ATMOSPHERIC MERCURY
BEST PRACTICES AND SOP WORKSHOP

Summary of Workshop

Chicago
October, 2007

Considerations – Please Read

- There will be ample opportunity for peer review and field testing feedback on the topics that were reviewed and the decisions that were made by consensus.

- This document only covers critical areas with a low level of consensus or where consensus was high but required active peer review. Thus, many operational or quality assurance topics are not covered in this document.

- The warning and control limits are intended to be used for near real-time feedback by the NADP program office to the site operators so that any corrective action can be done quickly.

- We want to begin this network with very high standards to motivate new and existing operators to run their instruments with the greatest of attention and take corrective action in a timely fashion. As the network evolves, it is much easier to adjust tight criteria as new knowledge is gained

Site Liaison (Atmospheric Inferential Deposition Expert - AIDE)

There was a brief discussion about NADP providing an atmospheric mercury site liaison to field questions regarding instrument performance, QA, troubleshooting and so forth, with this person having a direct connection to Tekran for rapid parts replacement and technical support.

It was suggested that the site liaison could also tap into experienced users to help resolve problems.

There was a sidebar discussion about having a "User Forum" or Wiki-site.

TOPIC 1: Basic sampling, temperature, calibration and thermal desorption settings.

Below is the consensus for Tekran 2537-1130-1135 settings

Consensus NADP-AMN TEKRAN MODEL 1130/1135 CONTROLLER PROGRAM WORKSHEET

Controller S/W revision:

Description of this Method:

NOTES: 1) Flow rate set for near sea-level sites. Sites at higher elevation may adjust to keep volumetric flow at 10 lpm. 2) A 1-hour adsorb time - 1 hour desorb cycle is an acceptable alternative for special source-receptor study sites. The sample duration is set to 12 2537A cycles, the autocal must be adjusted to 36 cycles and 2537 factors increases to 8.333.

Model 2537A Settings

Cycle Time: (sec)	300
Flow Rate: (L/m)	1.00

Pump Module Settings

Sample Flow: (L/m):	9.00
Desorb Flow: (L/m)	6.00

Model 1130 Denuder Module Temperature Settings (deg C)

SP1	Case Heater:	38
SP2	Case Fan:	40
SP1	Heated Line:	50
SP1	Denuder Keep Warm:	50
SP2	Denuder Heat:	500
SP1	Ext. Heat:	75
SP2	Ext Keep Warm:	50

Model 1135 Particulate Module Temperature Settings (deg C)

SP1	Pyrolyzer Keep Warm:	50
SP2	Pyrolyzer Heat:	800
SP1	Part-Trap Keep Warm:	50
SP2	Part-Trap Heat:	800
SP1	Case Heater:	38
SP2	Case Fan:	40

Calculated Values

5.00	Model 2537A Sample Volume (L)
10.00	Denuder Flow Rate (L/m)
1,200	Denuder Total Volume (L)
0.00417	Model 2537A Factor (for ng/m3)
4.167	Model 2537A Factor (for pg/m3)
120	Denuder Sample Time (min)
60	Desorb Analysis Time (min)
180	Total Cycle time (min)
72.0	Auto-Recal interval (hours)

Note: Denuder figures above also apply to the particulate trap.

Au Cartridge Status (RGM & PHg 1st Heat)

Step	Cartridge	Cartridge	Cartridge
1	A	B	A
2	B	-	-
3	A	B	A
4	B	A	
5	B		
6	A	B	-

Controller Settings

Step No.	Step Label	Step Duration	Duration Units	Event Flags 0 - 7	Sync N=0, Y=1	1130 H/C Mask	1135 L/C Mask	Cumulative Time (sec)	Notes	Time (hrs)
	Auto-Cal	24	RGM-Cycles	n/a	n/a	n/a	n/a			
0	Sample Duration	24	2537A Cycles	0	0	0	0	7200	RGM and PHg Adsorb time	2.00
1	Flush	590	sec	1	1	9	0	7800	Three cycle initial flush	2.17
2	Pyro-Ht	590	sec	2	1	9	4	8400	Pyrolyzer preheat	2.33
3	Part-Ht	890	sec	2	1	9	12	9300	Particulate trap heat	2.58
4	RGM-Ht	600	sec	3	0	13	12	9900	Start RGM Heat	2.75
5	RGM-Ht2	290	sec	3	1	13	0	10200	RGM Ht - Stop Py/Pt Ht	2.83
6	Cool	590	sec	1	0	3	2	10790	Two cycle cool	3.00
7	Wait	1	sec	1	1	1	0	10800	Zero air during Sync Period	3.00

Notes:

1) If the Model 2537A is not in **RUN** mode, or if it stops drawing air through its **Sample** Inlet (eg: it stops or the **Zero** solenoid is activated, the controller will immediately jump to the **WAIT** (**7**) state and wait there until the Model 2537A reenters normal **RUN** mode.
2) A step duration of **0** will cause the step to be skipped entirely.

Event Flags:

1) If the controller changes state midway through a 2537A sample cycle, the resultant event flag will be the logical **OR** of the flag settings for the individual steps.
2) Event flag status is not sampled for the initial few seconds of each 2537A cycle. If step changes are to occur asynchronously with respect to the sample cycle, the change should occur 1 second ***after*** a cycle change to prevent spurious flag values from being registered. If **Sync=1**, the transition will always occur at the correct time.

Sync:

If **Sync** is set to **Yes** (**1**), the controller will pause at the current step until a Model 2537A cycle transition is detected, even after the duration time expires. The duration should expire at least a few seconds *before* the expected cartridge switchover.

Model 1130: H/C Mask Functions:

Add numeric values to determine total functions activated during the step

1 Zero Air ON, Desorb Flow RateSelected
2 Denuder Cooling
4 Denuder Heat
8 External Heat

Model 1135: L/C Mask Functions:

Add numeric values to determine total functions activated during the step

1 Aux-1
2 Particulate Cooling
4 Pyrolyzer Heat
8 Particulate Heat

TOPIC 2: RGM and PHg calculation routine.

Below is the consensus that was reached for the arithmetic routine to reduce and blank correct the PHg and RGM desorption results.

A set of logical criteria is being built to screen and flag data for high blanks, carryover, outliers and unusual ratios.

Tekran Desorb Program			Tekran RGM and PHg Data Reduction Routines		
Cycle ID	Description		USER-ID	PHg Calculation	RGM Calculation
A	Flush				
B	Flush		Consensus	(E+F+G)-3*D	(H+I+J)-3*K
C	Pyro-Ht				
D	Pyro-Ht				
E	Part-Ht				
F	Part-Ht				
G	Part-Ht				
H	RGM-Ht				
I	RGM-Ht				
J	RGM-Ht2				
K	Cool				
L	Cool				

TOPIC 3: Detector and Flow Calibration.

The following was the consensus reached for calibration of flow and Tekran 2537 detector – by internal permeation source and external injection of mercury standard for permeation source verification. *When reading the following topic it is important to remember that the warning and control limits, with flagging, will be done automatically as the data is received and then emailed so that corrective action can be taken. Also, the site operator and scientist will have the ability to comment on their data with respect to quality and other factors for circular review. Finally, the data flagging may or may not downgrade the data from say A to B.*

Noted Comments:

- Most Tekran users are not auditing their flow meters at all or on a set frequency.
- Accurate flow measurement is directly related to the accuracy of the reported mercury concentration measurements
- Collocated Tekran measurements may not agree due to a lack of the users auditing their flow measurements, not due to differences in detector response. Intercomparison studies such as Aspmo et al., 2005, AE, did not indicated flow calibration, so the differences may be partly due to lack of appreciation of the flow measurement accuracy.
- Flow may be set lower than 9 liter/minute (0° C, 1 atm) standard value for higher elevation sites as long as volumetric inlet flow remains at 10 ± 1 liter/minute.
- Adjusting to maintain a volumetric flow at the inlet between 9.0 to 11.0 liters per minute is crucial to maintain a scientifically valid particulate cut point of 2.5 μm.
- Improved flow properties (less pump strain) can be achieved using a less restrictive RPF and filters in flow path (Note: Tekran is acting now to make improvements)

1) Tekran 2537 mass flow meter audit
    a. Frequency = Quarterly
    b. Method = Bios or equivalent - correct to T=0°C and P=760 mmHg.
    c. Record offset value and use to correct final data or re-adjust flow meter by applying adjustment factor using AD1-USc option in Tekran. Must document!

2) Tekran 1130 mass flow meter audit
    a. Frequency = Quarterly
    b. Method = Bios or equivalent – correct to T=0°C and P=760 mmHg.
    c. Record flow meter offset at current setting of 9.0 liters/minute to be used to correct final data (must be adjusted as a dilution ratio)

3) Tekran 1130 inlet volumetric flow audit
    a. Frequency = At least monthly – ideally at each glassware change

b. Method = Get URG adaptor for inlet – Use Bios or equivalent. Critical that this is done to avoid extremes in either T or P with respect to average seasonal temperatures (e.g. do not perform at early morning temperature minimum). Further details will be developed for SOP.
c. Record volumetric flow rate at actual inlet temperature and pressure. Value should be within 9.0 to 11.0 liters per minute volumetrically. As needed, adjust 1130 flow meter to maintain within this range. Record new setting and volumetric flow rate.

4) Tekran 2537 ***internal perm*** source calibration
   a. Frequency = 72 hours
   b. Permeation time = 120 seconds
   c. Sample Restart on XX:00 = Set ROUND function to 60 minutes

5) Tekran 2537 ***internal perm*** source calibration factor (function of detection limit)
   a. CF must be greater than 6×10^6 (Span area/ng of mercury)
   b. Data flags – not discussed
   c. Corrective action require if CF is below this value

6) Tekran 2537 zero air value criteria for ***internal perm*** calibration
   a. Warning limit if above 0.25 pg (1500 area units at CF=$6x10^6$)
   b. Control limits will be: a) 3 consecutive warning limits observed or b) values will be flagged if zero value is greater than 1% of span value for either the a or b channel.
   c. Corrective action required if control limit is breached.

7) Tekran 2537 ***internal perm*** calibration Au cartridge difference (CF_{CartA}/CF_{CartB})
   a. Warning limit if CF_{CartA}/CF_{CartB} is outside of 0.96 to 1.04 range
   b. Control limit if CF_{CartA}/CF_{CartB} is outside of 0.95 to 1.05 range
   c. Data is flagged above the control limit.
   d. Corrective action required if control limit is breached since this is often a harbinger of a valve problem, for example.

8) Tekran 2537 ***internal perm*** calibration-to-calibration variability (CF_{new}/CF_{last})
   a. Control limit if CF_{new}/CF_{last} is outside of 0.95 to 1.05 range for either the A or B channel
   b. Data will be flagged above the control limit
   c. Corrective action require above any of these criteria, except in cases where the operator has noted that the control limit breach was expected due to changes made to the instrument (e.g. new gold traps, cuvette cleaning, lamp adjustment, etc.)

9) Mercury saturated vapor verses temperature curve
   a. High consensus – All use Dumerey Hg vapor saturation curve used by mercury researchers for past 30 years. This is the basis for the curve in the Tekran 2537 manual and Tekran 2505

b. NIST has published a paper (without doing any research of their own) that lists a saturated Hg vapor curve which is approximately 7% different in the "room temperature range" compared to the Dumerey saturated Hg vapor curve. This has also now been published in the CRC Handbook. Tekran has generated a very thorough study of the Dumarey curve, please request a copy.

10) Tekran 2537 ***front panel inject*** "perm-source verification" frequency and acceptance criteria
    a. Frequency of every 3 months by skilled on-site operator using NIST traceable source following detailed protocol based on Tekran manual with review and input by leading scientists. There was a strong consensus in the survey to do at least 5 injections per gold cartridge.
    b. Annual external perm-source verification and audit by an independent technician and saturated mercury vapor source. An external audit program will probably consist of one to two highly trained technicians.
    c. A specific control limit was not agreed upon – 5% was thought to be reasonable. A suggested criterion = 0.97 to 1.03 for average $(Inj_{cartA,\ n=5})/(Perm_{cartA,\ n=5})$ and %RSD of $(Inj_{cartA,\ n=6})$ <10% was offered.
    d. The following gathered comments are relevant:
        i. It is rare to see any drift or any change in the rate of emission from the mercury permeation source over many months (even years). Some have observed a few percent at most and if it is above this level it will be off by a "ton" and be due to a major failure.
        ii. We will highly recommend to NOT reset the mercury permeation source rate on the basis of a single quarterly "perm-source verification" if the result is outside of set criteria (to be determined – say 5%).
        iii. Perm-source verification results outside the set criteria may be the result of an inaccurate, plugged or improperly conditioned syringe. It was suggested that the syringe be calibrated yearly.
        iv. It is recommended that for a set of front panel injection results which is outside of the control limit (5%?) should trigger the following corrective action
            1. Document results – do not change permeation rate
            2. Ensure Tekran 2537 is under control – don't do a front panel perm source verification on a known poorly functional instrument
            3. Review calibration procedure, Tekran 2505 settings, internal room temperature, digital syringe settings – check for temperature related effects – make sure the correction for room and syringe temperature difference is applied (now done automatically on newer 2505s) - check for zero air related effects.
            4. Send your syringe in to be recalibrated (or possibly NADP provides a known calibrated alternative)

5. Attempt the front panel injections again with an alternative, recently calibrated and conditioned syringe.
6. If the perm-source verification falls outside the control limit again, request NADP to send their external QA program technician to verify the perm source emission rate – or – can send instrument to Tekran for recertification.

11) Tekran 2537 zero air criterion for ***front panel inject*** "perm-source verification"
    a. Control limit should be 0000 area counts
    b. Corrective action taken until zero air reads 0000 area counts

12) Tekran 2537 ***front panel inject*** "perm-source verification" Au cartridge difference (Mean $Area_{CartA}$/Mean $Area_{CartB}$)
    a. Range of 0.95 to 1.05 as acceptable
    b. Corrective action – either injections are being done improperly (likely) or instrument is behaving poorly which should have already been evident.

ASIDE: Detector calibration under negative or positive pressure

There was an extended conversation during our workshop about whether to provide zero air for calibration under slight positive or negative air pressure upstream of the gold cartridges. Positive pressure (0.5 PSI max) zero air is supplied by the 1130 pump module through the pressure regulator, zero air canister and DFU filter. Negative pressure operation can be setup by having the inlet open to ambient room air to draw air through the pressure regulator, zero air canister and DFU filter.

We determined that some explanation from Tekran would be useful to help us reach a consensus. Here are some of our own comments and information from Tekran.

1) The exact amount of mercury provided by the internal mercury permeation source will be very slightly different depending on the pressure difference between the zero air in the sample line and the mercury permeation chamber.

    a. When the valve is opened on the internal mercury permeation source for calibration purposes, the slight pressure difference between the permeation chamber and the zero air in the sample line causes a short pressure rebalancing and subsequent mercury "foosh" effect. If the sample line pressure is less than ambient, gas from the chamber will suddenly empty out into the sample line until the pressures equalize. This will deliver more mercury than would be expected considering only the steady state permeation emission rate. Conversely, if the sample line is positively pressurized with respect to ambient, there will be a slight inflow of zero air into the perm chamber until its pressure rises to match that in the sample line.

b. When the permeation time is set at the standard 120 seconds, this foosh effect is minuscule. However, the "foosh" effect is different in direction and magnitude depending on whether the zero air is supplied at a positive or negative pressure relative to the permeation chamber pressure.

c. This small and highly reproducible swoosh effect is taken into account when the mercury permeation rate is certified at the factory.

d. At the Tekran factory, the internal mercury permeation rate is certified using positive zero air pressure.

e. Historically, Tekran chose to recommend positive pressure because of more consistent results compared to negative zero air pressure operation. The first Tekran 2537A systems requested the user supply a gas cylinder of zero air or a compressed zero air source for a positive pressure zero air source. Tekran then developed the 1100 zero air generator to rid user of the need to have a gas cylinder. With the advent of the Model 1130, positive zero air supply for calibration was built into the system. **Note:** the zero air that supplies the 2537 (whether it be from an external compressor, a Model 1100 or the Model 1130) must be passed through the Tekran supplied "BBQ" regulator followed by the Model 2537's final stage zero air canister. This will reduce the pressure to just a few inches of water.

f. Thus, for accurate results, Tekran users should calibrate their instruments using positive zero air pressure – AND – most importantly subsequent front panel injections for permeation source verification should also be done using positive zero air pressure.

g. Operating the Tekran using negative zero air pressure is perfectly acceptable and will provide accurate results as long as the internal mercury permeation rate is also re-certified using negative zero air pressure.

h. Thus, either positive or negative zero air pressure can be used, as long as the permeation rate is certified under the same conditions and the system continues to operate under the chosen method. Tekran recommends positive zero air pressure.

2) It appeared that most Scientists are using positive zero air pressure for calibration and internal permeation source verification by front-panel injection.

3) The notion that using negative zero air pressure for calibration more closely mimics conditions during operation is a red-herring. The response of the detector for calibration is done under the same conditions as a sample, 80 ml/min of argon flow, exact same pressure conditions. The internal permeation source calibration

is not intended as a check of the integrity of the sampling system, but is simply a determination of the detector's mercury sensitivity. Doing standard additions using the Tekran Model 1110, front-panel injections or inlet injections should be used for auditing and testing the integrity of the entire system.

4) One advantage mentioned for using negative pressure is the ability to change out quartz-ware in the 1130/1135 in the field when the Tekran 2537 is doing a calibration, increasing field efficiency. This is not a factor. When changing the glassware the very slight positive pressure that is present at the "Tee" zero air distribution fitting at the back of the 1130 pump module will not change significantly. The length of the heated sample line, plus the restriction of the final 47 mm Teflon filter in the DM case, ensure that, as long as the 1130 pump is running, you will have enough zero air pressure, even as you change the glassware. (The BBQ regulator supplies only a few inches of water pressure.)

5) A small internal leak in the 2537 sample path will cause high zeros if using negative pressure since lab air and dust may be sucked in. Positive pressure will cause air to leak outwards.

END OF ASIDE

TOPIC 4: Automated and Remote Data Capture and Reduction.

The goal of this topic was to come to a consensus about the system we will use to automatically and remotely capture, screen and display draft data. This topic was more of a conversation about what direction we are headed and the options. There was no consensus on using the exact same system (e.g. Campbell Data Logger) at each site. It would be too difficult for NADP to support the various options. The bottom line is to have complete Tekran data files available to NADP in a prescribed format so they can be easily downloaded and then perform the data reduction, quality assurance and operator feedback routines.

1) The data stream format will be the responsibility of NADP to provide – with input from users. All network sites must conform to the data stream format requirement

2) Data will be screened automatically each day for basic performance checks based on logic supplied by a subgroup of users (ad-hoc advisory group) with experience developing such tools. Detailed data plots, ancillary performance data and data flags will be compiled and sent to the site sponsor and site operator daily. Bob Larson NADP programmer offered the following comments as recorded:
    a. NADP has been working with different programs to collect the data
    b. Work has been underway to develop another program to process the data, then put it into SQL --- then use the mercury processing logic to flag the data

c. We'd like to have a program to send information to a user about his/her data, then send a detailed bunch of information where the user can look at the NADP site to interpret
d. QA/QC of data
e. We will always have the ability to pull up your own data to mark/flag this data and provide comments to your own data on the website
f. We want to build the capability to fill in an online field book where the site operator and scientist will have up to 30 days to comment on your own data. This is a critical feedback mechanism. The user should have some ability to disqualify data due to known problems (same occurs in MDN – field and lab folks can put down C for a suspected contaminated sample based on their own knowledge)

3) Weekly plots of preliminary screened data using low temporal resolution will be posted on the NADP website in picture format, with the proper caveats embedded in the picture (e.g. provisional data, data is not final, do not quote, cite or interpret and etc). Several scientists indicated that the real-time pictures are critical to improve the value of the program to outsiders.

4) We will use local standard time and the data will be adjusted to have the timestamp be the start time (not end time).

5) We are anticipating a goal of data being posted for anyone's use/download within 30 days of sampling in hourly format with all flags and quality assurance information provided. Currently all data is password protected (0rain). NADP must give final approval of the network before we can publish data for open use – we are still in "Developmental" network mode and will be for the foreseeable future.

6) Raw data will never be made available.

7) A strong encouragement will be included with all downloads to contact the site operator and scientist for collaborative data interpretation. Prestbo idea – post workshop: Upon data download – the person getting the data would be notified that an email will be sent to the site operator and scientist responsible for the site to promote collaboration and open knowledge of data use.

8) Final data flagging and quality assurance logic is the subject of another workshop or NADP meeting.

Data logger option (Miller):

- uses the Campbell CR1000
- reads the time stamps from the Tekran
- puts this data into a data table automatically
- users a Loggernet software
- the data logger can handle the calibration schemes (which Miller has written to work with this input information)

- Prefers the CR1000 over FTP transfer of Tekran data; the downside of this is that the site operator isn't able to see the data (on a computer) – doesn't have a computer

Data logger option (Watkins – OAQPS):

- There's a PC-based data logger software, using serial ports, Invidas for Windows

Cellular data link options (Felton and Miller):

- AirLink Raven cellular - $600 for the unit, cheap monthly fees
- internetinmotion.net – always on – allows your IP address to be found, unlimited data, $1200/unit; $50/month by Sprint, 144kbs upload speeds

TOPIC 5: Soda Lime (SL) Trap. The goal of this topic was to learn about current practices and then have a plan moving forward to have a harmonious approach regarding soda lime use. This topic has some relevance to Topic 6 "Zero Air System" which will be dealt with separately. Several important comments were made about SL, they are:

1) Historical Information:
    a. SL was chosen early on because it had been very well characterized in the mercury analytical realm and had already been proven to scrub acid gases and halide compounds while still passing elemental mercury quantitatively.
    b. SL use has been shown to prevent gold-trap passivation due to the release of deleterious compounds co-captured or formed from the heating of the denuder and RPF. No passivation is observed in locations as diverse as Detroit, Chicago, Okinawa and Everglades when using SL. Gold traps have lasted from 1.5 to 2 years with this protective SL trap installed.
    c. Without SL, gold cartridge passivation may occur even if the zero air system is modified to be very dry and lacking any halide release (see Topic 6 below). Thus, it is critical that we develop a standard SL trap and protocol for use that works throughout the ambient mercury network.

2) Tekran is willing to provide SL traps that conform to the strict preparation, packing and date tracking requirements as defined by the user community. The SL traps will be provided at low cost and available without delay via Tekran or NADP.

3) SL management and observations
    a. It should be noted that passivation of gold cartridges is not always related to the absence of a SL trap. For example, making certain the nichrome wire heating system is functioning properly to burn off (clean) the gold cartridges each 5-minute sample is important to avoid gold cartridge passivation.

b. Proper storage seems to be an important factor. The SL must stay dry. The SL must not be allowed to absorb mercury from the air in the storage location
c. SL should be changed out weekly or possibly every other week since adsorption of water and CO_2 will transform it to other compounds – it will eventually turn into $Ca(OH)_2$ or $CaCO_3$ and no longer be soda lime. Removing water from the zero air may also improve SL longevity.
d. Exposure of SL to high levels of halides (e.g. in mercury + halide rate experiments) has been shown to ruin the SL ability to pass elemental mercury quantitatively
e. Teflon tubes holding SL should be pre-cleaned in acid, rinsed, dried and packed as needed. Teflon tubes are tossed after one use.
f. Recommend keeping SL in a desiccated box, mercury free air
g. Baked quartz wool was recommended over glass wool.
h. SL Brand: No consensus, but suggest using Mallinckrodt AR 7337 non-indicating, 4-8 mesh (Note Mallinckrodt and JTBaker merged).
i. Most users employ a SL trap and the trap is kept at room temperature.

SL Consensus: In the near term, all users in the network will use SL following a standard protocol most closely resembling the one used in Landis et al., 2002 for type, packing, pre-purge and change frequency. The performance of the SL traps should be recorded and shared (ideally in a user forum). It was recommended that one entity should produce the SL traps for consistency (individual users can still make their own if desired). Tekran has offered to follow the set protocol, including pre-purge, made to order, fresh SL, air-tight seal, documented SL age and "use-by" time stamp. Tekran will offer a very low-cost tube-only replacement (on-site compression fittings can may be cleaned and re-used).

TOPIC 6: Zero Air System: There was a good bit of conversation surrounding the Tekran 1130 pump module, 1102 air dryer and zero air canisters which make up the "Zero Air System". There was a high level of consensus that the proper operation and maintenance of the zero air system is critical for continuous, high quality mercury speciation measurements. A summary of the conversation and action items are listed below.

1) Maintaining very dry zero air has been shown to improve the performance of the Tekran Speciation System. It is presumed that providing dry air to the 1130 pump module prevents the release of halogen compounds from the zero air canisters which may adsorb on the soda lime trap or the gold cartridges to cause temporary and transitory low biased elemental mercury values. (Experiment: when passivation occurs after a denuder desorption cycle, disconnect the soda lime trap and see if the Tekran recovers immediately – some have observed this effect).

2) The addition of the Tekran 1102 air dryer has improved overall performance in the majority of uses as documented in the questionnaire. However, additional

drying after the Tekran 1102 has been added by many users with even greater overall performance. Typically the additional drying agent is drierite or similar. Although some have tried Nafion tubes or external compressors to provide dry air as worthy alternatives.

3) According to the questionnaire responses, most users do not change their zero air canisters on a set schedule. However some respondents maintain that frequent changing improves performance, especially with respect to observed passivation. We agreed that the zero air canisters must be changed at least every 6 months.

4) The use of an activated carbon instead of iodinated carbon in the second stage zero air canister was postulated as a possible improvement to avoid the release of halogen compounds. Tekran briefly offered these canisters, but learned that they did not work as well. Several scientists offered to order activated carbon canisters and try them in different ways. Post meeting note: Tekran has installed an activated carbon canister on their system in Toronto and found again that it did not provide mercury free air and may actually be releasing mercury.

5) The questionnaire documented that the Tekran 1102 air drying unit has been found to be helpful. In comparison to other options considered for water removal, the 1102 is compact, quite, modular and simple to operate. However, in some extreme cases the 1102 has been found to under perform. It has been suggested that the cycling time of the 1102 could be adjusted for better performance. It was also suggested that the molecular sieve in the 1102 will eventually need replacing. It was also suggested that the addition of a small pump to supply forced air during the heating cycle of the 1102 would help drive collected water off of the molecular sieve to improve performance.

Based on the workshop conversation the following set of solutions is recommended for improved zero air system performance. Prestbo will coordinate the following:

1) Development of an improved Zero Air System (and retrofit if possible) to include
    a. Optimize the heat cycle of the 1102 air dryer, if possible
    b. Determine whether a small pump and switching valves can be added to the 1102 to provide forced air to drive out water during the heat cycle
    c. Determine if an activated carbon canisters plus protective DFU filter can be used as a final polishing step and still provide high quality zero air. Coordinate use and information exchange with scientists trying this approach.
    d. Develop a refillable canister with indicating molecular sieve to be used in place of silica gel or drierite as the polishing drying capacity. Molecular sieve has greater water absorption capacity than silica gel or drierite.
    e. Develop a retrofit for the 1130 pump module that will allow plumbing such that multiple drying and mercury removal canisters can be mounted externally (probably on the 1102 panel) for easy change out.

f. Develop a final disposable prophylactic sorbent trap containing soda lime, activated carbon or other compound which will ensure the zero air is free of halogen or other deleterious compounds, while maintaining mercury free air. The final prophylactic sorbent trap should maintain performance for at least 2 weeks in the very dry and clean zero air stream.

TOPIC 7: Field Site and Physical Setup. Because all three mercury fractions, Hg^0, $PHg_{2.5}$ and RGM are know to have surface effects, the **location** and **height** of the inlet of the Tekran 1130/1135 must be carefully considered and criteria will be adopted. However, there are also constraints, namely the cost of installing a tower and length of heated line of 15 meters (power and flow). A productive workshop discussion ended with consensus on several key items and additional information. The siting criteria will continue to develop over time; the following is only our starting point. Also, the capability to petition for an exception will most likely be offered, especially since existing sites may not be able to easily make changes.

1) The minimum inlet height above the native ground level will be set at 4 meters and the normal range will be 4-10 meters. The ideal inlet height should be 10 meters above the native ground level based on its acceptance for many other air measurement networks.

2) The minimum inlet height above any surface (e.g. instrument shelter, tower deck) will be 2 meters.

3) The minimum distance from co-located instruments and other field site obstructions was not set, but guidance is available in CFR QA handbook volume 4 and also NADP siting criteria.

4) The inlet should be located in a clearing such that the any object above natural ground level shall be at least 5 times the difference in distance between the instrument inlet height and the object (e.g. tree). For example, a 30 meter tree should be 100 meters from the instrument with an inlet height of 10 meters (5 x (30-10) = 100).

5) We generally have the common opinions that:
    a. A an ideal fetch around the sampling site would have a minimal amount of surface roughness (e.g. short grass)
    b. Sampling at a low height near or within a densely forested locale should be avoided
    c. The air you sample may be impacted by whatever is in the horizontal line of site from the instrument inlet. Thus, sampling on a local high spot (mountain) will be more representative of the regional air mass compared to sampling at the local low spot (valley).
    d. Models (e.g. Hysplit) and or modelers may be able to provide critical decision input on ideal sample height and field site location.

e. The resources put into a sustained measurement of atmospheric mercury justify the additional expense and effort to find and maintain ideal site locations and siting criteria.

6) The location of new and existing sites was discussed and is summarized below. We decided that:
   a. We should characterize the currently operating atmospheric mercury field sites with respect to typical descriptors (e.g. lat., long. and possibly the following:
      i. Designate as local, regional representative
      ii. Distance from mercury point sources types and magnitudes
      iii. Ecosystem (urban, agricultural, forested, desert)
   b. We must provide strong guidance to site sponsors on where they should locate new sites with respect to both their own and network goals
   c. Co-location with MDN sites or at other atmospheric measurement sites has many advantages, but we should not constrain ourselves unduly.
   d. NADP should consider using simple atmospheric modeling to help select new measurement sites.
   e. We agreed to generate a list of ideal site criteria and distribute for review. The siting criteria that NADP uses can serve as a template. This should be a priority.

TOPIC 8: Gold Trap Quality Assurance: A number of basic checks and maintenance procedures for the Tekran 2537 gold (Au) cartridges are currently not aligned across the user group.

1) We reach a consensus for the on-going determination of gold trap bias. For each 24 hour period, calculate the ratio $Hg^0_{CartA}/Hg^0_{CartB}$ using the middle 80% of each 2 hour Hg^0 data set. The $Hg^0_{CartA}/Hg^0_{CartB}$ value should be within the range 0.95 to 1.05. If it falls outside of this range on two consecutive days, a warning limit notification will be sent to the site operator. If the ratio falls outside of this range for 3 consecutive days, a control limit notification will be sent to the site operator and corrective action will be required.

2) Harmonized solutions to protect gold cartridges from passivation were presented in Topics 5 and 6 covering soda lime traps and the zero air system, respectively. Some additional comments and possible solutions offered by the workshop participants are:
   a. Keep gold traps at a 3% warm value during sampling (default is 1%) to minimize condensation (of compounds?) during sampling that can interfere with the amalgamation of mercury
   b. Use longer gold cartridge heating times and maintain the nichrome heating element to keep them working properly
   c. Cleaning gold cartridges that have been confirmed as truly passivated is likely to be a stopgap until new gold cartridges can be installed.

d. Purge the entire system with zero air after denuder and soda lime change to minimize passivation. (Note: not sure how this is done, but it is assumed that crude is flushed to air rather than going through the gold cartridges).
e. It has been observed that trace contaminant gases in argon can quickly ruin gold traps or reduce fluorescence sensitivity due to quenching. Using a prophylactic molecular sieve trap for oxygen and moisture as well as a used, heat-blanked gold cartridge may be prudent.
f. Changing zero air canisters frequently
g. Rinse and clean 1130 pump module tubing when replacing zero air canisters.

ADDITIONAL TOPICS

1) Can Tekran recycle used gold cartridges with a rebate? Doubtful, but will be researched.

2) Less pressure drop and equal performance can be obtained if the 0.2 um Teflon filters that Tekran supplies are replaced with a 2 um Teflon filter. The pore size rating is not related to the size or efficiency of particle size capture. Using a 2.0 um pore size equivalent Teflon filter allows us to get quantitative capture of particulate matter (99.999%) down to 0.3 um with an order of magnitude less pressure drop than the 0.2 pore size equivalent Teflon filters.

3) A quick survey at the workshop indicated that no one present uses vacuum grease on their impactor plates to minimize large particle bounce.

4) There was a fruitful discussion about the need to do quality assurance standard additions of mercury using syringe injection or the Tekran Model 1120 to have feedback on recovery. Several groups have also done injections of mercury at the inlet or in front of the soda lime in zero air to ensure there are no losses of elemental mercury through the sample lines, filters, soda lime trap. This is an important topic that will be part of the QA program for the network.

5) Check your denuders to see that they are perfectly cylindrical – this is important for proper sampling and good airflow.

6) The connection between the denuder and RFP is a leak point that needs improvement if possible.

7) A very important topic of reporting units, method detection limits and uncertainty was brought forward, but not discussed at length. This is an important topic that will probably require an ad hoc group to address (volunteers?).

8) A maintenance schedule is desired.