made by adding 35 mL Baker Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. Nitric acid is reused for up to six months and is stored in a carboy dedicated for HNO_3. At the end of the three-day soak, the supplies being cleaned are rinsed three times with Milli-Q water and transferred into a Class 100 Clean Room.

Inside the clean room, the supplies are again rinsed three times with Milli-Q water. The tubs containing the supplies are filled with 0.56M Baker Instra-Analyzed HNO_3 that is kept in the clean room and is dedicated for this final step only. The supplies are then allowed to soak in this acid for seven days. This acid is prepared by adding 35 mL of the Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. At the end of the seven day acid soak inside the clean room, the supplies are rinsed five times with Milli-Q water and allowed to air dry on a clean surface. When the supplies are dry, they are triple bagged in new polyethylene bags and removed from the clean room, ready for use in sampling.

2.2 Preparation of Gold-Coated Bead Traps and Pre-Filters

Gold-coated borosilicate glass bead traps are constructed at The University of Michigan Air Quality Laboratory and tested prior to use in the field. The gold-coated beads used in the traps are made by generating a gold plasma under vacuum conditions that uniformly deposits onto the surface of the beads. The thickness of the coating generated using this process is about 300 Å. The gold-coated beads are contained in a quartz tube which is 10 cm long with an inner diameter of 5 mm and an outer diameter of 7 mm. Teflon heat-shrink tubing is attached to both ends of the tube into which Teflon endplugs are placed when the trap is in storage or connectors when the trap is being used to collect a sample. Each trap contains approximately 0.7 g of gold-coated borosilicate glass beads which are held in place using quartz wool and two sets of three radial indentations in the quartz tube. The gold-coated beads, quartz tubes and quartz wool are baked at 600ºC for one hour prior to making the trap. In addition, Teflon endplugs and heat shrink tubing are acid cleaned as previously described. After each trap is made, it is given a unique number identifier in order to chart the history and performance of the trap. New traps are first conditioned by drawing approximately 0.4 m^3 of air through the trap then heating the trap to 500°C for five minutes. Inert gas is purged through the traps at 300 cc/min during heating procedure to remove

moisture and other volatile constituents. The conditioning procedure is performed twice prior to testing the trap. The trap is then tested by injecting a known amount of elemental mercury vapor and comparing the result to an analytical standard. The trap must exhibit duplicate measurements that are within 5% of the standard and the replicate measurements must also be within 5% of each other. Following this test, the trap is then blanked (described below) and stored for seven days. After seven days, the trap is analyzed for a storage blank (sample analysis is described in the *Standard Operating Procedure for Analysis of Vapor Phase Mercury*). The storage blank must be less than 15 pg for the trap to be accepted for use in field sampling. Gold traps are stored with endplugs in place, triple bagged in polyethylene before and after sampling.

Just before going into the field to collect vapor phase mercury samples, gold-coated bead traps are blanked again. Blanking a trap removes all mercury from the gold-coated bead surface and will also remove water vapor and other unwanted constituents. Traps are blanked by placing them in the analytical train and heating them to 500°C for two minutes, identical to a normal sample analysis.

Vapor phase mercury samples collected onto gold-coated borosilicate glass bead traps must be prefiltered to exclude particles. Glass fiber filters (Gelman Sciences) are pre-treated to remove all mercury prior to use in sampling. Glass fiber filters, 47 mm in diameter, are placed in a clean crucible with a lid. The crucible is placed in a muffle furnace which is heated to 500°C and the filters are allowed to bake at this temperature for one hour. While hot, filters are removed from the crucible with acid-cleaned Teflon-coated forceps and placed in an acid-cleaned Teflon jar which is closed and sealed with Teflon tape. The Teflon jar is triple bagged and stored at -40°C until use. Filters are stored no more than three months prior to use and frequent blanks are taken to ensure the filters remain clean.

3.0 Vapor Phase Mercury Sample Collection

During sample collection the filter packs and gold bead traps are housed in a sampling box that is mounted on a pole or tower at least 3 meters above ground level. The sampling boxes were custom-made at UMAQL from fiberglass enclosures (Stahlin Enclosures) using quick connect couplings to connect the vacuum lines from the pump to the sampling devices. Sample intakes are at least 30 cm apart and are not positioned near any potential contaminant sources.

A flow rate of approximately 300 cc/min. is typically used to sample with gold-coated bead traps, however, in highly contaminated areas flow rates less than 300 cc/min. may be desirable. Sample duration and flow rate depend on the study design. The sampling flow rate is maintained with a mass flow controlling device in order to maintain constant flow throughout the sampling period. During the Lake Michigan Loading Study all samples collected will consist of two traps in series. The front trap (A) is used to remove mercury from the air stream and the second trap (B) is used as a back up to characterize any breakthrough from the front trap. The flow rate through the inlet of the front trap must be confirmed before setting up each sample using 'test' traps instead of the sample traps, since any flow measuring device in front of the inlet could potentially contaminate the sample. Air is not drawn into a gold trap without a pre-filter attached since this will result in particle buildup inside the trap. All pumps used for sampling are allowed to warm up for at least 30 minutes prior to use.

3.1 Setting Up Gold-Coated Bead Samples

During all phases of sample set-up and removal, the operator stands downwind of the sample in order not to contaminate the sample by shedding particles from clothing, etc. In addition, particle-free gloves are worn when handling gold bead traps and prefilters. An acid-cleaned filter holder is loaded with a fired glass fiber filter for each new gold bead trap sample to be collected. The filter pack is placed in one of the inner holes in the mercury sampling box (Appendix B). An acid cleaned piece of 0.64 cm Teflon tubing is placed in the ferrule fitting on the outlet of the filter pack and is tightened down with a ferrule nut. The 'test' traps are removed from their plastic tubes, the endplugs are removed from the trap and placed in the plastic tube which is then capped and returned to a clean plastic bag. The Teflon sleeve of the front test trap is placed snugly over the 0.64 cm Teflon tube on the outlet of the filter pack. A piece of 0.64 cm Teflon tubing is placed in the back end of the front trap and a second trap is attached to this piece of Teflon tubing. Another piece of Teflon tubing is secured to the vacuum line and attached to the back end of the second trap (Appendix C). A calibrated rotameter is attached to the inlet of the prefilter pack by a 9 cm long piece of black latex tubing. The flow rate is allowed to stabilize and is then read from the rotameter. After recording the flow rate, the test traps and the rotameter are removed and sample traps are installed in their place in the same manner as described. A trap heating assembly is placed over the front sampling trap. The heating assembly consists of a 12.5 cm length of 0.9 cm ID stainless steel tube wrapped with 1.27 cm silicon heating tape and covered with insulated vinyl tape. A variable transformer is set (~3-4 V) to maintain a constant temperature of 93°C to prevent condensation of water vapor in the sampling traps. The sample number, date, time, flow rate, meteorological information and any other pertinent information are recorded on a log sheet (Appendix D).

3.2 Taking Down Gold Bead Trap Samples

Particle-free gloves are worn during this procedure. The gold-coated bead traps are removed from the sampling stream and the endplugs are replaced. The juncture of the Teflon plugs/gold trap is wrapped with Teflon tape. The trap is placed in its plastic shield which is capped, and the sample number is placed on the plastic tube. As soon as the trap is removed from the sampling stream, the time is recorded. The tube containing the sample is then sealed in polyethylene bags and is immediately shipped to the UMAQL for analysis. Test traps are placed in line after the filter and the flow rate is read using a calibrated rotameter. All other pertinent information is recorded on the sample log sheet. After the flow rate has been checked, the pump is turned off. The prefilter is discarded.

3.3 Taking Blanks

A minimum of 25% field blanks and 10% shipping/storage blanks are taken to ensure samples are being collected in a contaminant-free manner. Field blanks involve setting up a gold bead trap in the same manner as a sample. The filter pack and attached gold trap are placed in the sampling box for two minutes *without the vacuum line attached*. After the two minutes, the sample is taken off, labeled and stored as described for samples. Shipping/storage blanks are traps that have been blanked, Teflon taped and triple bagged. The traps are then sent to the sampling site along with sample traps but are never removed from the triple bag nor is the Teflon tape removed. The traps are then sent back with sample traps to the UMAQL for analysis.

3.4 Trouble-Shooting

If flow through the gold trap or filter pack sample is low:

3.4.1 Check to make sure that all the connections are sealed tightly (make sure the ferrule nut fittings are tightened down, tubing connectors are tightly inside tubing from gold trap and on filter pack tubing, 'flow check' filter pack is screwed together tightly, tubing from the pump to the sampler is intact and connected securely.)

3.4.2 Make sure that the exhaust of the rotameter is not impeded in any way when using the rotameter to check flow.

3.4.3 Check the black latex tubing in the sampling box for cracks or tears due to weathering.

3.4.4 Make sure the mass flow controller is on and reading the normal output for the sample.

If all systems seem to be working properly and the flow remains low or erratic, operators are instructed to notify Matthew Landis at UMAQL (313) 763-7714 or at home (313) 663-9615 immediately.

4.0 Performance Criteria, Quality Assurance and Quality Control

4.1 Field operators are carefully instructed in the techniques of contaminant-free vapor phase mercury collection. All of the operators are currently operating sampling equipment for either the National Dry Deposition Network, the National Atmospheric Deposition Program, the Integrated Atmospheric Deposition Network or the Great Lakes Acid Deposition Network.

4.2 Every six months UMAQL personnel will inspect the sampling sites to audit the sampling equipment and make all necessary repairs or adjustments.

4.3 Co-located samples are collected from one sampling site during the study to quantify method precision. Reported concentrations are based on the mean of the two co-located samples.

4.4 Precision and accuracy levels will be set and maintained for each type of analysis. A relative precision for total mercury of less than 10% is maintained for samples with values at least three standard deviations greater than the detection limit. Analysis of standards and controls is within 5% of the stated value.

4.5 A minimum of 25% of all samples analyzed are field blanks or analytical blanks to ensure that samples are collected in a contaminant-free manner.

4.6 Every three months maintenance on the CVAFS analyzer is conducted, including replacement of the UV lamp, the Teflon tubing, and the detection cell.

4.7 Gold traps are checked prior to every sample with 0.8 ng of mercury in order to ensure that their use during the previous sample collection has not diminished trap performance.

5.0 References

5.1 Bloom, N.S. and Fitzgerald, W.F. (1988) Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection. *Anal. Chem. Acta*. 208, 151.

5.2 Dumarey, R., Temmerman, E., Dams, R. and Hoste, J. (1985) The Accuracy of the Vapour-Injection Calibration of Mercury by Amalgamation/Cold-Vapour Atomic Absorption Spectrometry. *Anal. Chem.. Acta*. 170, 337-340.

5.3 Dumarey, R., Dams, R., and Hoste, J. (1985) Comparison of the collection and desorption efficiency of activated charcoal, silver, and gold for the determination of vapor-phase atmospheric mercury. *Anal. Chem*. 57, 2638-2643.

5.4 Fitzgerald, W.F., and Gill, G.A. (1979) Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis. *Anal. Chem*. 15, 1714.

5.5 Lindberg, S.E. (1981) Author's Reply 'Mercury partitioning in a power plant plume and its influence on atmospheric removal mechanisms.' Atmos. Environ. 15, 631-635.

5.6 Rossmann, R. and Barres, J. (1991) Trace element concentrations in near-surface waters of the Great Lakes and methods of collection, storage, and analysis *J. Great Lakes Res.* 14,:188.

5.7 Schroeder, W.H. (1982) Sampling and analysis of mercury and its compounds in the atmosphere. *Environ. Sci.. Technol*. 16, 394-400.

Appendix A. Facilities, Equipment and Reagents

Following is a list of the required facilities, equipment, supplies and reagents for sample preparation, sample collection and sample analysis that are outlined in this document. The make and model of the following items are those used at The University of Michigan Air Quality Laboratory. Many of these items are available from a variety of sources.

1. Preparation of Field Supplies

- Class 100 Clean Room, Work Stations
- Clean Room Gloves
- Particle-free Wipes
- Clean Room Cap, Gown and Boots
- Milli-Q Water (18.2MÙ/cm)
- Exhaust Hood
- Acetone
- Alconox
- Polyethylene Tubs
- EM Science Tracepur and Suprapur Hydrochloric Acid
- Polytherm Water Bath (Science/Electronics)
- Baker Instra-Analyzed or EM Science Suprapur Nitric Acid
- New Polyethylene Bags
- 20 L Polyethylene Carboys

2. Sample Collection

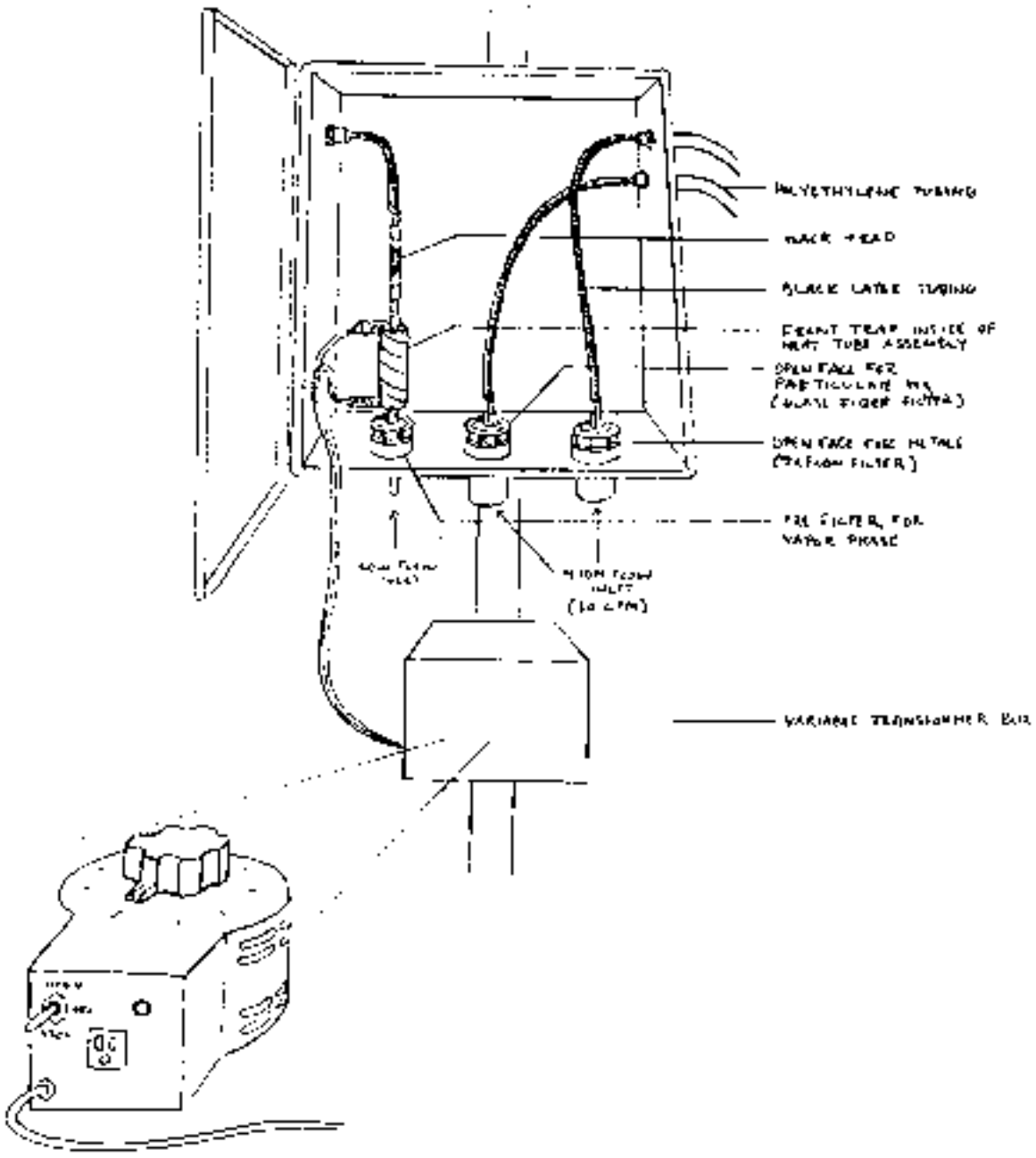
- Mass Flow Controlled Vacuum Pump (URG, Model 3000-02M)
- Calibrated 300 cc/min. Rotameter (Matheson)
- HDPE Tubing with quick connects
- Black Latex Tubing
- Mercury Sampling Box (UMAQL, See Appendix B)
- Acid-Cleaned 47 mm Teflon Filter Holders (Savillex, PFA Labware)
- 47 mm Preheated Glass Fiber Filters (Gelman Sciences A/E)
- Acid-Cleaned Teflon Jars (Savillex, PFA Labware)
- Teflon-Coated Forceps
- 'Blanked' Gold-Bead Traps (UMAQL)
- Teflon Endplugs
- Trap Heater & Variable Transformer
- Acid-Cleaned Teflon Tubing
- Particle-Free Gloves
- Teflon Tape
- Sample Labels
- Field Operator Log Book
- Shipping Boxes

Appendix A. Facilities, Equipment and Reagents (Cont'd)

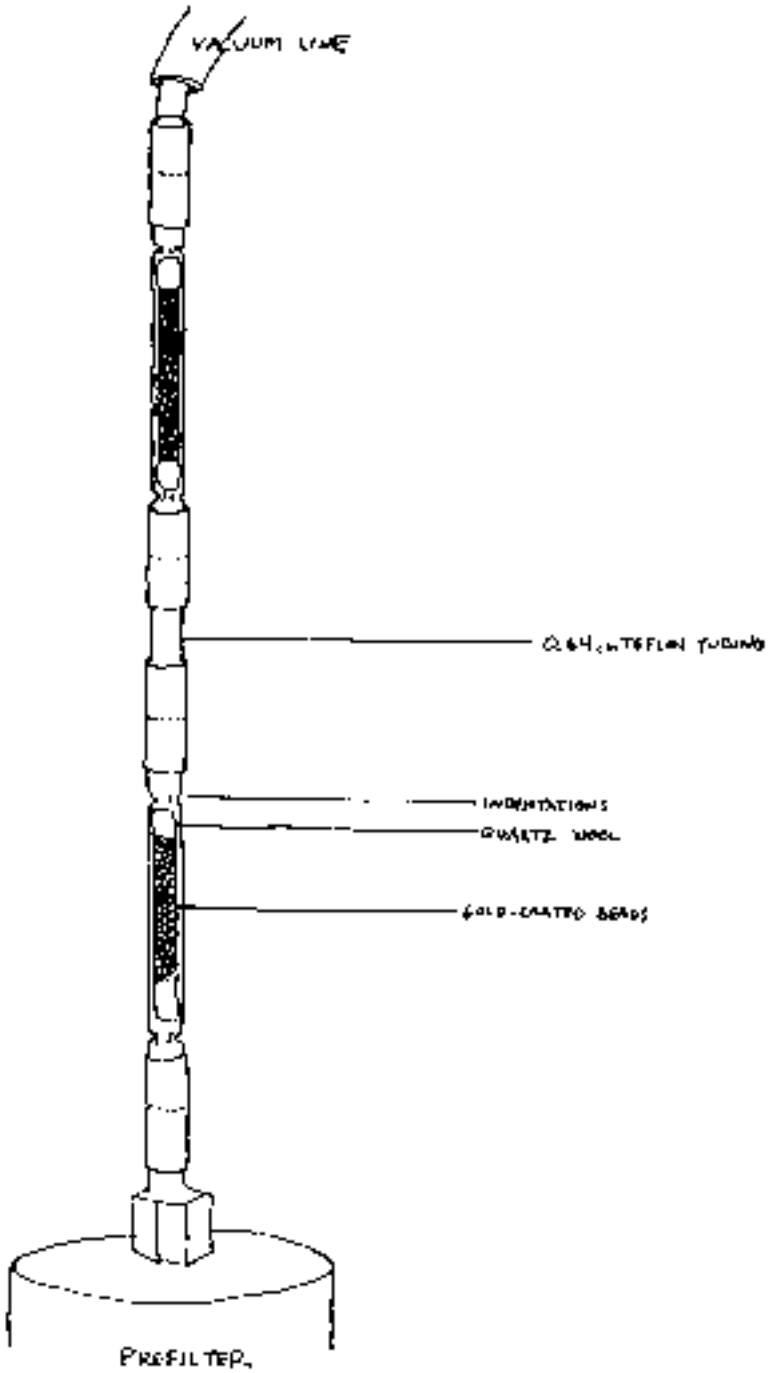
3. Sample Analysis

- Cold Vapor Atomic Florescence Detector (Brooks Rand, LTD.)
- Line Tamer/Conditioner (Shape Magnetronics Model PCLT 150)
- Integrator (Hewlett-Packard Model 3390A)
- Helium, Ultra High Purity Grade (99.999%)
- Mass Flow Controller (Tylan)
- Nichrome Coils (UMAQL)
- Electric Leads
- Variable Transformers (Staco Energy Products Co. Type 3PN1010)
- Cooling Fans
- Gold-Coated Glass Bead Traps (UMAQL)
- Gas Tight Syringe (Hamilton series 1800)
- Injection Port (UMAQL)
- Constant Temperature Circulating Water Bath (Fisher Model 901)
- Instrument Grade Metallic Mercury (Triple Distilled)
- Mercury Flask (UMAQL)
- Certified Immersion Thermometer (Kessler Instruments, Inc. 15041A)

Appendix B. Diagram of Mercury Sampling Box



Appendix C. Diagram of Assembled Gold-Coated Bead Traps



Appendix D.

LAKE MICHIGAN LOADING STUDY

IIT-CHICAGO

Vapor Phase Mercury

Sample No.	Au Trap #A/B	Date On/Off	Time On/Off	Flow On (LPM)	Flow Off (LPM)	Wind Speed	Wind Direction	Sky Conditions	Notes	Init.

PUMP SYSTEM USED:_____

ROTAMETER #:_____ CALIBRATION CURVE=_____

Appendix D. (Cont'd)

LAKE MICHIGAN LOADING STUDY *SAMPLE TRACKING FORM*

ITT--CHICAGO

Vapor Phase Mercury Samples: Gold-Coated Bead Trap

Sample Number*:_____
Gold Trap Number:_____
Operator:_____

Date On:_____ Date Off:_____
Time On:_____ Time Off:_____
Rotameter Reading On:_____ Rotameter Reading Off:_____

*If Blank Sample Note Type and How It Was Handled (Shipping Blank, Field Blank, etc.)

_____

Notes: (ambient conditions, anything out of the ordinary, using freshly cleaned filter packs, etc.)

_____

For Use at Univ. Of Michigan Air Quality Lab

Date Sample Received:_____ Rec'd By:_____

Date Sample Analyzed:_____ Rec'd By:_____

Analyzer #:_____

Notes: (Appearance of Sample, Are Endplugs Teflon-taped, etc.)