



# **GMOS Standard Operational Procedure**

Methods for the determination of speciated ambient Hg

## Foreword

This Standard Operational Procedure (SOP) is for the continuous measurement of mercury species at GMOS monitoring sites using the Tekran 2537/1130/1135 instrumentation. This SOP is based largely on the United States Atmospheric Mercury Network (AMNet) Standard Operational Procedure [1-2]. The AMNet SOP clearly describes the measurement of speciated ambient mercury for large-scale network of sites, and thus is a useful guide for establishing a protocol for the GMOS global monitoring sites. Additional information was obtained from the procedures used at the Canadian monitoring station at Alert in the northern Nunavut Territory [3-4]. Furthermore, this GMOS SOP was revised during a workshop in Brussels, Belgium on 7-8 April, 2011 in which the participating GMOS partners provided input and suggestions on the procedures described in this document.

The present version of this GMOS SOP can be used as a reference guide for initiating and performing speciated mercury measurements for the GMOS site network. It also contains quality control protocols to be used in the field when performing speciated mercury measurements. More detailed technical information can also be found in the Tekran 2537A/B and Tekran 1130/1135 manuals. Where specific AMNet protocols are referenced, these documents can be found online at: <https://nadp.isws.illinois.edu/amn/docs.aspx>

It should be noted that in this SOP, requirements and recommendations are both provided where appropriate. Requirements (typically noted by the words “shall” or “must”) are guidelines that must be followed at all sites. Recommendations are suggestions that allow for some flexibility in the procedures based upon the specific characteristics of each site. Careful attention should be paid to these guidelines for GMOS monitoring sites.

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## 1. Scope

This Standard Operational Procedure describes methods for determining gaseous elemental mercury (GEM), particulate bound mercury less than 2.5  $\mu\text{m}$  (PBM<sub>2.5</sub>), and gaseous oxidized mercury (GOM)\* in ambient air using the Tekran 2537/1130/1135 automated system. The proper operation and maintenance of the Tekran system is described below. This operating procedure is designed to support consistent and systematic sampling among the contributing GMOS sites. Results shall be reported with respect to air at 273.15 K and 101.325 kPa. The sampling times should be reported with respect to GMT time and concentrations should be reported as  $\text{ng m}^{-3}$  for GEM and  $\text{pg m}^{-3}$  for PBM<sub>2.5</sub> and GOM.

\*Note: GEM, Hg<sub>p</sub>, and RGM are the nomenclature that until recently has been widely used for the ambient mercury species which are quantified using the method described here. The contributors of AMNet propose that Hg<sub>p</sub> and RGM should instead be more accurately referred to as particulate bound mercury less than 2.5  $\mu\text{m}$  (PBM<sub>2.5</sub>) and gaseous oxidized mercury (GOM), respectively. The GMOS project will adopt the nomenclature proposed by AMNet, and it will be used throughout GMOS documentation, including this SOP.

## 2. Abbreviations and Definitions

### Mercury Species:

Hg	Mercury
TGM	Total Gaseous Mercury: the summary of gas phase species of mercury, including ground state and reactive forms
GEM	Gaseous Elemental Mercury (Hg <sup>0</sup> ): gas phase mercury in its ground electronic state
GOM	Gaseous Oxidized Mercury: oxidized gas phase mercury compounds
PBM <sub>2.5</sub>	Particulate Bound Mercury less than 2.5 $\mu\text{m}$ : mercury that is bound to particles with a mean aerosol diameter of 2.5 $\mu\text{m}$ or less

### Analytical Terms:

CVAFS	Cold Vapour Atomic Fluorescence Spectrometry
MFC	Mass flow controller
MFV	Mass flow meter
Zero air	Pre-filtered mercury free air used for calibration
UHP	Ultra High Purity (e.g. for Argon gas used by the Tekran; grade 4.8 (99.998%) or higher)
MDL	Method Detection Limit: the minimum concentration of a substance that can be measured and reported with 99% confidence that the concentration is greater than zero
QA	Quality Assurance
QC	Quality Control

### Units:

ng	nanogram; $10^{-9}$ g
$\text{ng m}^{-3}$	nanograms per cubic meter

pg	picogram; $10^{-12}$ g
pg m <sup>-3</sup>	picograms per cubic meter
°C	degrees Celsius
cm	centimeters
L	liters
lpm	liters per minute
psi	pounds per square inch
kPa	kilopascals
V	volts

### 3. Gases and chemicals

- 3.1 Grade 4.8 (99.998%) or higher ultra high purity (UHP) Argon for use as a carrier gas for the 2537.
- 3.2 Elemental mercury, of purity 99.9999 %, for preparation of gaseous mercury vapour standard.

*WARNING — Mercury is toxic by skin absorption and inhalation of vapour. Use suitable personal protective equipment (including gloves, face shield or safety glasses, etc.) and minimize exposure by using a fume hood.*

- 3.3 Reagent grade water: ultrapure deionised water with resistivity greater or equal to 18 MΩ cm that originated from a pre-purified (distilled, reverse osmosis, etc.) source.
- 3.4 Laboratory grade methanol: to use for tubing and glassware cleaning and drying.
- 3.5 Soda lime: soda lime traps are often placed upstream of the detector sample filter to remove free halogens that can shorten the life of the gold trap cartridges. Soda lime should be non-indicating, 4-8 mesh, and free of mercury. Laboratories should contact one of the GMOS work package leaders for information about where and how to purchase acceptable soda lime for the Tekran system. See Annex E for information on soda lime trap assembly.
- 3.6 2.4M Potassium Chloride (KCl): used for coating the GOM annular denuder. Prepare by dissolving 90 g of high purity (ACS grade) KCl in 500 mL of reagent grade water. See Annex E for instructions on coating GOM annular denuders.
- 3.7 Internal permeation source: the 2537 analyzers are equipped with internal permeation sources capable of calibrating the system automatically at a preset time or manually when initiated by the operator.

## 4. Principles of speciated ambient mercury measurements

This SOP applies to the sampling of ambient mercury using the Tekran 2537/1130/1135 automatic speciated ambient mercury monitoring unit. This method allows for determination of mercury from 0.001 to 50 ng m<sup>-3</sup> of air [1].

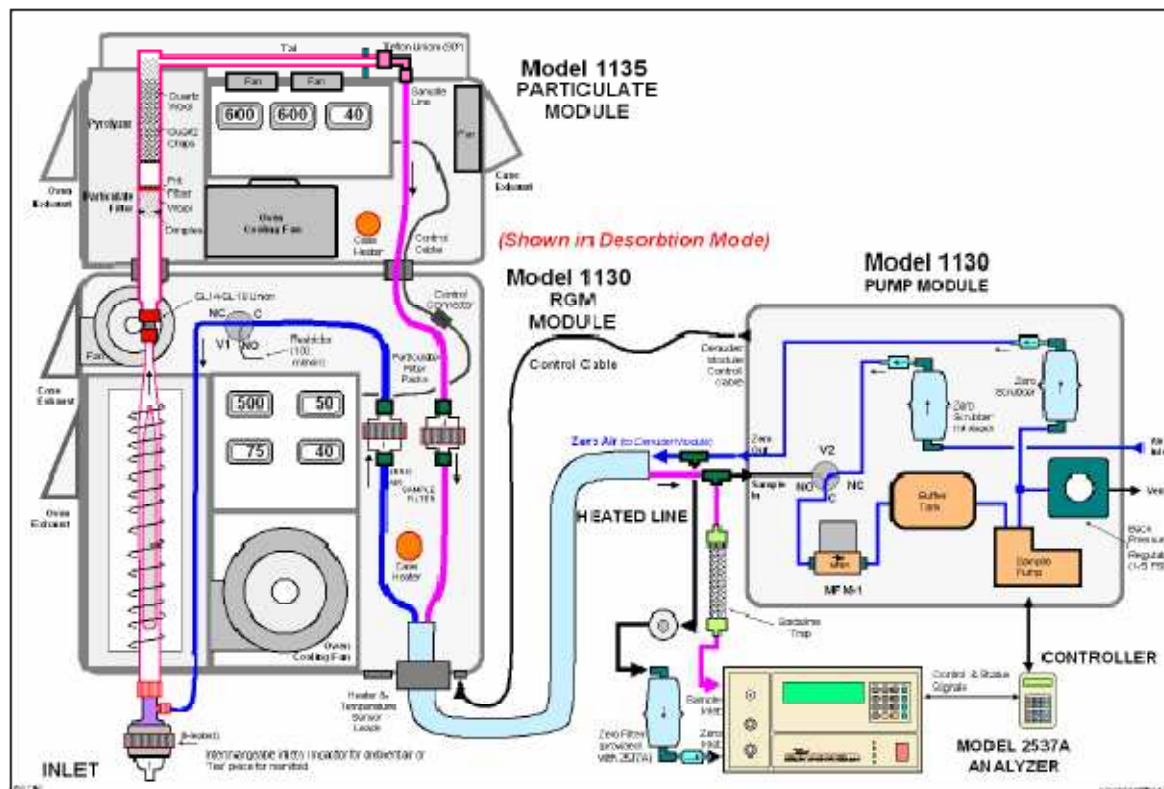


Figure 4.1 Tekran automatic speciated ambient mercury analyzer.

The method employed for the Tekran system within the GMOS project is based predominantly upon the method used by the NADP AMNet [1-2]. This method allows for real-time sampling of GEM, GOM, and PBM<sub>2.5</sub> with detection by automatic gold cartridge pre-concentration and CVAFS. A list of appropriate equipment and parts is provided in Tables 1 and 2 of the AMNet Site Operations Manual [2]. These tables are also provided in Annex A. The GMOS operating sites are required to obtain their own replacement parts from Tekran and other supplying companies.

With the Tekran speciation system, ambient air is pulled through a glass elutriator inlet which removes particulate matter that is > 2.5 µm. The ambient air subsequently is pulled through a KCl coated quartz annular denuder which selectively adsorbs GOM while GEM and PBM<sub>2.5</sub> are able to pass through. Downstream of the denuder, a regenerable particulate filter (RPF) selectively captures PBM<sub>2.5</sub> while the remaining GEM is able to pass through to the 2537 where it is captured onto gold cartridges. The gold cartridges are thermally desorbed, and UHP argon gas transports the released GEM to the detection cell where the Hg concentration is quantified using CVAFS [1].

While GOM and PBM<sub>2.5</sub> are continuously captured by the denuder and RPF, respectively, GEM is collected onto alternating gold traps (A and B) within the 2537. The concentration of GEM on the gold traps is quantified automatically on predetermined intervals (in the

GMOS project, 5-minute sampling intervals are recommended for GEM). After a fixed amount of time which is programmed into the instrument, the Tekran ceases to sample ambient air and switches to a mode for GOM and  $\text{PBM}_{2.5}$  analysis. The RPF and denuder are subsequently heated to very high temperatures to convert the existing Hg to the GEM form which can be captured on the gold traps and quantified using CVAFS. During this time, mercury-free zero air is pushed through the 1130/1135 system to transport Hg to the analyzer [1].

The volumetric flow rate through the inlet should be 10 lpm. The 2537 should pull at 1 lpm for GEM sampling, while the 1130 pump module pulls at 9 lpm. However, high altitude sites exist within the GMOS project where due to lower atmospheric pressure it may be difficult to achieve 10 lpm at inlet. In these specific cases it is acceptable to utilize a lower flow rate; however a volumetric flow rate through the roof inlet of 10 lpm should be achieved to the best extent possible.

The temperature of the instrument during sampling should be 50°C. During the desorption cycle, the denuder tube furnace should heat to 500°C and the RPF tube furnaces should heat to 800°C.

For all GMOS sites, it is recommended that GEM be sampled on 5-minute intervals. The 2537 sampling cycle for GEM should always start at the top of the hour to ensure ease of data comparability. At most GMOS sites, a 2-hour sampling period is recommended for GOM and  $\text{PBM}_{2.5}$ , during which time GEM is continuously sampled on the recommended 5-minute intervals. However, at more remote sites it may be necessary to use a 3-hour sampling period. This sampling frequency should be determined on a site-by-site basis. The sampling cycle should be followed by a 1-hour desorption cycle in which GOM and  $\text{PBM}_{2.5}$  are quantified. The 1-hour desorption cycle should be programmed as follows, with each step requiring 5 minutes [1]:

- 3 zero air flushes
- 1 pyrolyzer heat cycle
- 3 particulate heat cycles
- 3 GOM denuder heat cycles
- 2 zero air flushes (while the furnaces cool)

The concentration of  $\text{PBM}_{2.5}$  should be calculated as the sum of the concentration of the three particulate heat cycles minus 3 times the value of the third zero air flush (from the beginning of the desorption cycle) [1]. The concentration of GOM should be similarly calculated as the sum of the concentration from the three denuder heat cycles minus 3 times the value of the third zero air flush (from the beginning of the desorption cycle) [1].

## 5. Siting requirements for speciated ambient mercury measurements

Two types of sites shall exist within the GMOS project:

**Master Sites** will measure continuous speciated ambient mercury (GEM, GOM, and PBM<sub>2.5</sub>) and total mercury in precipitation.

**Secondary Sites** will measure total gaseous mercury (TGM) and GEM in the ambient atmosphere and total mercury in precipitation.

The following siting requirements shall be followed when establishing new GMOS sites:

1. It is recommended that the GMOS monitoring sites be located in background areas which are not directly impacted by anthropogenic emissions of mercury or other airborne pollutants. The sites shall be representative of a large area, i.e. the concentration(s) of mercury obtained at the site shall be representative for the region where the measurements are performed. Measurement sites close to natural mercury emission sources, such as active volcanoes, are not recommended unless the measured ambient mercury is actually representative for a large area.
2. GMOS sites shall be chosen based on existing sites that can provide available ancillary measurements. Examples include EMEP and GAW sites. In this way, the site will have the necessary existing infrastructure for atmospheric mercury monitoring, including available power, shelter, and site personnel.
3. It is recommended that GMOS sites be selected based upon the criteria set forth by GAW with respect to distances from major natural and anthropogenic sources. Stations within the GAW framework are categorized as either global or regional with respect to the remote nature of the sites and the relative impact of sources and pollutants. Within GMOS, it is strongly recommended that sites satisfy the minimum-distance guidelines of global background stations; however, regional background stations may be permitted depending on the specific site characteristics (Table 5.1).
4. The monitoring sites shall be as exposed as possible without influence from surrounding topography or other obstacles within a 2 km radius around the site. Naturally vegetated areas with level ground are recommended [5]. Vegetation surrounding the site should be maintained at < 0.5 m and not higher than half the height of the measurement device (e.g. precipitation collector) [5].
5. The sites must have sufficient power available to support the operation of desired sampling equipment. Responsible personnel must review the instrument specifications to determine whether the site has the necessary capabilities.
6. All activities near the site shall be recorded on a regular basis. This includes active natural and anthropogenic sources, motor vehicle traffic, distance to population centers, activity of major wildlife, and frequency of people visiting the monitoring site. This is critical for understanding variability in the measurement data.



Table 5.1: Minimum-Distance Guidelines for GMOS Stations. (GAW, 2004) [5]

Parameter	Minimum Distance to Site (km)		Comments
	<i>Regional/Rural Background Stations</i>	<i>Global/Remote Background Stations</i>	
SO <sub>2</sub> or NO <sub>x</sub> Point Source			If emission sources (such as power plants, refineries, chemical plants, smelters or other major industrial facilities) are located in the general upwind direction from the collector, then the regional distances indicated should be doubled
>100 tonnes per year	20	50	
>1000 tonnes per year	50	100	
Major Industrial Complex	50	150	
Town, population 1,000-10,000	10	25	Future population growth and associated land development should be considered carefully, especially for towns and villages near a station. If population centres are located in the general upwind direction from the collector, then the regional distances indicated should be doubled
Town, population 10,000-25,000	20	50	
City, population 25,000-100,000	50	100	
City, population >100,000	100	200	
Parking lot or large paved area	0.2	0.5	On-site parking lots and maintenance yards also need to be kept at least 300 meters from the collector
Secondary road, lightly travelled	0.5	1	The local road network around the site is of particular concern. Traffic volume and type as well as road surface will largely determine the impact at the site
Secondary road, heavily travelled	1	5	
Major highway, airport, railway, shipping lane, harbour	5	25	Moving sources of pollution, such as air, ground, or water traffic or the medium on which they traverse (e.g. runway, taxiway, road, tracks, or navigable river), should not be within 500 metres of the collector
Feedlot operations	2	50	Acceptable distances will vary greatly depending on size of the operation. Even small concentrations of animals should be housed no closer than 500 metres. If the feedlot, dairy barn or animal waste pile can be smelled at the collector, it is too close
Intensive agricultural activities	2	10	Surface storage of agricultural products, fuels, vehicles or other source materials should be kept at least 500 metres from the collector
Limited agricultural activities	0.4	1	Storage of small amounts of agricultural products, fuels, or other source materials should be kept at least 500 metres from the collector
Sewage treatment plant	2	20	
Active volcano, fumarole, etc.	20	100	Geothermal sites including geysers and springs may have significant emissions and should be avoided
Natural salt, dust, alkali sources	2	2	Windswept materials from salt and alkali flats as well as sea spray from coastlines can contaminate samples
Vertical objects (Includes towers, wires, fences, trees), angle of projection from instrumentation	$\leq 45^\circ$ from top of instrument		For an angle of $45^\circ$ from horizontal, the object must be a distance equal to the object's height away from the instrument
Buildings, angle of projection from instrumentation	$\leq 30^\circ$ from top of instrument		For an angle of $30^\circ$ from horizontal, the object must be a distance equal to twice the object's height away from the instrument

## 6. General requirements regarding speciated ambient mercury measurements

The Tekran 2537 and 1130 pump module should be housed in a sheltered, mercury-free ( $< 15 \text{ ng/m}^3$ ), temperature controlled structure ( $15^\circ\text{C} - 30^\circ\text{C}$ ) [3]. Power requirements for the Tekran system are 100/120 V, 50-60 Hz and 250 VA max, 100 VA average [3]. Outside the shelter, the inlet of 1130/1135 system should be positioned such that the inlet is  $\leq 45^\circ$  from vertical objects and trees, and  $\leq 30^\circ$  from buildings [5,6]. Putting the inlet on top of the measurement cabin may be an optimal solution to meet these requirements, and this may also minimize the length of the sample line.

The Tekran instrument should be installed according to the descriptions given in the user manual provided with the instrument. A 25 ft heated  $\frac{1}{4}$ " Teflon sample line (provided by Tekran) is recommended. A 50 ft heated line is also available but should only be used if necessary, as the longer sample line can increase flow resistance. Teflon fittings are required for all tubing connections.

Sites may exist in GMOS where due to extreme weather conditions it is necessary to sample ambient air through a high-flow manifold. However, in these specific cases the use of a manifold and the location of the manifold must be approved by the GMOS science advisory team. It is possible to custom order a manifold from Tekran which is specifically designed and approved for use of the Tekran 1130/1135 instrument in extreme weather locations. It is recommended that, if a manifold is needed at a given site, the site operators utilize the manifold provided by Tekran or ensure that their existing manifold complies with the suggestions below.

The high flow manifold available through Tekran has the following characteristics:

- The manifold is comprised of highly cross-linked, superior fluoro-polymer coated aluminum pipe.
- The manifold has a highly cross-linked, superior fluoro-polymer coated conical inlet, which is designed to give laminar flow in the range of 80-120 lpm.
- The manifold is fully heated and insulated with PID temperature control. The section outside of the building is weatherproof and encased in aluminum pipe.
- The modified inlet for the Tekran 1130 consists of either a longer glass elutriator or a Teflon-coated straight-arm cyclone.
- The manifold is equipped with a blower, flow sensor, and manual flow adjustment

It is recommended that GEM concentrations be measured at the site using the Tekran 2537 prior to deployment of the 1130/1135 speciation system. This will allow for characterizing the GEM levels in the chosen location and determining whether the site in fact represents a background area. It is also recommended that the site operators occasionally (e.g. every 3 months) monitor the GEM concentration inside the monitoring shelter to determine whether there is any risk of contamination or bias from within the shelter [1]. Shelter air should contain  $< 15 \text{ ng/m}^3$  of Hg.

Trace metal clean techniques must be used at all times in the laboratory and in the field when handling or preparing supplies and performing necessary tasks for mercury speciation sampling. Clean techniques are critical for preventing the contamination of sampling equipment and ensuring the collection of the highest quality data. This includes wearing appropriate clean, non-talc gloves (e.g. nitrile) when handling any component that will come

in contact with the sampling stream. In the laboratory, such components should be handled in a clean room, clean bench, or glove box to avoid exposure to contaminated air.

## 7. Operation and routine maintenance of the Tekran2537/1130/1135 speciation system.

To assure collection of the highest quality data, the instrument must be inspected and maintained on a regular basis. A trained operator must visit the measurement site weekly. In addition, remote monitoring of the data is recommended where possible, as it allows for observing the performance of the instrument in between visits to the measurement site. An example weekly site checklist for the field operator is given in Annex G. The operator should bring this document to the site each week and appropriately note the maintenance performed.

Each time the operator visits the monitoring site, he/she is responsible for inspecting the condition of the site (noting any unusual activity), verifying the operation of the sampling equipment, performing the appropriate maintenance procedures, compiling the field form(s), and when necessary troubleshooting, repairing, and/or replacing equipment. Below, the recommended instrument settings and routine maintenance required of the operator is outlined, following the procedures established by AMNet [2]. A list of consumable materials for maintaining operation of the Tekran system is provided in Table 2 of the *AMNet Site Operations Manual* [2] and in Annex A. Site operators are responsible for purchasing and having available all necessary replacement parts in their own laboratories

### 7.1 Recommended instrument settings for the Tekran 2537 A/B

The parameter settings recommended at a typical background site are listed below. The Autocal feature should be set to “Yes” to indicate that the internal permeation source used for automatic calibrations is chosen (See section 7.6 below). Note that the sample timing in Table 7.1.1 could be optimized for more remote sites where it is difficult to obtain Argon (e.g. longer sampling time to reduce the frequency of Argon usage). However, more frequent heating is better for the gold cartridges and as such Tekran recommends a 5-minute sampling interval. As such, 5-minute sampling is recommended for the majority of GMOS sites.

**Table 7.1.1** Recommended parameter settings for the Tekran model 2537A/B instrument

#### Method. Edit. Timing-1

Sample:	300 s	FlushHi:	40 s
Calib:	300 s	Meas-dly:	5 s
Zero-sub:	No <sup>(a)</sup>	BL-Time:	20 s

#### Method. Edit. Timing-2

Intg-Dly:	15 s	Pk-Time:	35 s
HtADur:	32 s	Cool-Dn:	80 s
HtBDur:	32 s	Round:	5 min

Method. Edit. other

Car-Meas:	80 ml/ min	SmplRate:	1.00 l/min
Car-Idle:	5 ml/ min	WarmA:	3 %
CarFlush:	100 ml/ min	Warm B:	3 %

Method. Edit. Perm-Src

Autocal:	No/Yes	PermTime:	120 sec
Cal-Conc:	Instrument specific	CalibInt:	72.0 hr

- (a) Zero-sub should be set to “No”. During normal performance the zero values (BlArea) should be very low(< 1500). If high zero values persist it might indicate problems with leaking or contamination. Consult the Tekran manual for appropriate maintenance

## 7.2 Weekly Maintenance (Each Visit)

Each week the operator is responsible for the following primary tasks to maintain the performance of the Tekran speciation system. A more specific list of instrument parameters and checks are provided in Table 5 of the *AMNet Site Operations Manual* [2], which is displayed in Annex B. Additionally, the operator can consult the *AMNET Site Report A: Each Visit/Weekly Maintenance* [7] for specific details and procedures.

- Completesteeklysite report
- Examine instrument data and parameters (e.g. samplevolume, baseline voltage, zero air flush values, peak status, argon tank, temperatures, errorlights, etc.) and note on checklist
- Confirm that the 2537 baseline is between 0.100 - 0.250 V
- Confirm that the standard deviation of the baseline is < 0.100 mV
- Check the 2537 lamp voltage
- Examine a recent period of consistent data collection without any obvious disturbances (e.g. sudden peaks in concentration). Compute the average of 5 consecutive A trap concentrations and 5 consecutive B trap concentrations. Confirm that the average concentrations of the 5 consecutive the A/B trap measurements are different by < 10%.  
For example:  
mean (A)= Average (A1, A2, A3, A4, A5)  
mean (B) = Average (B1, B2, B3, B4, B5)  
 $APD = \frac{\text{mean}(A) - \text{mean}(B)}{\text{Average}\{[\text{mean}(A) + \text{mean}(B)]\}}$   
Where “APD” = Average Percent Difference
- Examine the every 72-hour automatic calibrations– confirm that the calibration zeros are 0.000 and that the A and B trap spans are different by  $\leq 5\%$ .
  - NOTE: If the trap spans differ by 5-10%, the operator does not necessarily need to take action but he/she should note this difference in the event that the traps continue to differ by a greater percentage or in the event that there is a sudden change in trap performance. If the trap spans differ by more than 10% then the operator may need to take corrective action and should consult the Tekran 2537 manual for guidance.

- Look for clear PBM<sub>2.5</sub> and GOM peaks and zero air flushes in the desorption cycles. During the desorption cycles of each species, the mercury removed during the three consecutive cycles should be desorbed as 70%, 20%, and 10% of the total concentration, respectively.
- Examine the argon tank and regulator pressures
- Confirm that all error lights are off, the Perm light is blinking, and all switches are in the correct position
- Confirm that the 1130/1135 case and heater temperatures are correct

### 7.3 Bi-weekly and Monthly Maintenance

Bi-weekly the operator is responsible for the following tasks in addition to the weekly tasks:

- Replace soda lime trap
- Replace GOM denuder
- Replace inlet glassware
- Replace 1130 quartz sample filter
- Perform leak check of the system at the sample inlet ( $\leq 0.3 \text{ ng/m}^3$  expected)
- Confirm that the instrument meets all specifications

At the end of each month, the operator is responsible for the following tasks in addition to the bi-weekly and weekly tasks:

- Replace RPF
- Clean GL 14-18 union
- Install new 1130 zero air filter

Specific details for performing these tasks can be found in the *AMNet Site Report B: Glassware Change-out/Monthly Maintenance*[8].

NOTE: Some of these biweekly and monthly tasks may need to be performed on a greater frequency depending on specific site characteristics. For example, sites with high humidity (e.g. coastal and marine sites) may require the soda lime trap to be changed weekly instead of bi-weekly. Other sites with high particulate levels may require the 1130 filter to be changed weekly, or sites with higher RGM concentrations may also require weekly replacement of the GOM denuder. All new sites should initially follow the guidelines above, but consider these types of adjustments once initial data is collected and site specific procedures can be determined.

### 7.4 Quarterly Maintenance

The operator is responsible for the following tasks on a quarterly basis in addition to the weekly, bi-weekly, and monthly tasks described in 7.2 and 7.3. More detailed descriptions of these tasks are also provided in Table 7 of the *AMNet Site Operations Manual* [2] as well as the *AMNet Site Report C: Quarterly Maintenance* [9]. Note that not all tasks listed below are performed every quarter so it is important that the operator be aware of when these procedures are required.

#### **Each quarter –**

- Measure, verify, and calculate % difference of the 1130 flow rate
- Measure, verify, and calculate % difference of the inlet flow rate
- Perform elemental injections on gold trap cartridges A and B (see Annex C for instructions on the use of the mercury vapor source for elemental injections)
- Examine gold cartridge heating coils and confirm that they are bright orange when heating
- Confirm that instrument shelter air contains  $\leq 15 \text{ ng/m}^3$  of mercury
- Install new 2537 sample filter
- Clean Teflon line from 2537 to soda lime trap
- Perform leak check of the 2537 analyzer. This can be done by disconnecting the sample line from the back of the instrument (where the filter housing is located) and physically blocking the filter inlet with a Teflon cap. The pump flow should drop to zero (pump will begin to race). At that time the Teflon cap can be removed and sample line can be reattached.
- Confirm that the 1130 flow rate is within 3% of the set point

#### **2<sup>nd</sup> quarter only –**

- Change 1130 zero air canister
- Clean 1130 pump tubing
- Replace 1130 DFU filters
- Measure, verify, and calculate % difference of the 2537 flow rate
- Verify 2537 scalefactor

#### **4<sup>th</sup> quarter only –**

- Change 2537 heater coils, zero air canisters, DFU filter
- Replace RPF elbow and tubing
- Replace 1130 pump diaphragm and pump brushes  $\leq 1.0 \text{ cm}$
- Replace denuder-to-RPF union
- Measure, verify, and calculate % difference of the 2537 flow rate
- Verify 2537 scalefactor
- Calibrate flow meter
- Rinse heated sample line
- Verify standard addition performance
- Site audit (See section 9)

## **7.5 As-Needed Maintenance**

The following tasks should be performed by the operator as needed. These tasks are also listed in Table 8 of the *AMNet Site Operations Manual* [2] and described in detail in the *AMNet site report D: Annual/As-Needed Maintenance*[10].

- Reset or replace 2537 lamp
- Install new matched pair of gold cartridges
- Clean or replace 2537 Teflon valves
- Clean or replace cuvette
- Service or repair the 2537 pump
- Replace septum

- Check perm source temperature and perm vent flow
- Replace filter holders and fittings
- Replace 1130 heater
- Replace the 1130 or 1135 caseheaters
- Rinse heated sample line
- Replace Argon gas cylinder when pressure is < 200 psi
- Swap equipment (record new serial number)

## 7.6 Calibration

The Tekran 2537 should be regularly calibrated by the following method involving the internal permeation source:

- An automatic internal calibration using the internal permeation source, which utilizes known amounts of mercury vapour. It is recommended that this calibration be performed automatically by the instrument at least every 72 hours with a permeation time of 120 seconds [1]. The operator should keep a record of these calibrations (spans and blanks) in order to observe patterns in instrument behaviour over time [1].

Occasionally, it is also necessary to perform Manual Injections or Standard Additions of known amounts of mercury vapour obtained from a temperature controlled mercury vapour source (e.g. Tekran model 2505). This procedure is used to verify the permeation source and confirm that it is stable. This procedure is not recommended as a means to regularly calibrate the 2537 instrument. This should be performed quarterly by a trained technician or field operator [1]. The procedure is described in the Tekran 2537 manual, Chapter 5. Information on the characteristics of the mercury vapour source and how it should be used with the Tekran 2537 are also presented in Annex C.

## 8. Data download, storage, and management

Data from the Tekran speciation system should be captured using a desktop computer, laptop computer, or data logger at the monitoring site.

The GMOS sites are free to quality assure and use their data in their own manner, but all GMOS data should be processed by GMOS project managers in the same way.

The most important process related to data management within the GMOS project is the transfer of collected data to a central database. As such, GMOS will provide an Interoperable System (ICT) to all the partners which allow the sharing of:

- (1) information and data from historical databases,
- (2) measurements collected at GMOS ground-based sites and measurement campaigns,
- (3) model output.

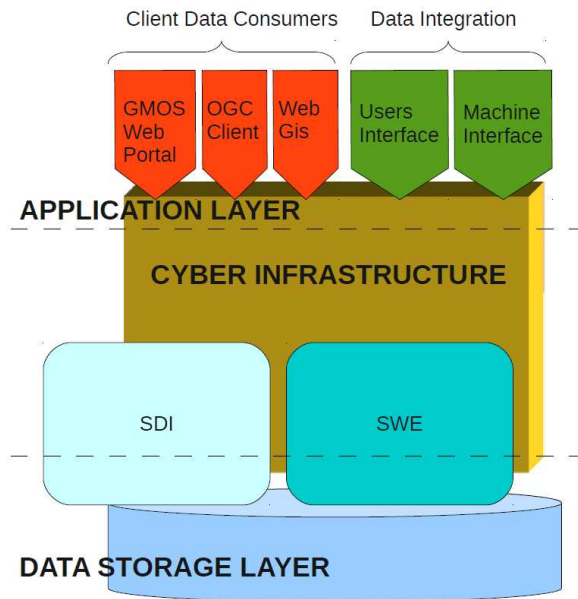
The development of the ICT system will consider a range of data formats given that data will be provided from in-situ or mobile sensors, from oceanographic or aircraft measurement campaigns, or from numeric models.



The GMOS ICT System will be based on a Spatial Data Infrastructure (SDI), which contains two central databases:

- I) a Database Management System (DBMS) for most of the data; and
- II) a *Sensor Web Enablement* (SWE) system for data coming from monitoring stations.

This Data Storage Layer (see **figure below**) will be managed by Cyber Infrastructure, which will serve as an integration system for data coming from GMOS partners' activities. Administrators will have an account in the Cyber Infrastructure in order to manage data processes and data integration.



Data stored in the Data Storage Layer and managed by the Cyber Infrastructure will be provided to users by means of different devices contained in an Application Layer. Each device represents a different view of the data managed by the Cyber Infrastructure. The GMOS web site can be used as device where data will be provided to users as simple link for data link, or by a Web visualization system to visualize information (Human to Machine process, H2M). Additional devices will be oriented to a machine access (Machine to Machine process, M2M) like Web Services OGC compliant.

## 8.1 How to upload data in the GMOS ICT System

The Cyber Infrastructure will have a simple Web Interface through which users can produce metadata (following an INSPIRE scheme), upload data, and assign rights to their data.

Two main methods will be used for uploading data to the GMOS ICT System:

1. Directly upload data using the Web User Interface. In this case a user will access a dedicated web page through a username and a password. He/she will fill in a few mandatory fields to construct the metadata and upload the file. The Cyber Infrastructure will manage and store the data.
2. Upload data through an automatic connection (by using common communication protocols like FTP, HTTP, etc.). The system can be configured in a *data-pull* event (in



which the system will periodically call dedicated computers and folders to retrieve data) or in a *data-push* event (in which the users can notify the system by an e-mail that new data have been loaded in a folder).

Under two of the Deliverables from the WP9, GMOS will report in detail the SDI architecture and the metadata requirements.

## 9. Quality control and quality assurance

Laboratories involved in preparing supplies for operation of the Tekran speciation system must demonstrate adherence to quality control and assurance procedures, including regular analysis of any reagents, standards, or blank solutions required for operating the instrument [1].

Site operators should also be thoroughly trained by a technician or GMOS project coordinator who is familiar with the operation of the Tekran speciation system. The operator is responsible for reviewing all Standard Operating Procedures, troubleshooting guides, and site maintenance documents provided. The site operator is responsible for evaluating the raw instrument data on a weekly basis. This includes examining all of the parameters described in section 7.1 and the table in Annex A. Any abnormalities should be noted on the weekly field sheet, and as necessary the site operator should troubleshoot and perform instrument maintenance to resolve any persistent problems. The 2537 analyzer must also be calibrated regularly as described above in section 7.6.

The GMOS team will regularly and systematically perform QA/QC procedures on the speciated ambient Hg measurements collected at all sites. The QA/QC procedure will be designed to generate error flags for problematic data. This systematic examination of the data over time will allow for determining the benchmarks for high quality data within the GMOS project. Through frequent and systematic examination of the data it will also be possible to ensure that the site operators are operating the instrumentation correctly and collecting consistent high quality data. The quality of performance at each site will be in part determined by the percentage of complete data that is collected, which will be determined by the presence of complete sampling cycles free of instrument or measurement error. Throughout the course of the project, GMOS will work with other networks such as AMNet to determine appropriate detection limits for measurement parameters as well as acceptable limits of precision and uncertainty, because widely accepted values have not currently been established for measurements with the Tekran speciation system.

### Regular Site Audits

Regular site audits by a trained technician are recommended in order to ensure continued instrument performance and the collection of high quality data. The following procedures are recommended during regular (e.g. annual or bi-annual) site audits [2-3]:

General site inspection:

- Verify overall operation of the equipment
- Inspect area around the station and confirm compliance with siting criteria
- Determine height of sample inlet
- Identify location of sample inlet with respect to the laboratory building
- Identify type and size of inlet hood

- Identify type and length of sample line
- Observe movement of people and vehicles near site

Instrument inspection:

- Determine sample volume
- Check for contamination of sample filter
- Leak test on each gold cartridge
- Determine difference between cartridges (expect difference within 10%)
- Permeation test
- Cartridge integrity and interference
- Inspect sample line integrity
- Verify performance of the Standard Addition Unit (calibration unit should stabilize overnight before injections are performed)
- Compare performance of syringes
- Compare calibration set-ups

## 10. References

- [1] NADP AMNet Standard Operating Procedures for Field Analysis of Gaseous and Fine Particulate-Bound Mercury. Version 1.1 January 2011. Written and edited by Mark L. Olson and Mark F. Rhodes.
- [2] Atmospheric Mercury Network Site Operations Manual. Version 1.0 February 2011. Written and edited by Mark L. Olson and Mark F. Rhodes.
- [3] Standard Operating Procedures Manual for Total Gaseous Mercury Measurements. Canadian Atmospheric Mercury Measurement Network (CAMNET). Version 4.0 March 1999. Written and edited by Sandy Steffen and Bill Schroeder.
- [4] Tekran Mercury Speciation Unit Protocol for 1130/1135 Operation at Alert Site. Provided by Sandy Steffen, Environment Canada.
- [5] Manual for the GAW precipitation programme. Guidelines, Data Quality Objectives and Standard Operating Procedures. WMO TD No. 1251. WMO/GAW Report nr 160. WMO, 2004.
- [6] NADP Site Selection and Installation Manual. September 2009. Written by Mark F. Rhodes.
- [7] NADP AMNet Standard Operating Procedure Site Report A: Each Visit/Weekly Maintenance. Version 1.3 February 2011. Written and edited by Mark L. Olson and Mark F. Rhodes.
- [8] NADP AMNet Standard Operating Procedure Site Report B: Glassware Change-out/Monthly Maintenance. Version 1.3 February 2011. Written and edited by Mark L. Olson and Mark F. Rhodes.
- [9] NADP AMNet Standard Operating Procedure Site Report C: Quarterly Maintenance. Version 1.3 February 2011. Written and edited by Mark L. Olson and Mark F. Rhodes.
- [10] NADP AMNet Standard Operating Procedure Site Report D: Annual/As Needed Maintenance. Version 1.3 February 2011. Written and edited by Mark L. Olson and Mark F. Rhodes.

## Annex A

Figure A.1. Equipment and parts recommended for use in GMOS ambient speciated mercury measurements [2].

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Table 1. NADP approved equipment for use in the AMNet.

Equipment	Manufacturer*	Model Number
Continuous Mercury Vapour Analyzer	Tekran	2537A or 2537B
Air Dryer	Tekran	1102
Continuous Oxidized Mercury Speciation Module	Tekran	1130
Continuous Particulate Mercury Module	Tekran	1135

\* Disclaimer: The use of a trade or manufacturer's name does not constitute an endorsement by the University of Illinois, the Illinois State Water Survey, or the NADP.

Table 2. Recommended inventory for AMNet consumable materials.

Description	Part Name	Tekran Part Number	Quantity
For operation of the Tekran 2537A	UV analytical lamp, 1"	90-25180-01	1
	Gold cartridge, matched pair	35-25500-00	1
	Zero air canister	90-25360-00	1
	Dry filter unit filter	90-25115-04	1
	Particulate filter, pore size 0.2 µm, diameter 47 mm	90-25102-100	10
	Injection port septum	90-25110-100	10
	Cartridge heater, pair	model specific	1
	Pump diaphragm and brushes	model specific	1
	V2 valve	80-25600-00	1
	Soda lime cartridge	90-13310-64	1
For operation of the Tekran 1130	¼" Teflon ferrules	30-25300-05	2
	Impactor disks	30-13127-10	10
	Particulate filter, borosilicate glass, pore size 1.0 µm, diameter 47 mm	90-13110-100	10
	Zero air canister	90-25360-00	2
	Dry filter unit filter	90-25115-00	2
	Impactor inlet assembly	several	1
	Pump diaphragm and brushes	model specific	1
For operation of the Tekran 1135	Quartz denuder (body only)	30-13100-00	2
	Quartz filter disks for regenerable particulate filter, pore size 0.1 µm, diameter 21 mm	90-13500-25	10
	Quartz wool regenerable particulate filter fill material	90-13510-25	1
	GL14-GL18 union	30-13510-00	1
	Teflon 90 reducing union ⅜" – ¼" elbow	30-13520-00	1
	Quartz regenerable particulate filter assembly	30-13500-00	2

## Annex B

Figure B.1. Weekly activities as suggested by AMNet [2].

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**Table 5.** Weekly activities as reported in AMNet Site Report A.

Equipment	Maintenance Check
General	2537 date time correct
	Baseline voltage 0.100-0.250 V
	Baseline deviations < 0.100 V
	Peak status = OK, OKF, or NP
	Sample volume 5.0 L (adjustable)
	Calibration zero = 0.000
	SPAN RF $\geq 6 \times 10^6$
	Span difference A vs B $\leq 5\%$
	Desorbition blank C = 0.000 pg/m <sup>3</sup>
	PBM clear peak
	GOM clear peak
	Argon tank $\geq 200$ psi
	Regulator $\geq 30$ psi
	2537 lamp light off
	2537 perm light blinking
	1130/1135 switches to auto
	1130 pump switch on
	1130 flow auto
	1102 warm to touch
	1102 drierite blue
1130 unit	Denuder temperature (sample) 50 °C
	Denuder temperature (desorb) 500 °C
	Elutriator heater temperature (sample) 50 °C
	Elutriator heater temperature (desorb) 75 °C
	1130 Case temperature 35-41 °C
	Sample line temperature 50 °C
1135 unit	Pyro temperature (sample) 50 °C
	Pyro temperature (desorb) 800 °C
	Part temperature (sample) 50 °C
	Part temperature (desorb) 800 °C
	1135 Case temperature 35-41 °C

## Annex C

### General characteristics of mercury vapour sources

A small amount of liquid elemental mercury is kept in a closed thermostatted container, according to Figure C.1. The mercury concentration in the source is determined by the mercury vapour pressure ( $P_{\text{Hg}}$ ) over the liquid mercury phase. Since  $P_{\text{Hg}}$  is strongly dependent on temperature, it is necessary to know exactly the temperature in the calibration vessel (i.e. the temperature of the liquid mercury phase). The temperature should be measured by the accuracy equal to or better than  $\pm 0.1$  °C. A thermometer that is certified traceable to an international standard shall be used. The pressure in the source shall be maintained equal to the ambient by help of a narrow capillary tube. The principles of using the saturated mercury source for calibration are described below.

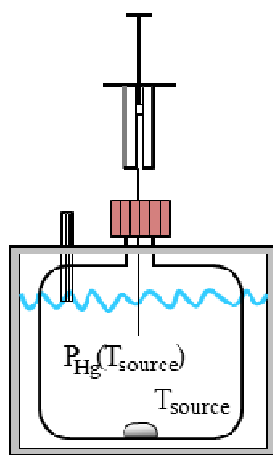


Figure C.1. A saturated mercury vapour source consisting of pure liquid mercury housed in a thermostatted water bath.

Figure C.1 shows how a sample of gaseous mercury is collected from a saturated mercury vapour source. A syringe is inserted via a septum on top of the flask containing liquid elemental mercury in equilibrium with its vapour. The syringe is conditioned by slowly moving the plunger up and down one or two times. A certain volume is then collected and used as a standard amount of mercury. The mercury concentration in the source  $C_{\text{Hg}}$ , can be calculated by help of the Ideal Gas Law according to,

$$C_{\text{Hg}} = \frac{P_{\text{Hg}}(T_{\text{source}})}{R T_{\text{source}}} A_{\text{Hg}} \quad \text{ng } \mu\text{l}^{-1} \quad \text{Equation C.1}$$

Where  $A_{\text{Hg}}$ ,  $R$  and  $T_{\text{source}}$  are the standard atomic weight of Hg (200.59 u),  $R$  is the ideal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $T_{\text{source}}$  is the temperature in K [1].

It should be noted that the mercury concentration in the syringe will only be equal  $C_{\text{Hg}}$  when the temperature of the syringe is equal to  $T_{\text{source}}$ . Hence, if the temperature of the syringe happens to be lower than  $T_{\text{source}}$ , some of the gaseous mercury may condense on the surfaces inside the syringe. On the other hand, if the mercury source temperature is lower than the ambient the concentration in the syringe will be lower than in the source. An accurate and

precise correction for the temperature difference between the syringe and that of the source can be made [1] and the result is,

$$C_{\text{Hg}}(\text{syringe}) = \frac{P_{\text{Hg}}(T_{\text{source}})}{R T_{\text{syringe}}} A_{\text{Hg}} \quad \text{ng } \mu\text{l}^{-1} \quad \text{Equation C.2}$$

To use equation C.2,  $P_{\text{Hg}}(T_{\text{source}})$  must be substituted by a mathematical function that describes the saturation pressure of mercury. If using the expression proposed by Ebdon et al., 1989 [2], the following equation is obtained.

$$C_{\text{Hg}}(\text{syringe}) = \frac{D}{T_{\text{syringe}}} 10^{-(A + \frac{B}{T_{\text{source}}})} \quad \text{ng } \mu\text{l}^{-1} \quad (T_{\text{syringe}} \geq T_{\text{source}}) \quad \text{Equation C.3}$$

$T_{\text{syringe}}$  is the temperature of the syringe in Kelvin;

$T_{\text{source}}$  is the temperature of the mercury source in Kelvin;

A is a constant with numerical value -8.134 46;

B is a constant equal to 3 240.87;

D is a constant equal to 3 216.523;

Equation C.3 shall be used to calculate the mass concentration of mercury vapour samples collected from a mercury vapour source using a syringe.

Equation C.3 is identical to that recommended in the recent European Standard NEN-EN 15852 [1] and resembles the equations recommended in many mercury instrument manuals and standards.

Remarks:

- Equation C.3 takes account of two different temperatures – the temperature of the mercury source and that of the syringe.
- Equation C.3 is only valid for situations where  $T_{\text{syringe}}$  is equal to or higher than the temperature of the mercury source ( $T_{\text{source}}$ ).
- It is recommended to keep the temperature of the mercury source at least some degrees Celsius below room temperature.

High accuracy is required for the determination of  $T_{\text{source}}$  as mentioned above. This is because the vapour pressure of mercury is exponentially dependent on temperature. Therefore,  $T_{\text{source}}$  appears in the exponential term of Equation C.3. The temperature of the syringe can normally be considered as equal to the room temperature and it is enough to measure this temperature with an accuracy of  $\pm 1$  °C.

## References

- [1] NEN-EN 15853 (en). Ambient air quality - Standard method for the determination of mercury deposition. ICS 13.040.20, June 2010.
- [2] Ebdon L.; Corns W. T.; Stockwell P. B.; Stockwell P. M.; Application of a computer-controlled adsorber/desorber system to monitor mercury in air or gas samples: Part 1. Calibration and system description; Journal of Automatic Chemistry (1989), Vol. 11, No 6, p. 247-253



## Characteristics of the Tekran 2505 mercury vapor source

It is recommended that the Tekran Model 2505 Mercury Vapor Primary Calibration Unit be used to perform manual injections and standard additions on the 2537. With this instrument a small amount of liquid elemental mercury is kept in a closed thermoelectric temperature controlled container, and no water bath is needed. The mercury concentration in the source is determined by the mercury vapour pressure ( $P_{\text{Hg}}$ ) over the liquid mercury phase. Since  $P_{\text{Hg}}$  is strongly dependent on temperature, it is necessary to know exactly the temperature in the calibration vessel (i.e. the temperature of the liquid mercury phase). The temperature of the source is determined automatically by the 2505 and reported digitally. The 2505 is powered by 110 V line power. The temperature resolution of 0.001 °C and an accuracy of  $\pm 0.05$  °C. A Hamilton digital syringe is used to draw predetermined amounts of mercury vapour from the device. The concentration of mercury obtained by the syringe can be determined by the temperature of the mercury chamber. Manual injections and standard additions should be performed by a trained technician following the instructions in the Tekran 2505 User Manual.



Figure C.2. The Tekran 2505 Mercury Vapor Primary Calibration Unit



## Annex D

### **Cleaning of gold traps**

A pair of gold cartridges (gold traps), i.e. glass tubes containing a large gold surface, is used in the Tekran 2537 mercury analyser to trap gaseous mercury from ambient air. The two cartridges continuously undergo adsorption/desorption cycles during the measurements. After prolonged use, deactivation may occur. One option is to remove the gold traps and install a new matched pair (this is typically performed annually or as needed). In certain situations cleaning of the cartridges may be an alternatively suitable solution. A possible monthly standard cleaning procedure is presented here.

To perform continuous mercury measurements two pairs of sample gold traps are required. After cleaning the cleaned gold traps should be tested against a reference pair of gold traps, i.e. an additional pair that is not used for sampling. *If the tested cartridges show a deviation of more than 5 % a more profound treatment with Aqua regia (three parts of concentrated hydrochloric acid (HCl) and one part of concentrated nitric acid (HNO<sub>3</sub>) is needed.*

### **Cleaning procedure of gold cartridges in an ultrasonic bath**

Prior to cleaning the cartridges are rinsed with deionised water (3.5) using a clean syringe and immersed overnight in deionised water (3.5). The actual cleaning takes place the next day in an ultrasonic bath with a solution of deionised water (3.5) and an alkali detergent<sup>1</sup>. The solution consists of 300 ml of deionised water and 12 ml of the detergent.

***Use disposable (rubber) gloves during the whole procedure!***

### **The complete cleaning procedure:**

#### **I**

- a. With a 12 ml plastic syringe draw 10 ml of the solution into the cartridge and immediately force it out again; repeat this procedure 10 times;
- b. Fill the cartridge again with the solution and place in into the ultrasonic bath for 9 minutes;

Repeat procedure a. and b. 10 times for both cartridges (A and B). Make sure not to mix the cartridges. Finish by rinsing with deionised water.

#### **II**

- a. With a new 12 ml plastic syringe draw 10 ml of deionised water into the cartridge and immediately forced it out again. Repeat this procedure at least 10 times using fresh deionised water each time.
- b. Finish the cleaning by flushing pure Argon or Nitrogen (3.1)/(3.2) gas through the cartridges. The Argon/Nitrogen gas should be flushed through each of the cartridges for at least 5 minutes.

## Testing of the cleaned cartridge pair

The cartridges are tested in a Tekran 2537A analyser (preferably with an analyser not used for sampling). In this test the adsorption capacity of the cleaned cartridges are compared with a reference gold cartridge pair that not is used for continuous sampling.

### Testing procedure

Start background air sampling with the reference cartridge pair. The instrument should be run using the same frequency and timing that is normally used during sampling (5 min sampling cycles at a sampling rate of 1.0 L per min). Check the performance of the instrument, i.e. that it is yielding expected background TGM values and that the zero air values are sufficiently low (should be close to zero).

- a. Measure a sequence of five complete cycles on each cartridge;
- b. Install the cleaned cartridge pair. Start the instrument and perform a zero air test. Measure a sequence of five complete cycles on each cartridge.

The average values from the cleaned cartridges should be within  $\pm 5$  when compared to each other and should also not differ more than 5 % in comparison to the reference cartridges.

<sup>1</sup>Labosol-U-Ultraschall-Reiniger. This detergent is provided by the German company neoLab ([www.neolab.de](http://www.neolab.de)).

## Annex E

### Laboratory cleaning procedures for speciated mercury measurements

All components that are in contact with the sample air shall be cleaned extensively before use. Plastic or nitrile non-talc gloves shall be used at all times when preparing and handling equipment that will come in contact with the sample stream.

The following laboratory procedures are based upon the procedures suggested for the AMNet sites. Further details can be found in *AMNet Site Report B*[9].

#### Denuder coating

- 2.4M KCl Coating solution – dissolve 90 g of ACS grade KCl in 500mL of reagent grade water
- Follow Tekran Technical Note 307: EPA Denuder Recoating Procedure

#### Soda lime

- non-indicating
- 4-8 mesh
- Low mercury
- pre-purged with argon
- refer to Tekran Technical Note 204: Model 2537/1130 Soda lime trap

#### Inlet glassware cleaning

- separate elutriator into its four components (union, upstream tee, impactor body and impactor inlet)
- replace the impactor disk
- thoroughly rinse all components with reagent grade water then laboratory grade methanol. If any debris remains following the rinse with reagent grade water and laboratory grade methanol, wipe the inside of the glassware with a long cotton swab.
- allow components to dry
- reassemble elutriator
- place inlet assembly in zip-lock bag for storage and transport

#### Cleaning and repacking the RPF

- Remove inlet cap
- Use the nichrome wire tool to remove quartz wool plug and quartz filter
- Cut a clean room wipe into 4x8cm pieces
- Put a piece of clean room wipe on the end of the nichrome and put a few drops of reagent grade water on the wipe – clean the inside walls of the RPF inlet
- Put another piece of clean room wipe on the nichrome and put a few drops of methanol on the wipe – clean the inside walls of the RPF inlet
- Perform the same two steps with smaller pieces of clean room wipe on the tail of the RPF
- Purge RPF with zero air to dry
- Insert a new quartz filter disk using the nichrome wire – ensure it is flat on the frit
- Insert a new piece of quartz wool
- Heat the main body of the RPF in a tube furnace to 800°C for 30 min while pushing Hg-free air through the RPF at 1 lpm
- Allow RPF to cool and cap both ends
- Store carefully until use

## Annex F

### Recalculation of concentrations and air volumes to reference conditions

TGM and GEM concentration values are presented as the mass of  $\text{Hg}^0$  per volume. Since actual air volumes vary with temperature and pressure, standardised volumes are used. With instruments using MFC and MFM the air volume is often standardised to a certain reference temperature and pressure. The default setting of, for example the Tekran model 2537A/B instrument, is 273.15 K and 101325 Pa. Concentration values can easily be recalculated to a certain reference condition according to,

$$C_{\text{ref}} = \frac{P_{\text{ref}} T}{T_{\text{ref}} P} C \quad (\text{ng m}^{-3}) \quad \text{Equation E.1}$$

Where  $T_{\text{ref}}$  and  $P_{\text{ref}}$  correspond to the desired reference condition and  $T$ ,  $P$  and  $C$  relate to the actual temperature, pressure and concentration, respectively [1]. To convert GEM concentrations obtained at varying temperature and pressure each individual value must be recalculated using Equation E.1. Whereas when recalculating from one reference condition to another the relation between  $C_{\text{ref}}$  and  $C$  is a constant.

Likewise, may a volumetric flow rate value be recalculated to a standardised flow rate, according to,

$$F_{\text{ref}} = \frac{T_{\text{ref}} P}{P_{\text{ref}} T} F \quad \text{Equation E.2}$$

Where  $T_{\text{ref}}$  and  $P_{\text{ref}}$  correspond to the desired reference condition and  $T$ ,  $P$  and  $F$  relate to the actual temperature, pressure and volumetric flow rate, respectively [1].

The GMOS reference temperature and pressure are 273.15 K and 101325 Pa, respectively.

## Annex G      Tekran Check and Maintenance List

<b>Site Name:</b>	<b>Country:</b>
<b>Operator:</b>	<b>Date:</b>

### Each Visit Checklist:

2537 Analyzer and Data	Check (X) if OK	1130 Pump	Check (X) if OK
2537 date time correct		1130/1135 switches to auto	
Peak status = OK, OKF, or NP		1130 pump switch on	
Sample volume 5.0 L		1130 pump flow switch to auto	
Baseline voltage 0.100-0.250 V		<b>1130 Unit</b>	
Baseline deviations < 0.100 V		Denuder temperature (sample) 50°C	
Calibration zero = 0.000		Denuder temperature (desorb) 500°C	
SPAN RespFctr $\geq 6 \times 10^6$		Inlet heater temperature (sample) 50°C	
Span difference A vs B $\leq 5\%$		Inlet heater temperature (desorb) 75°C	
Desorption blank C = 0.000 pg/m <sup>3</sup>		Sample line temperature 50°C	
PBM <sub>2.5</sub> clear peak		<b>1135 Unit</b>	
GOM clear peak		Pyro temperature (sample) 50°C	
Argon tank $\geq 200$ psi		Pyro Temperature (desorb) 800°C	
Regulator $\geq 30$ psi		Part temperature (sample) 50°C	
2537 lamp light off		Part Temperature (desorb) 800°C	
2537 perm light blinking		1135 Case temperature 35-41°C	
1102 warm to touch			
1102 drierite blue			

**Comments:**

## Annex G      Tekran Check and Maintenance List

<b>Site Name:</b>	<b>Country:</b>
<b>Operator:</b>	<b>Date:</b>

### Biweekly and End of Month Checklist:

Biweekly – 1 <sup>st</sup> Change	Check (X) if OK	Monthly	Check (X) if OK
Change soda lime		Change RPF	
Change denuder		Change GL 14-18 union	
Change inlet glassware		Change 1130 Zero air filter	
Change 1130 sample filter			
Leak check at inlet $\leq 0.3 \text{ ng/m}^3$			
Instrument meets weekly specifications			
Biweekly – 2 <sup>nd</sup> Change			
Change soda lime			
Change denuder			
Change elutriator glassware			
Change 1130 sample filter			
Leak check $\leq 0.3 \text{ ng/m}^3$			
Instrument meets weekly specifications			
<b>Comments:</b>			

# Annex G Tekran Check and Maintenance List

<b>Site Name:</b>	<b>Country:</b>
<b>Operator:</b>	<b>Date:</b>

## Quarterly Checklist:

Each Quarter	Check (X) if OK or Insert Value	Second Quarter	Check (X) if OK or Insert Value
1130 flow rate, instrument (lpm)		Change 1130 zero air canisters	
1130 flow rate, measured (lpm)		Clean 1130 pump tubing	
1130 flow rate, % difference (%)		Replace 1130 DFU filters	
Elutriator flow rate (lpm)		2537 flow rate, instrument (lpm)	
Measured flow rate (lpm)		2537 flow rate, measured (lpm)	
Percent difference flow rate (%)		2537 flow rate, % difference (%)	
Cartridge A, mass injected (pg)		2537 scale factor	
Cartridge A, 2537 concentration (pg/m <sup>3</sup> )		Fourth Quarter	
Cartridge A, manual injection % diff.		Change 2537 heater coils	
Cartridge B, mass injected (pg)		Change 2537 zero air canister	
Cartridge B, 2537 concentration (pg/m <sup>3</sup> )		Change 2537 DFU filter	
Cartridge B, manual injection % diff.		Replace RPF elbow and tubing	
Trap heating coils bright orange		Replace 1130 pump diaphragm	
Instrument shelter air $\leq 15$ ng/m <sup>3</sup>		Replace 1130 pump brushes	
Change 2537 sample filter		2537 flow rate, instrument (lpm)	
Clean Teflon line from 2537 to soda lime		2537 flow rate, measured (lpm)	
2537 leak check		2537 flow rate, % difference (%)	
1130 flow rate within 3% of set point		2537 scale factor	
		Rinse heated sample line	
<b>Comments:</b>			

# Annex G      Tekran Check and Maintenance List

<b>Site Name:</b>	<b>Country:</b>
<b>Operator:</b>	<b>Date:</b>

## As-Needed Checklist:

Clean or Replace Components	Check (X) if OK	Replace Equipment (Record New Serial Number)	Check (X) if OK
Change 2537 lamp		Replace 2537	
Install new matched gold cartridges		Replace 1130 Pump Module	
Clean 2537 Teflon valves		Replace 1130 Sampling Unit	
Replace 2537 Teflon valves		Replace 1135 Sampling Unit	
Clean 2537 cuvette			
Replace 2537 cuvette			
Service 2537 pump			
Replace septum			
Check perm source temperature			
Check perm vent flow			
Replace filter holders and fittings			
Replace 1130 heated boot			
Replace 1130 case heater			
Replace 1135 case heater			
Rinse heated sample line			
Replace Argon cylinder (< 200 psi)			
<b>Comments:</b>			



