

WP 4.1 Testing of mercury resistant materials

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Testing of mercury resistant materials

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Summary

The main objective of WP 4.1 of the EMRP project PartEmission is to assess the characteristics of suitable materials for the sampling of low level mercury concentrations.

A materials study was carried out to select the best candidate materials to be tested with respect to their suitability for the sampling of mercury in ambient air and exhaust emissions.

Based upon the study several types of Teflon tubes were tested by VSL, whereas glass and passivated glass were tested by JSI. Both institutes used a similar measurement approach.

FEP and PFA types of Teflon proved to be suitable materials as no effects were found due to absorption or permeation under standard test conditions.

Non-passivated glass also proved to be a suitable material as no effects were found due to adsorption or permeation under standard test conditions.

JSI will conduct further studies that will include testing of the non-passivated and passivated glass material under increased temperature conditions, in the presence of water vapour, and other gases (CO_2 , NO_x , ...) that are found in automotive exhaust.

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1. Introduction

The main objective of WP 4.1 of the EMRP project PartEmission is to assess the characteristics of suitable materials for the sampling of low level mercury concentrations.

A materials study was carried out to select the best candidate materials to be tested with respect to their suitability for the sampling of mercury in ambient air and exhaust emissions. During visits of the Mercury 2011 conference (Halifax, Canada), Linde Electronics and Specialty Gases (USA), NIST (USA), US EPA (USA) and Tekran (Canada) it became clear that glass could be used in conjunction with Teflon tubes, e.g. FEP-type and PFA-type. In most cases a preference was found for the Teflon PFA-type tubes.

Based upon the study several types of Teflon tubes were tested by VSL, whereas glass was tested by JSI.

Both JSI and VSL used a Tekran 2537B CV AFS instrument for mercury measurements. In the manual of this instrument it is advised to use an FEP type of Teflon because it has smoother walls and is less porous than PTFE types of Teflon. Furthermore ¼ inch (6,35 mm) OD Teflon lines are advised with a recommended wall thickness of 0,030 inch (0,76 mm). In addition to the Tekran 2537B monitor, JSI also used a Brooks Rand CV AFS detector Model I.

2. Materials and Methods

2.1. Instruments used

2.1.1. Tekran 2537 B

The Tekran 2537B monitor is a CV atomic fluorescence detector (AFS). It can be calibrated in two ways. First is automatic calibration using an in-built Hg permeation source and the second is manual calibration using manual injection of mercury vapour from an external mercury calibration unit. Manual injection is considered the primary standard method since it is directly based on the vapour pressure of mercury at a known temperature.

A full calibration cycle of the Tekran 2537B consists of six steps: two Clean steps, two Zero steps and two Span or Calibration steps. The Clean steps serve to remove any residual mercury from cartridges before the calibration begins. The Zero steps provide both check of internal instrument contamination and residual mercury levels in the zero gas supply. The Span steps provide measurement sensitivity of the instrument.

Calibration of the instrument can be performed as mentioned either manually or automatically. When manual calibration of the instrument is performed it is important that each injection be performed in a repeatable and consistent manner. It is therefore preferred that all injections for a particular calibration are performed by a single individual. The amount of mercury to be injected, in ng, is calculated by looking up the concentration within the source (pg/μl) at the source temperature and multiplying by the number of microliters to be injected. In order to determine what concentration in air a particular cartridge loading represents it is necessary to know the volume of air in each sample. This is simply the method sample rate multiplied by the number of minutes per sample. The conversion from m³ to liters (1000) and from ng to pg (1/1000) cancels to unity. Hence:

Air concentration = Amount * 1/Sample Volume

ng/m³ = pg * litres/m³ * ng/pg/ litres

Calibrations using the internal permeation source are considerably more convenient than manual calibrations, and can be performed automatically by the instrument without user intervention. It should be noted that permeation source calibrations are currently having a relatively large measurement uncertainty. The low emission rates of the permeation tubes used to calibrate Tekran 2537B analysers preclude an accurate gravimetric determination of emission rates. Therefore the permeation source rate must be determined by calibration against the best primary calibration source currently available, a temperature controlled saturated mercury vapour source. The applied method consists of multiple manual injections from this temperature controlled primary mercury vapour source. Hereby the permeation rate of the tube, supplied in the instrument, is verified. It should be noted that much of the difference in ambient air readings between analysers can be traced to differences in the determination of the permeation rate. Therefore it is advised to always use the same source, syringes and if possible the same operator when validating the permeation rates of multiple Tekran 2537B instruments.

Calibration:

Computations that calculate the calibration constants for the Blank Correction and the Response Factor, of each cartridge, are performed at the end of a successful calibration. These computations allow the conversion of subsequent desorption peak areas into final results calculated in ng/m³. The computations are performed independently for each cartridge of the instrument. It should be noted that sample volumes are referenced to 0 °C and 760 mm Hg pressure. These are the standard calibration and certification conditions for the Tylan mass flow meter. Instrument performance includes the following assumptions that have been verified and tested by the manufacturer:

1. The area of a blank peak is directly dependent upon the blank (zero) air volume sampled.
2. The response of the system is linear, allowing a two point calibration (zero plus one known span point) to be used.

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Blank Correction (it represents the expected background area per litre of sample, this blank value may be subtracted from all subsequent readings to correct for instrument background) is calculated using following equation:

$$\text{Blank Correction} = \text{Blank Area} / \text{Blank Volume}$$

Blank Area (The area of the peak detected during zero air measurement)

Blank Volume (The actual measured volume of zero air that passed through the cartridge during the operation in litres. This is normally a product of the flow rate and the sample time.)

Response Factor (it represents the response factor for the instrument, it is represented in ng/area) is calculated using following equation:

$$\text{Response Factor} = \text{Adjusted Area} / \text{Span Mercury Amount}$$

Adjusted Area (represents the span peak area minus the area that could reasonably be attributed to background, the calculation corrects for any differences in the sample volumes between the zero and span operations).

$$\text{Adjusted Area} = \text{Span peak Area} - (\text{Blank correction} * \text{Span sample volume})$$

Span Sample Volume (the measured volume of zero air that passed through the cartridge during the span phase, this air is spiked with mercury, either by injection or via the permeation source).

Span Mercury Amount (the amount of mercury that entered the cartridge during the span phase of the calibration. This is determined in one of the two ways, depending on whether the calibration was done via a manual or by permeation source injection).

Span Peak Area (area of peak detected during desorption after span phase).

- Sample Result Calculations

Once a calibration has been performed, the two quantities *Blank Correction* and *Response Factor* for each cartridge are all that are required to convert subsequent ambient peak areas into concentrations. The subtraction due to blank areas measured during the zero phase of the calibration is optional.

The calculation of the final result is broken into several simpler calculations:

$$\text{Mercury Amount (ng)} = \text{Sample Adjusted Area} / \text{Response Factor}$$

$$\text{Result (ng/m}^3\text{)} = \text{Mercury Amount (ng)} * 1000 * \text{Factor} / \text{Sample Volume}$$

Mercury Amount (it represents the total amount of mercury desorbed from the cartridge (ng), any loading attributable to the blank is not included in the Mercury Amount calculation).

Result (ng/m³) (it represents the calculated concentration of mercury in the sample (ng/m³), the factor of 1000 is due to the fact that 1 m³ = 1000 litres).

Sample Adjusted Area (The adjusted or blank corrected area may subtract out the area of a peak that can be attributed to blank).

Sample Peak Area (The area of the peak measured for the sample).

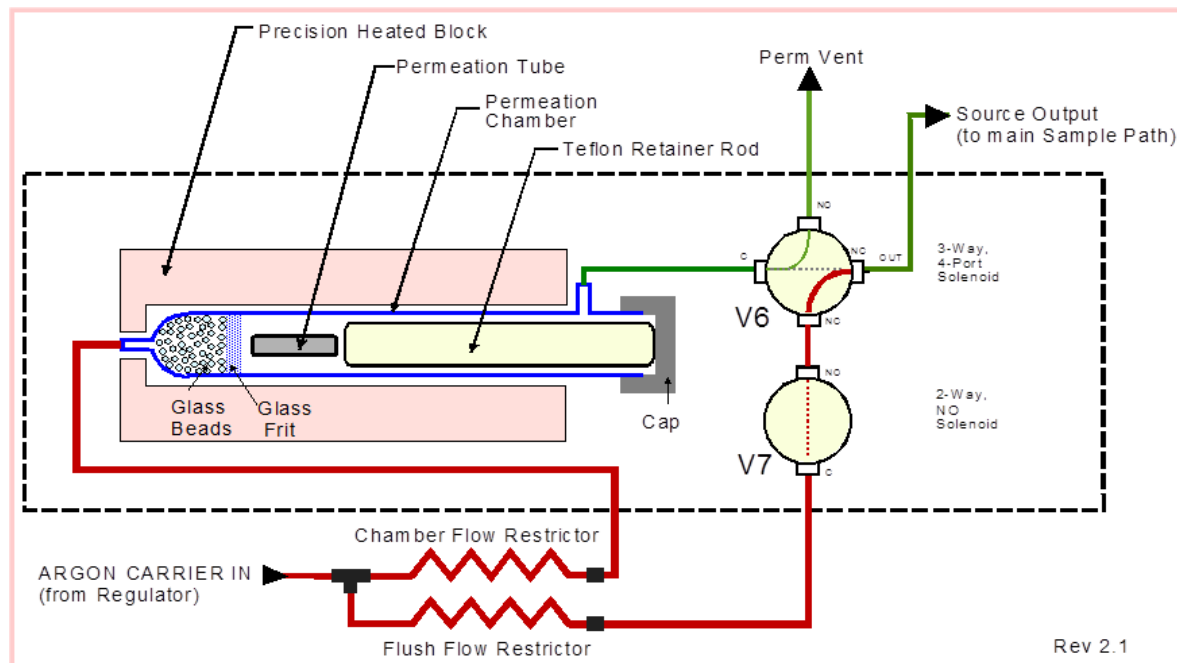
Sample Volume (The measured volume of sample drawn through the cartridge filters).

Factor (it represents the numerical “factor” that is used to compensate for preconcentration or dilution front end samplers).

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Permeation Source flow diagram



Source: Tekran Instruments Corporation

2.1.2. Brooks Rand Model I

Brooks Rand Model I detector is a CV atomic fluorescence detector (AFS). The CV AFS detector unit was coupled with an in house made desorption system consisting of two desorption coils made from cantal wire and connected to the controller unit, two gold sand traps for mercury desorption and sorption, Teflon tee piece equipped with silicon septa for mercury vapour injection and instrument calibration and analogue recording unit connected to the detector for signal recording. The whole system was connected to a mercury vapour free pure argon flow for proper operation at 60 ml/min. Tubing used was Teflon 100, FEP (1/16 x 1/8").

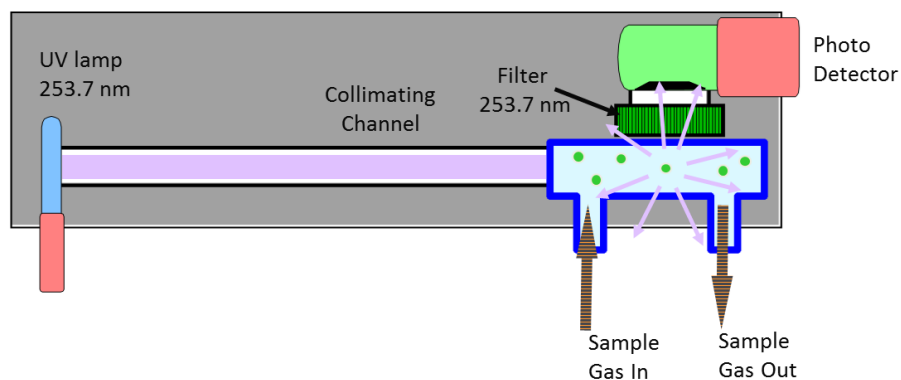
The calibration of the detector was performed manually using mercury vapour injections. Tee piece equipped with silicon septa served as injector port for injections of mercury vapour. The amount of mercury injected was calculated by taking a certain volume (typically 5 μ L) of mercury vapour with a gas tight syringe from the source (mercury vapour primary calibration unit) at the given temperature and multiplied by the number of microliters injected. Calculations of absolute concentrations (in pg) were made using the appropriate table, providing the required information of mercury vapour dependence on temperature. Signals heights recorded from repeated mercury vapour injections served as reference concentration points for further analysis.

The principle operation of AFS detectors (Tekran and Brooks Rand) is shown in the diagram below.

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Diagram of AFS detector



Source: Tekran Instruments Corporation

2.1.3. Calibration units

During the experiments two types of mercury vapour calibration units were used.

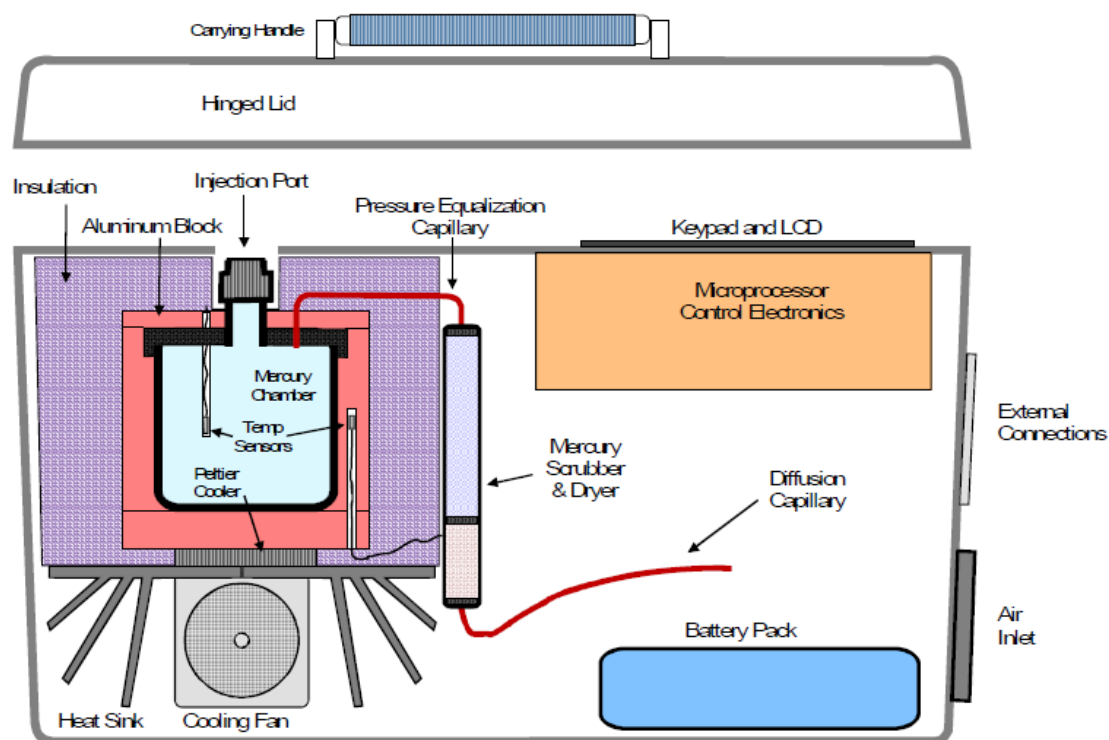
Tekran 2505 Mercury Vapour Calibration Unit

Tekran 2505 Mercury Vapour Calibration Unit is a saturated gaseous mercury source. The temperature of the source is controlled thermoelectrically to provide capability of withstanding changing ambient temperatures. The cooled/heated mercury reservoir has two temperature sensors (resolution of 0.001 °C) calibrated against a US National Institute of Standards and Technology (NIST) traceable source. The calibration unit registers the reservoir temperature and calculates the amount of mercury in a defined injection volume. The mercury vapour is taken from the calibration unit and delivered manually using a high precision digital/manual gas tight syringe. This calibration unit is used as a primary calibration standard for routine calibration. It requires a power source for proper operation.

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Diagram of Tekran 2505 Mercury Vapour Calibration Unit



Source: Tekran Instruments Corporation

Mercury Instruments Calibration Unit

Mercury Instruments Calibration Unit is also a saturated mercury source. The temperature of the source is not controlled and is dependent on the ambient temperature. For proper use, the temperature of the source must be measured using an external thermometer which is calibrated against a traceable source. The mercury vapour is taken from the calibration unit and delivered manually using a high precision digital/manual gas tight syringe. The amount of mercury taken from the source is a function of temperature and volume. Proper calculation of the amount of mercury taken requires the use of the appropriate table which provides the required information of mercury vapour dependence on temperature. The Calibrator does not require a power source for operation.

2.1.4. Syringes for gas sampling

Sampling of the mercury vapour was performed using different types of gas tight syringes with Teflon plunger. Syringes used:

- 1700 gastight Hamilton syringe, 25 μ L, Model 1702 RN SYR
- 25 μ L, Model 1702 RN Digital SYR, equipped with 25 μ L 1700 gastight Hamilton syringe, with 5 cm standard needle or 7 cm side vent needle

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2.1.5. Other materials and gases

Gases used for CV AFS (Brooks Rand or Tekran 2537B) instrument operation :

- Ar gas of purity of 5.0 or more

Carrier gases used during the materials testing:

- ECD grade N₂
- Ambient air

Other materials used:

- Puresep-T Septa, 1/4"
- Teflon 100, FEP (1/16 x 1/8") tubing
- 1/8" PFA Compression Tee
- Gold sand traps
- Calibrated digital thermometer

2.1.6. Teflon tubes tested by VSL:

- | | |
|------------------------|---|
| • Teflon 350, PFA tube | 4,75 x 6,35 mm (wall thickness 0,80 mm) |
| • Teflon 350, PFA tube | 3,96 x 6,35 mm (wall thickness 1,19 mm) |
| • Teflon 100, FEP tube | 4,83 x 6,35 mm (wall thickness 0,76 mm) |
| • Teflon 100, FEP tube | 3,96 x 6,35 mm (wall thickness 1,19 mm) |

The Teflon 100 FEP tube is a general purpose resin, used for industrial and medical tubing.

The Teflon 350 PFA tube is a high molecular weight resin with highest resistance to stress cracking, also used for tubing.

All tube material was supplied by Polyfluor Plastics in the Netherlands.

2.1.7. Glass materials tested by JSI:

- 2' x 1/4" x 2 mm (ID)HP Glass column

Both institutes used a similar measurement approach with the Tekran 2537B. A slightly different approach was used with the Brooks Rand CV AFS detector.

3. Experimental

3.1. VSL Test set-up

The testing started with the development of a measurement procedure. The following experimental conditions were chosen:

- 1 meter of Teflon 100 FEP tube (4,83 x 6,35 mm), attached to the Tekran 2537B sample inlet
- a (well conditioned) calibrated digital 25 µL gas tight Hamilton syringe, supplied by Tekran
- Tekran's Mercury Vapor Primary Calibration Source
 - Starting at a recommended temperature (according to the manual) of 2-3 Degrees Centigrade below RT
 - Note: During the PartEmission Kick-off meeting a use at 4 – 11 degrees Centigrade had been recommended
- normal routine conditions
 - 7,5 Liter of air sampled in 5 minutes

The measurement results of the digital 25 µL gas tight Hamilton syringe showed very poor repeatability. Therefore another syringe was selected: a 1700 gastight Hamilton syringe of 25 µL (Model 1702 RN) with a 5 centimeter type 2 needle.

It should be noted that the digital Hamilton/Tekran syringe has a needle of 7 centimeter to optimize the distance from the tip of the needle to the place where the temperature is being measured. Nevertheless the manual gastight Hamilton was selected as the repeatability proved to be much better than the repeatability using the digital syringe, even after thoroughly cleansing this digital syringe.

Furthermore a temperature of 2-3 degrees Centigrade below room temperature in the Mercury Vapour Primary Calibration Source was found inappropriate as repeatability was low compared to the later selected temperature of 13 degrees Centigrade.

After these tests the following experimental conditions were used:

- 1, 5 or 10 meter of each type of tube, attached to the Tekran 2537B sample inlet. In each case the tube material was new tube that had been packed until the moment of use
- a (well conditioned) manual uncalibrated 25 µL gas tight Hamilton syringe, supplied by Tekran, whereby the syringe was filled with 10 µL of mercury vapour
- Tekran's Mercury Vapor Primary Calibration Source
 - conditioned at 13,026 degrees Centigrade under normal test conditions
 - with also some testing at 18 degrees Centigrade for comparison reasons
- normal routine conditions
 - laboratory temperature of 19,6 degrees Centigrade
 - 7,5 Liter of air sampled in 5 minutes

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3.2. JSI Test set up

The testing started with the development of a measurement procedure.

3.2.1. Tekran 2537B experimental set up

The following experimental conditions were chosen:

- 2' x 1/4" x 2 mm (ID) HP glass column, was used for testing of non-passivated glass material. Teflon gas line with a tee piece for Hg vapour injection with 6 mm silicon septa with was attached on one side and gold sand trap on the other via Teflon fittings. ECD grade N₂ was used as carrier gas at the rate 120 mL/min for 2 min.
- Gold sand traps were used for Hg vapour capture
- Homemade desorption unit was used for gold sand traps desorption after mercury vapour capture, temperature of desorption coils was set at ~ 500 °C in order to preserve gold trap integrity and avoid memory effects.
- A (well-conditioned) manual calibrated 25 µL gas tight Hamilton syringe with 5 cm type 2 needle and Digital Hamilton casing fitted with 25 µL gas tight Hamilton syringe with 5 cm type 2 needle,

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- Mercury Instruments, Manual Calibration Unit, ambient temperature calibration unit
- Hg vapour temperature was at ambient room temperature (23 °C – 25 °C) since the calibration unit does not enable temperature control. Appropriate index tables were used to determine Hg concentration injected.
- Normal routine working conditions were followed.
- ~ 4 Litre of air/N₂ gas sampled in 5 minutes when Tekran 2537B was used.

The measurements with the digital 25 µL with 7 cm needle gas tight Hamilton syringe were discontinued after accidental contamination of the syringe with liquid mercury, all attempts to clean the syringe to date failed. Therefore another syringe was selected: a 1700 gastight Hamilton syringe of 25 µL (Model 1702 RN) with a 5 centimetre type 2 needle. This syringe type was then fitted to the digital Hamilton casing and used as digital set up and compared to manual injection with the same syringe type.

It should be noted that the digital Hamilton casing outfitted with 1700 gastight Hamilton syringe of 25 µL performed comparable to the manual injection.

Injections of Hg vapour were performed at ambient room temperature using the Mercury Instrument calibration unit, which does not enable temperature control of the mercury vapour source. The calibrated digital thermometer was used to record the ambient temperature of the source, for latter calculation of the actual Hg concentration injected.

Initially Tekran 2537B was used as a detector, but since the results from direct on line Hg vapour injection and desorption of Hg vapour from gold trap, after trapping of Hg in N₂ gas flow, differed considerably, the Brooks Rand model I AFS detector with double amalgamation system was used.

3.2.2. Brooks Rand Model I experimental detector set up

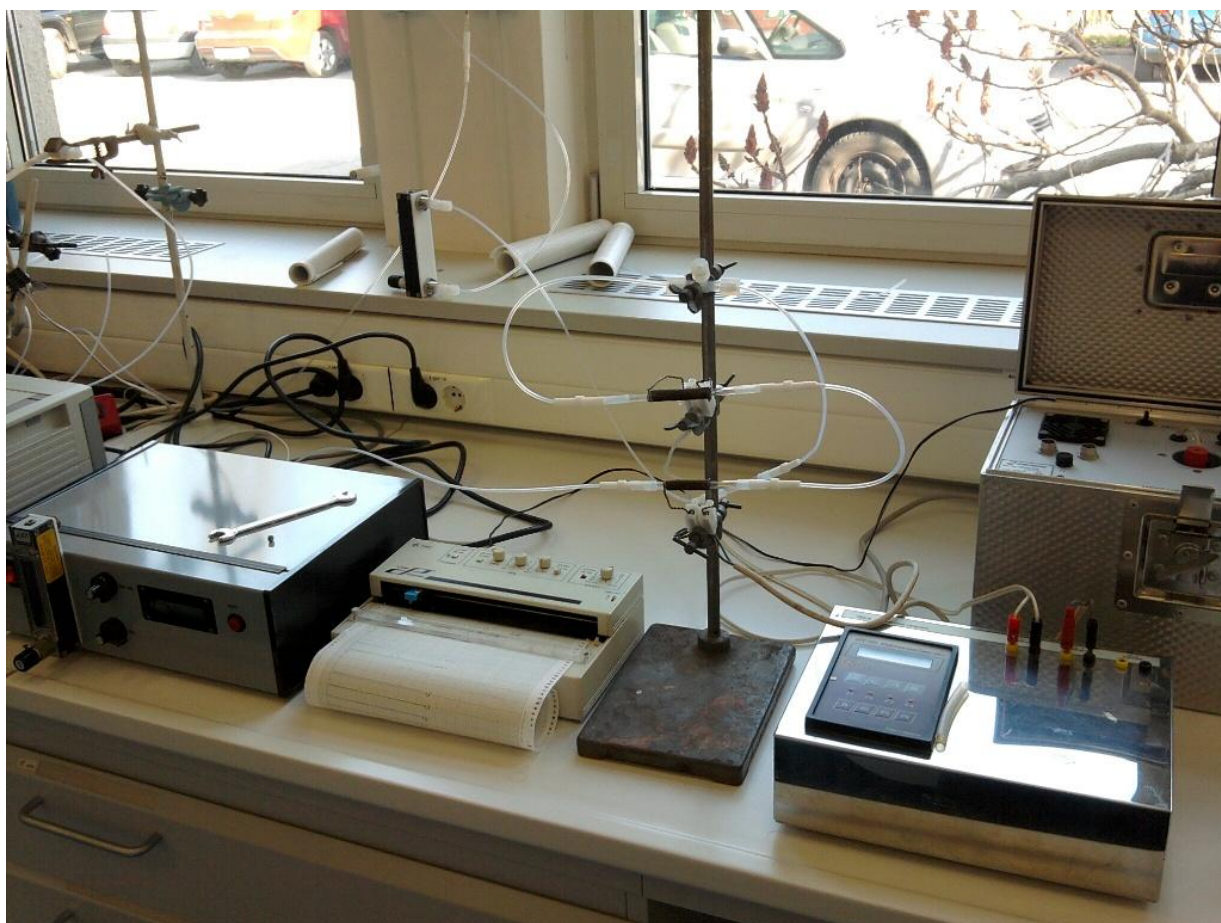
After initial tests and detector change, the following experimental conditions were used:

- 2' x 1/4" x 2 mm (ID) glass column, was used for testing of non-passivated glass material. Teflon gas line with a tee piece for Hg vapour injection with 6 mm silicon septa which was attached on one side and gold sand trap on the other side via Teflon fittings. ECD grade N₂ was used as carrier gas at the rate 120 mL/min for 2 min.
- Gold sand traps were used for Hg vapour capture
- Homemade desorption unit was used for gold sand traps desorption after mercury vapour capture, temperature of desorption coils was set at ~ 500 °C in order to preserve gold trap integrity and avoid memory effects
- A (well-conditioned) manual calibrated 25 µL gas tight Hamilton syringe with 5 cm type 2 needle and Digital Hamilton casing fitted with 25 µL gas tight Hamilton syringe with 5 cm type 2 needle
- 5 µL of mercury vapour at room temperature was injected into the glass column
- Mercury Instruments Manual Calibration Unit Hg vapour source at room temperature which changed during the day between 23.0 – 25.5 °C. Calibrated digital thermometer was used to record the temperature of the Hg source
- Normal routine working conditions were followed
- 60 ml/min flow of Ar carrier gas was used for Brooks Rand model I AFS detector
- Brooks Rand model I AFS detector
- Analogue recorder was use to record the instrument response. Recorder was set to 50 mV over 200 mm scale

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Brooks Rand Model I set up



4. Results

4.1. VSL testing set up results

4.1.1. VSL Teflon tubing tests

In the following tables the measurement results are shown for the tests of 1 meter, 5 meter and 10 meter of each tube material.

Each test series consisted of two ambient air measurements, followed by 6 - 8 injections, and finally concluded by another two ambient air measurements. The measurement result of each type and length of tube tested is composed of the mean of the measured values (with an injection of 10 microliters of mercury vapour) after subtraction of the mean of the “blanks” (ambient air measurement results) prior and afterwards (“corrected”).

The measurement value of the mercury injected was corrected for the laboratory temperature. The loss due to expansion (in percentage) equals $((T_{\text{labtemp}} - T_{\text{reservoir}})/T_{\text{labtemp}}) \times 100$.

Table 1: Tests with 1 meter of tube material

1 Meter	FEP-tubing 4.83-6.35 mm 806cb483x635	FEP-tubing 3.96-6.35 mm 806cb396x635	PFA-tubing 4.75-6.35 mm 806cc475x635	PFA-tubing 3.96-6.35 mm 806cc395x635
	14.5	18.2	17.0	18.7
	14.0	17.5	17.6	18.4
	14.0	17.9	17.7	18.4
	14.1	17.8	17.3	18.1
	14.7	17.9	18.5	18.5
	15.1	17.6	17.2	17.8
		17.6	18.1	18.4
		17.5	18.0	17.8
mean (ng/m ³)	14.4	17.8	17.7	18.3
std	0.451	0.246	0.506	0.331
ambient air (ng/m ³)	2.9	4.1	4.4	4.5
ng/m ³ "primary injection"	9.5	9.5	9.5	9.5
ng/m ³ measurement result	11.5	13.7	13.3	13.8

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Table 2: Tests with 5 meter of tube material

5 Meter	FEP-tubing 4.83-6.35 mm 806cb483x635	FEP-tubing 3.96-6.35 mm 806cb396x635	PFA-tubing 4.75-6.35 mm 806cc475x635	PFA-tubing 3.96-6.35 mm 806cc395x635
	16.9	17.4	16.9	17.5
	17.9	16.8	17.5	17.6
	18.5	17.6	18.7	17.6
	18.2	17.1	17.8	16.4
	18.4	17.6	18.0	17.4
	18.1	16.7	18.0	17.1
	18.1	17.6	18.0	17.6
	17.0	17.3	17.6	16.9
mean (ng/m ³)	17.9	17.3	17.8	17.2
std	0.606	0.378	0.523	0.433
ambient air Hg (ng/m ³)	4.5	4.5	4.2	4.2
ng/m ³ "primary injection"	9.5	9.5	9.5	9.5
ng/m3 measurement result	13.4	12.8	13.6	13.0

Table 3: Tests with 10 meter of tube material

10 Meter	FEP-tubing 4.83-6.35 mm 806cb483x635	FEP-tubing 3.96-6.35 mm 806cb396x635	PFA-tubing 4.75-6.35 mm 806cc475x635	PFA-tubing 3.96-6.35 mm 806cc395x635
	16.4	16.4	17.3	16.5
	17.1	16.9	17.3	17.0
	17.7	16.9	17.6	16.9
	16.9	15.9	17.4	16.7
	17.0	16.3	16.3	17.4
	17.3	16.5	17.1	16.9
	17.3	16.6	16.7	17.5
	17.3	16.7	16.7	17.4
mean (ng/m ³)	17.1	16.5	17.0	17.1
std	0.376	0.331	0.433	0.369
ambient air (ng/m ³)	3.4	3.7	3.7	3.8
ng/m ³ "primary injection"	9.5	9.5	9.5	9.5
ng/m3 measurement result	13.7	12.8	13.3	13.3

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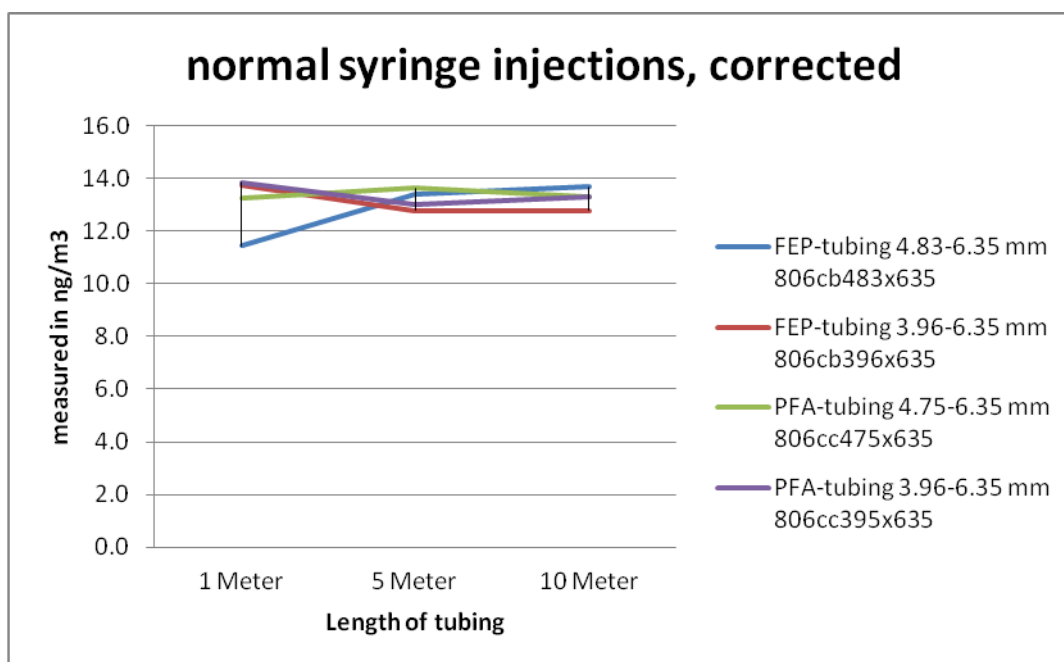
Table 4: Overview of measurement results

	FEP-tubing 4.83-6.35 mm 806cb483x635	FEP-tubing 3.96-6.35 mm 806cb396x635	PFA-tubing 4.75-6.35 mm 806cc475x635	PFA-tubing 3.96-6.35 mm 806cc395x635
1 Meter	11.5	13.7	13.3	13.8
5 Meter	13.4	12.8	13.6	13.0
10 Meter	13.7	12.8	13.3	13.3

Except for the low measurement result for the 1 Meter test of FEP-tubing (4,83 x 6,35 mm) all measurement results in Table 4 do seem to indicate that no difference is present between the different types of Teflon material with respect to their interaction with mercury vapour at the level investigated.

See also Figure 1 for an overview of the measurement results, corrected for the ambient air level of mercury vapour.

Figure 1: Overview of measurement results



4.1.2. Handheld versus digital syringe (VSL experience)

During the first measurements with a digital syringe the measurement results became higher and higher, which could be caused by poisoning. Therefore the digital syringe was cleansed thoroughly before it was used again in a comparison experiment with the handheld syringe.

The results are given in Table 5 for a test whereby 10 µL of mercury vapour was extracted from the Mercury Vapour Calibration Source at 13,026 degrees Centigrade.

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It should be noted that these measurement results are not comparable to those in paragraph 2.2 because the Tekran 2537B had been calibrated again by the internal permeation source prior to the experiments in this paragraph (see also paragraph 2.1.1).

The standard deviation using the manual syringe (Table 5) is much lower/better than the standard deviation found using the digital syringe. Therefore these measurements were repeated, using a similar approach, by JSI using a calibrated digital Hamilton/Tekran syringe.

Table 5: Use of manual versus digital syringe (Mercury Vapour Source at 13,026 degrees Centigrade)

	manual	digital	digital
1 Meter	FEP-tubing 3.96-6.35 mm 806cb396x635	FEP-tubing 3.96-6.35 mm 806cb396x635	FEP-tubing 3.96-6.35 mm 806cb396x635
	13.0	12.2	13.6
	14.3	17.6	13.2
	13.4	13.5	13.6
	14.4	23.0	13.9
	13.8	14.2	14.2
	14.4	15.1	21.5
	14.0	13.9	20.8
	14.3	14.0	16.3
mean (ng/m ³)	13.9	15.4	15.9
std	0.498	3.403	3.671
ambient air (ng/m ³)	2.8	2.8	3.1
ng/m ³ "primary injection"	9.5	9.5	9.5
ng/m ³ measurement result	11.1	12.6	12.8

It may be concluded from Table 5 that manual injections with a gastight Hamilton syringe provided lower repeatability of measurement results than using a digital gastight syringe. Further research will be performed to investigate whether this may be attributed to the particular (poisoned?) digital syringe used.

In Table 6 the results are given for the same experiment, albeit with a temperature of 18,015 degrees Centigrade of the Mercury Vapour Calibration Source and a length of 5 Meter of tube. In this experiment the measurement results are presented of a series of measurements whereby respectively ambient air, 10 µL injected manually, ambient air, 10 uL injected with a digital syringe, ambient air, 10 uL injected with a digital syringe, ambient air, 10 uL injected with a digital syringe, ambient air, and 10 uL injected manually were introduced in the mercury monitor.

These experiments seem to indicate that the particular digital syringe used may indeed be poisoned by mercury. After obtaining a very low repeatability for the first series of measurements using the digital syringe, the second series shows an improved (lower) repeatability whereas the third series of digital injections scores the lowest repeatability. Which repeatability is even lower than that found for the (consistent) low repeatability's obtained by manual injections. Furthermore, if only the handheld series and the last digital series are taken into account, the same calibration factor is found for the internal permeation system of (17,0/14,8=) 1,15.

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Table 6: Use of manual versus digital syringe (Mercury Vapour Source at 18,015 degrees Centigrade)

	manual	digital	digital	digital	manual
5 Meter	FEP-tubing 3.96-6.35 mm 806cb396x63 5	FEP-tubing 3.96-6.35 mm 806cb396x63 5	FEP-tubing 3.96-6.35 mm 806cb396x63 5	FEP-tubing 3.96-6.35 mm 806cb396x63 5	FEP-tubing 3.96-6.35 mm 806cb396x63 5
	20.3	106.8	24.9	20.1	21.6
	21.0	129.2	24.6	20.7	20.1
	18.4	79.7	27.1	21.2	20.0
	19.4	45.9	23.3	22.2	20.1
	20.1	29.9	22.6	19.6	19.3
	21.2	23.9	22.1	20.9	22.2
		52.7		20.3	18.9
		38.6		20.9	20.1
mean (ng/m ³)	20.1	63.3	24.1	20.7	20.3
std	1.044	38.163	1.802	0.789	1.091
ambient air (ng/m ³)	3.1	3.1	4.2	3.7	3.2
ng/m ³ "primary injection"	14.8	14.8	14.8	14.8	14.8
ng/m ³ measurement result	16.9	60.2	19.9	17.0	17.1

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4.2. JSI testing set up results

4.2.1. JSI Glass material testing

In the following tables the measurement results are shown for the tests made on a 1.2 m glass column used for testing of non-passivated glass material. 5 and 10 μL injections of mercury vapour at ambient temperatures between 23 – 25 °C were made using digital and manual 25 μL gas tight Hamilton syringes with 5 cm type 2 needles. Two experimental set up's were used.

4.2.2. Measurement results from Tekran 2537B experimental set up

In this set of experiments the Tekran 2537B was used as detector for mercury vapour and the experimental set up used was as described in paragraph 3.2.1. Mercury Instruments' Manual Calibration Unit was used as a source of mercury vapour. Since the unit operates at ambient temperatures a digital thermometer was used to record the temperature of the mercury source and appropriate index tables were used to calculate the amount of mercury injected into the glass column. Experimental measurements consisted of two procedures.

Procedure I – direct on line injection of Hg vapour:

In procedure I, 10 μL of mercury vapour at ambient temperature was injected directly into the Tekran 2537B using manual injections with the 25 μL gas tight Hamilton syringe with 5 cm type 2 needle, via short Teflon tubing connecting the instrument to the ambient air. The mass flow controller was set to 0.75 L/min and the carrier gas used was ambient air. This test consisted of three ambient air measurements, followed by 6 – 8 injections of mercury vapour, and finally concluded by another three ambient air measurements. The purpose of this procedure was to determine agreement between manual injections and the in built permeation source. The results obtained from the detector were in ng/m^3 and are shown in Table 7 in ng/m^3 as well as in pg.

Procedure II – injection of Hg vapour through glass column:

In procedure II, the experiment consisted of two steps. In the first step 10 μL mercury vapour was injected into glass non-passivated column at ambient temperature via a tee piece equipped with silicon septa on one side and gold sand trap on the other. Gas flow of ECD grade N_2 , at the rate of 120 mL/min, was run through the column as carrier gas for two minutes. In the second step of the experiment the gold sand trap was connected to the desorption unit and heated to 500 °C to desorb captured mercury under flow of ECD grade N_2 at approximately 0.75 L/min for 5 minutes. This test consisted of three ECD grade N_2 measurements, followed by 6 – 8 injections of mercury vapour, and finally concluded by another three ECD grade N_2 measurements. The results obtained from the detector were in ng/m^3 and are shown in Table 7 in ng/m^3 as well as in pg.

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Table 7: Tekran 2537B experimental set up, comparison of results between procedures I and II

Tekran 2537B	Direct Hg in system injection (Procedure I) (ng/m ³)	Direct Hg in system injection (Procedure I) (pg)	Hg gold trap desorption (Procedure II) (ng/m ³)	Hg gold trap desorption (Procedure II) (pg)
	39.1	147	28.3	106
	40.1	150	32.9	123
	39.0	146	35.6	133
	37.2	140	30.7	115
	38.2	143	30.3	114
	39.4	148	25.0	94
			30.4	114
			21.4	80
mean	38.8	146	29.3	110
std	1.0	3.8	4.5	16.7
ambient air or carrier gas	4.2	15.8	0.5	1.7
"primary injection"	43.6	164	43.6	164
measurement result	34.6	130	28.9	108

Table 7 presents results from procedures I and II, of Tekran 2537B experimental set up. Results obtained from direct injections of mercury vapour into the instrument in procedure I, had good repeatability with low standard deviation, but were also consistently low in comparison to calculated "primary injection" for a used volume of 10 µL per injection at ambient temperature. Results obtained from the subsequent desorption of trapped mercury from gold sand traps in procedure II of the experiment were less repeatable, had higher standard deviation and were even lower in comparison to calculated "primary standard" for a used volume of 10 µL per injection at ambient temperature, than measurements obtained in procedure I. Because of inconsistent and low results obtained in procedures I and II of the experiment, Tekran 2537B set up was found to be unsuitable for this type of experimental material testing. Consequently work on this approach was discontinued and a new set up, using simpler detector (Brooks Rand Model I), was constructed for testing of the glass material.

4.2.3. Measurement results from Brooks Rand Model I experimental detector set up

In this set of experiments Brooks Rand Model I was used as detector for mercury vapour and the experimental set up used was as is described in paragraph 3.2.2. Mercury Instruments' Manual Calibration Unit was used as a source of mercury vapour. Since the unit operates at ambient temperatures a digital thermometer was used to record the temperature of the mercury source and appropriate index tables were used to calculate the amount of mercury injected into the glass column. Experimental measurements consisted of two procedures.

Procedure I:

In procedure I, 5 µL of mercury vapour was injected into the instrument, using manual and digital 25 µL gas tight Hamilton syringes with 5 cm type 2 needles, at ambient temperature. Injection was made through a tee piece equipped with silicon septa, connected to a double gold sand trap amalgamation system and connected to 60 ml/min Ar carrier gas flow. After injection was made gold sand traps were desorbed at 500 °C in sequence one after another in order to release trapped mercury. This test consisted of at least three Ar gas measurements, followed by 6 – 8 injections of Hg vapour, and was finally concluded by

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another three Ar gas measurements. The purpose of this procedure was to compare repeatability of injections between manual gas tight syringe and digital gas tight syringe. Results obtained from Brooks Rand Model I detector were recorded as mercury peaks on analogue recorder set at 50 mV over 200 mm scale and are given in results tables as mV/mm of instrument response.

Procedure II:

In procedure II, the experiment consisted of two steps. In the first step 5 µL mercury vapour was injected into glass non-passivated column at ambient temperature via a tee piece equipped with silicon septa on one side and gold sand trap on the other. Both manual and digital syringes were used for injections of mercury vapour. Gas flow of ECD grade N₂ at the rate of 120 ml/min was run through the column as carrier gas for two minutes. In the second step of the experiment the gold sand trap was desorbed at 500 °C on double amalgamation system under 60 ml/min of Ar carrier gas flow. This test consisted of three ECD grade N₂ measurements, followed by 6 – 8 injections of mercury vapour, and finally concluded by another three ECD grade N₂ measurements. Results obtained from Brooks Rand Model I detector were recorded as mercury peaks on analogue recorder set at 50 mV over 200 mm scale and are given in results tables as mV/mm of instrument response.

All injections of mercury vapour were made at ambient temperature, which changed during the course of measurements and was recorded using a digital thermometer. Changing of the ambient temperature subsequently changed the concentration of mercury vapour in 5 µL gas tight syringes used for injections and as a result the response of the instrument changed during the course of the measurements. In order to compare the obtained results the following equation was used and the results are given in the Table 8 also as pg/mV:

Concentration (pg/mV) = (Concentration (Hg vapour at given T per µL)*5 µL)/peak response (mV)

Table 8: Brooks Rand Model I experimental set up, Phase I, comparison of results between manual and digital syringe injections of Hg vapour

Direct gold trap amalgamation of Hg vapour	Manual syringe injection (mV)	Manual syringe injection (pg/mV)	Digital syringe injection (mV)	Digital syringe injection (pg/mV)
	21.3	4.4	22.0	4.3
	21.3	4.4	22.3	4.2
	21.3	4.4	23.0	4.1
	21.5	4.4	22.5	4.2
	21.3	4.4	22.8	4.1
	20.0	4.7	22.8	4.1
	21.8	4.3	22.3	4.2
Temperature	24.1	24.1	24.5	24.5
mean	21.2	4.5	22.5	4.2
std	0.6	0.1	0.4	0.1
ambient air or carrier gas	0.5		0.5	
"primary injection" (pg)	92.3		95.3	
measurement result	20.7	4.5	22.0	4.2

Table 8 presents results from procedure I, of Brooks Rand Model I experimental set up. Results indicate good agreement between results for injection of 5 µL mercury vapour at ambient temperatures using either manual or digital 25 µL gas tight syringes. Measurements are repeatable with low standard deviation. It can be concluded that both *manual* and *digital* gas tight syringes give comparable performance.

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Table 9: Brooks Rand Model I experimental set up, Phase II, comparison of results between manual and digital syringe injections of Hg vapour

Glass column gold trap amalgamation of Hg vapour	Manual syringe injection (mV)	Manual syringe injection (pg/mV)	Temperature (°C)	Digital syringe injection (mV)	Digital syringe injection (pg/mV)	Temperature (°C)
	22.0	4.4	24.5	24.3	4.2	25.2
	23.3	4.2	24.5	23.0	4.5	25.2
	21.5	4.5	24.5	25.3	4.1	25.2
	22.3	4.4	24.5	23.5	4.4	25.2
	22.3	4.4	24.5	24.0	4.3	25.2
	23.8	4.1	25.0	24.3	4.2	25.2
	24.0	4.1	25.0	23.8	4.3	25.2
	23.8	4.1	25.0	23.5	4.4	25.2
	24.0	4.1	25.0			
mean	22.5	4.3		24.0	4.3	
std	0.8	0.2		0.8	0.1	
ambient air or carrier gas (mV)	0.5			0.5		
"primary injection" (pg)	95.3 & 99.3			100.9		
measurement result	22.0	4.3		23.5	4.3	

Table 9 presents results from procedure II, of Brooks Rand Model I experimental set up. Results obtained indicate that the subsequent desorption of trapped mercury from gold sand traps are repeatable and with low standard deviation between injections for 25 μL *manual* and *digital* gas tight syringes used for mercury vapour injections in procedure II. Comparison between Tables 8 and 9 shows good agreement between results obtained in procedures I and II of the experiment which indicates that mercury did not get adsorbed to glass and therefore it is concluded that glass is a suitable material under normal testing conditions.

Table 10: Overview of the results for Brooks Rand Model I experimental set up. Comparison of the results between procedures I and II

	Procedure 1		Procedure 2	
	Manual syringe injection	Digital syringe injection	Manual syringe injection	Digital syringe injection
pg/mV	4.5 \pm 0.1	4.2 \pm 0.1	4.3 \pm 0.1	4.3 \pm 0.1

Table 10 presents an overview of the results from procedures I and II, of Brooks Rand Model I experimental set up. Comparison indicates good agreement between results obtained for 25 μL *manual* and *digital* gas tight syringes used for injections of 5 μL of mercury vapour at ambient temperature.

However, JSI observed that in order to obtain repeatable results care must be taken when performing injections of Hg vapour with either manual or digital syringes. It is important to note that the septa used during the injection procedures are in good condition, since it was observed that shredded or damaged septa cause high standard deviation of the results. It is also important

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that care be taken that the needle point of the syringe does not touch anything during the injection (walls, lines,) , since that will increase the standard deviation of the results. And finally, when manual injection is used, the injection itself should be in contact with the fingers only at the top for as little time as possible while performing the injection procedure.

5. Conclusions

A materials study was carried out to select the best candidate materials to be tested with respect to their suitability for the sampling of mercury in ambient air and exhaust emissions.

Based upon the study several types of Teflon tubes were tested by VSL, whereas glass was tested by JSI. Both institutes used a similar measurement approach.

FEP and PFA types of Teflon proved to be suitable materials as no effects were found due to absorption or permeation under standard test conditions. Non-passivated glass also proved to be suitable material as no effects were found due to adsorption or permeation under standard test conditions.

It was observed by VSL that manual injections with a gastight Hamilton syringe provided lower repeatability of measurement results than using a digital gastight syringe. Further research will be performed to investigate whether this may be attributed to the particular (poisoned?) digital syringe used. JSI observed no such problems (Tables 8 and 9) as repeatability of measurement results were comparable between manual and digital Hamilton gas tight syringes used.

JSI will conduct further studies that will include testing of the non-passivated and passivated glass material under increased temperature conditions, in the presence of water vapour, and other gases (CO₂, NO_x, ...) that are found in automotive exhaust.

6. Literature

Tekran Instruments Corporation, User manual, Ambient Mercury Vapour Analyzer Model 2537B, Rev. 3.11, 2008