Report: Results of an intercalibration Hg campaign

19NRM03 SI-Hg

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Lead partner: CNR
Version No.: 3
Due date deliverable: 31-05-2023
Actual submission date: 27-11-2023

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation programme.

EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Summary

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1. Introduction

1.1. Task 1.4: Comparison at the CNR-IIA monitoring station in Rende

Mercury (Hg) is a pollutant of particular interest that, due to its chemical and physical properties and its ubiquitous presence in the environment, has combined qualities of toxicity and potential for bioaccumulation and biomagnification in aquatic and terrestrial biosystems. During the last decades the attention towards its monitoring has been constantly increased. A large number of activities have been carried out to characterize the levels of Hg species in ambient air and precipitation, to understand their variability over time and how they depend on physico-chemical parameters on temporal and spatial scale. The understanding of the pathways by which Hg is released into the atmosphere, transformed, deposited and eventually incorporated into biota is therefore of crucial importance to evaluate the impact on the environmental ecosystems [1]. The Article 19 of the Minamata Convention calls for a proper research, development and monitoring of Hg in the environment. Parties of the Minamata Convention are obligated to monitor levels of mercury and mercury compounds in vulnerable populations and in all environmental media, including biota, as well as to assess information on the environmental cycle, transport, transformation and fate of mercury and mercury compounds in a range of ecosystems, taking appropriate account of the distinction between anthropogenic and natural emissions and releases of mercury and of remobilization of mercury from historic deposition. This thorough assessment necessarily passes through its accurate and precise quantification in a rigorous and internationally comparable way. Indeed, previous studies regarding the intercomparison of Hg measurements reported the main causes of variability in results mainly depend on the experimental set up and calibration, rather than the type of instrument or the manufacturer [2]. More strictly, calibration step resulted to be fundamental, and its effectiveness depends on a combination of the analyst's skill and the reliability of the calibrators.

The aim of the task 1.4 was to determine the consistent quality of mercury measurements during a field campaign at the monitoring station located in Rende, Italy. This campaign consisted in the comparison of the performances of multiple Hg analyzers produced by different producers, operating in parallel under the same experimental conditions, each calibrated with SI-traceable certified gas generators. Participants were invited to perform field measurements using elemental gas generators and oxidized mercury generators for the determination of the mercury concentration at the monitoring station in Rende.

2. Involved Instrumentation

2.1 Sampling Site

The sampling site (Figure 1) selected for Hg measurements is a monitoring station located near the CNR-Institute of Atmospheric Pollution Research in Rende (Calabria, Italy, 39°21'27.2 "N 16°13'53.7 "E). It is a suburban site close to the urban and industrial area of Cosenza, near the A2 motorway, which crosses the area at about 1 km east of the measurements site with a considerable traffic flow per day and represents the major local source of air pollution in the area [3].

The sampling site is equipped with a meteorological station consisting of a thermo-hygrometer (LSI LASTEM DMA875) for the monitoring of temperature and relative humidity, an anemometer (LSI LASTEM DNA821) for the monitoring of wind speed and direction, barometer (LSI LASTEM DQA801) for the monitoring of the atmospheric pressure, and a pyranometer (LSI LASTEM DPA863) for measuring the total solar radiation.

Figure 1. Monitoring station in Rende

2.2 Gas Generators

The gas generators involved in the intercomparison included:

- Bell-jar 2505 Tekran Calibration Unit for Hg0 generation;
- Liquid evaporative HovaCAL SP gas generator for HgII generation;
- Non-thermal plasma oxidation of Hg0 on KCl-coated denuders for HgII generation.

The Bell-jar or Tekran® Model 2505 (Tekran Instrument Corp., Ontario, Canada) mercury vapor calibration unit is a gas generator used for periodic manual calibration of the active mercury analyzers through the use of a gas-tight micro-syringe. The operation of the Tekran 2505 unit is based on the Bell-jar principle, according to which the amount of elemental mercury (Hg^0) is calculated using the Dumarey equation. Based on this equation, the amount of elemental mercury withdrawn from the bell-jar using a micro-syringe can be easily calculated knowing the temperature of the source and syringe injection volume. Therefore, this kind of calibration unit is usually a first choice for the calibration of instruments that measure gaseous elemental mercury (GEM).

The HovaCAL SP is a portable gas generator by IAS GmbH for highly accurate gas-vapor mixtures with selectable humidity and especially designed for calibration of continuous emission monitoring systems [4]. This instrument is equipped with a sophisticated evaporation technology; indeed, its operation is based on the principle of dynamic evaporation of mercury chloride solution and mixture with carrier gas (ultra-high-purity air). For generating a defined reference gas and water vapor concentration, gas flow will be adjusted with the build in mass flow controller and the liquid flow will be achieved with a peristaltic pump. Liquid solution is continuously pumped into an electrically heated evaporator, vaporized, and mixed with carrier gas. Therefore, this generator is the most appropriate for the calibration of instruments that measure gaseous oxidised mercury (GOM).

Non-thermal plasma oxidation of GEM on KCl-coated denuders is a technique that is based in loading a denuder with a known amount of oxidized mercury, specifically mercury(II) oxide, HgO [5]. A non-thermal plasma utilizes the energy stored in energetic electrons (contrary to warm plasma in which the energy is dissipated as heat) to oxidize elemental mercury in the presence of reactive gasses, such as oxygen. The elemental mercury is produced by the reduction of NIST Standard Reference Material (SRM) 3133 with stannous chloride in hydrochloric acid solution, thus providing traceability of the non-thermal plasma oxidation system to the SI units. Production of GOM using non-thermal plasma and its loading on denuder is achieved simultaneously by attaching high-voltage electrodes directly on the denuder. The breakthrough (the amount of elemental mercury that is not oxidized in the plasma) is always collected on a gold-coated silica-sand trap and quantified to determine the exact amount of oxidized mercury collected on the denuder. Due to specific design of the non-thermal plasma oxidation system, a very small traceable amounts of GOM can be produced, thus making it appropriate for the calibration of instruments used for atmospheric GOM measurements.

Calibration with NIST SRM 3133 were also performed on the Hg analyzers to ensure SI traceability of the resulting measurement results. NIST SRM 3133 is the certified reference material in which the exact mass concentration of mercury is prepared gravimetrically, thus providing direct link with the SI units. NIST SRM 3133 has very low uncertainty which is only slightly increased when preparing dilutions of this certified reference material. Therefore, NIST SRM 3133 is very practical for the calibration of various instruments, especially because it can produce cold vapors when reacting with stannous chloride solution. For the calibration of instruments using NIST SRM 3133, a diluted NIST SRM 3133 solution with known Hg amount was reduced with stannous chloride in diluted hydrochloric acid to produce Hg(0) using a bubbler system. The produced Hg(0) vapors were collected on gold-coated silica-sand sorbent traps, which were then desorbed into the sampling port of each instrument. The obtained analytical signals were always collected by the appropriate procedural blank which included the bubbler blank released into the sampling port of the instrument in the same manner as the standard. As very small traceable amounts of mercury can be produced, this calibration approach is appropriate for the calibration of instruments used for atmospheric measurements.

2.3 Active Analyzers

The active sampling of gaseous Hg in the air was carried out using different Hg analyzers provided by Tekran Corporation, PS Analytical, Mercury Instruments, and Lumex. The sample inlet probe of each analyzer was installed individually near the monitoring station at about 2m above the ground.

A summary of the techniques used for active sampling is given in Table 1. Summary of the analytical methods for sampling and analysis of atmospheric mercury speciesTable 1. The mercury speciation analyzer system (Tekran Instrument Corp., Ontario, Canada) was used during the campaign, consisting of a Tekran® 2537X unit, a 1135 Particulate Mercury unit and a 1130 Speciation unit to simultaneously monitor Gaseous Elemental Mercury (GEM), Particulate Bound Mercury (PBM), and Gaseous Oxidized Mercury (GOM), respectively.

Speciation measurements were performed following the Global Mercury Observation System (GMOS) SOPs using a size-selective impactor inlet (2.5 µm cut-off aerodynamic diameter), a KCl-coated quartz annular denuder in the 1130 unit and a quartz regenerable particulate filter (RPF) in the 1135 unit [6]. During sampling, the denuder captured GOM, the PBM was trapped onto a RPF while allowing GEM to pass through, and being continuously quantified through the double amalgamation system and detected using cold vapor atomic fluorescence spectrometry (CVAFS) every 5 minutes. The GOM and PBM components were then sequentially desorbed at the end of the sampling cycle, which lasted 1-hour and was set at a flow rate of 10 sL/min. Subsequently, the 1130 and 1135 systems were flushed with Hg-free air for 1 hour, and PBM and GOM were sequentially desorbed at 800°C and 500°C, respectively, before being detected as GEM. During the campaign denuders and RPF were recoated and replaced every two weeks.

The Mercury Ultratracer UT-3000 (Mercury Instruments GmbH, Karlsfeld, Germany) uses a gold trap to capture total gaseous mercury (TGM) by the formation of an amalgam. The air sampled is pumped and pulled through a 0.45 µm polytetrafluoroethylene (PTFE) filter thus allowing mercury collection on the gold. The gold trap is then heated very quickly, and the mercury is released by thermal desorption. The elemental Hg is swept by the flow of purified air into the optical cell of the detector, and the Hg concentration is measured by cold vapor atomic absorption spectrometry (CVAAS) at the Hg absorption wavelength of 253.65 nm. Prior to each measurement, the instrument performs an auto-zero of its absorbance.

The RA-915M LUMEX analyzer is a portable multifunctional atomic absorption spectrometer that enables real-time monitoring and detection of GEM in air based on Zeeman background correction, which eliminates the effect of interfering compounds. This instrument does not require gold amalgam pre-concentration and subsequent regeneration steps and has a built-in test cell for performance verification and an autozero function for quick and easy calibration verification.

The 10.525 Sir Galahad II (SGII, PS Analytical, UK) analyzer is an automated instrument for measurements of Total Gaseous Mercury (TGM=GEM+GOM). The analyzer utilizes a gold on silica trap to collect the TGM before analysis and Atomic Fluorescence Spectrometry (AFS) detection. A pump and mass flow controller are used to measure the volume of gas sampled so that continuous online measurements can be performed. Thus, the TGM contained into the air sample is collected through a preconcentration trap and subsequently thermally desorbed into the SGII detector. An additional port allows for remote trap analysis by dual amalgamation.

2.4 Sorbent tube sampling

In addition to the sampling with active analyzers, during the campaigns also sorbent-based techniques were used for the Hg measurements. Remote tube samplers of Amasil (PS Analytical, UK) were involved. These remote tubes take advantage of Amasil (PS Analytical, UK) trap technology to collect TGM from the ambient air over a certain period. Two sampling approaches were compared using parallel trains including a battery operated micro pump charged by solar energy and a mass flow controller arrangement with a conventional pump run from mains voltage. These tubes use a porous silica coated in gold nanoparticles sandwiched between quartz wool plugs at the center of a quartz tube.

For deployment, remote tubes were secured to the metal support rack, at a height of about 2-3 m above ground to facilitate free air circulation. The Amasil traps were installed in an external shield to protect them from the weather. One of the advantages of this material is that it has a large surface area thereby providing a large adsorption capacity and once desorbed it can be reused.

After deployment, the mercury on Amasil trap was quantified by thermal desorption, heating within the PSA 10.525 SG-II remote port. The desorbed Hg was then collected onto a permanent gold trap, which was then heated to release Hg vapors, then detected by AFS.

Table 1. Summary of the analytical methods for sampling and analysis of atmospheric mercury species

Instrument	Measured Hg species	Analytical method
10.525 Sir Galahad II	TGM	CVAFS
UT-3000 Ultratracer Analyzer	TGM	CVAAS
Lumex RA-915M	GEM	Zeeman-CVAAS
Tekran 1130-1135-2537X Speciation Units	GEM, GOM, PBM	CVAFS
Amasil Remote tubes	TGM	CVAFS

2.5 Intercalibration Exercise Design

Compared to the protocol written in A1.4.1 [7] regarding the guidelines of the intercomparison campaign, the calibration scenario adopted was better defined, being known all the instruments involved. Furthermore, the ultimate goal of the campaign was adjusted in the evaluation of the comparability of calibrations, rather than measurements, conducted using the gas generators on the Hg analyzers from different companies. Specifically, the calibrations were carried out following the scheme in Figure 2. The Tekran 2505 bell-jar gas generators was used to calibrate all the involved analyzers while the non-thermal plasma gas generator and HovaCAL SP were used to calibrate Tekran Integrated system. Calibrations with NIST 3133 were performed on all the analyzers, except for Lumex, and compared with calibrations with the other gas generators in terms of the slope of the calibration lines. Linearity was also assessed for each experiment.

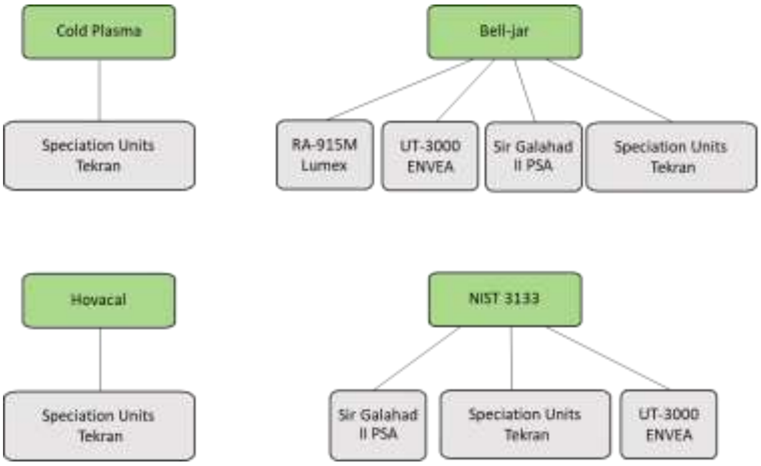

Figure 2. Calibration scenario adopted during the campaign

Given that the focus of the campaign turned into calibrations, simultaneous measurements of the instruments were not addressed, differently from what was stated in the protocol in A1.4.1 [7].

3. Experimental and results

3.1 Calibration by HovaCAL SP gas generator

Calibration for GOM measurements on the Tekran using HovaCAL SP gas generator was carried out through the connection of the HovaCAL SP outflow directly into the inlet of the integrated system (Figure 3). For these tests, the flow of the liquid solution in the HovaCAL SP was set at 0.06943 g/min and that of the gas flow at 7.67 L/min exceeding input flow of Tekran sampling unit. The sampling method of the Tekran integrated system was set to continuously sample the HovaCAL SP flow from a bypass flow for 1 h, during which GEM was measured every 5-min on the A and B traps alternately, while GOM and PBM were pre-concentrated on denuder and RPF, respectively. After this sampling step, thermal desorption was performed, first PBM was desorbed at 800 °C, the GOM from the denuder at 500 °C. Given the low ambient levels of GOM typically measured at the monitoring station (in the pg/m^3 range) and the even 1 000 000 times higher concentration levels produced by this gas generator for previous experiments (in the µg/m^3 range), it was first necessary to conduct cleaning operations to reduce its contamination. After this cycle, the GOM signal resulting from the sampling of the ultrapure water was used as an index of the effective cleaning. These procedures consisted in a flush of the evaporator with 10% v/v HNO_3 solution for 10 min and a flush with 10% v/v HCl solution for 10 min, each followed by rinsing with ultrapure water overnight. After these steps, a significant carryover contamination was still detected, the GOM signal was highly variable, and in addition, non-zero readings of GEM were measured, thus suggesting potential photo-reduction of GOM to GEM in the sample line. A further cleaning step was therefore necessary to reduce contamination and a coating of the sample line with aluminum foil to avoid photo-reduction (Figure 4). Ultrapure water was then used for a longer rinse time (30 h).

Figure 3. HovaCAL SP gas generator

Figure 4. Tekran Speciation Units System with aluminum-coated sample line

This step revealed to be useful to obtain a stable signal of the GOM, which permitted us to proceed with the analysis of the $HgCl_2$ solution at 0.1 µg/L (corresponding Hg concentration of around 1 ng/m^3 in air), for the low-level calibration with GOM. The first readings (Figure 5) consisted of non-zero values of GOM, GEM, PBM, which gradually decreased, and after six cycles zero values of GEM and PBM were obtained, while the GOM provided a final signal corresponding to 1.94 ng/m^3. Considering that the solution should have resulted in a 1 ng/m^3 reading, the discrepancy between GOM on the denuder and GOM produced by HovaCAL SP (94%) was considered high. However, from these tests also a quite long stabilization time of the gas generator resulted, thus our finding can be said to be promising for further studies of low-level calibrations.

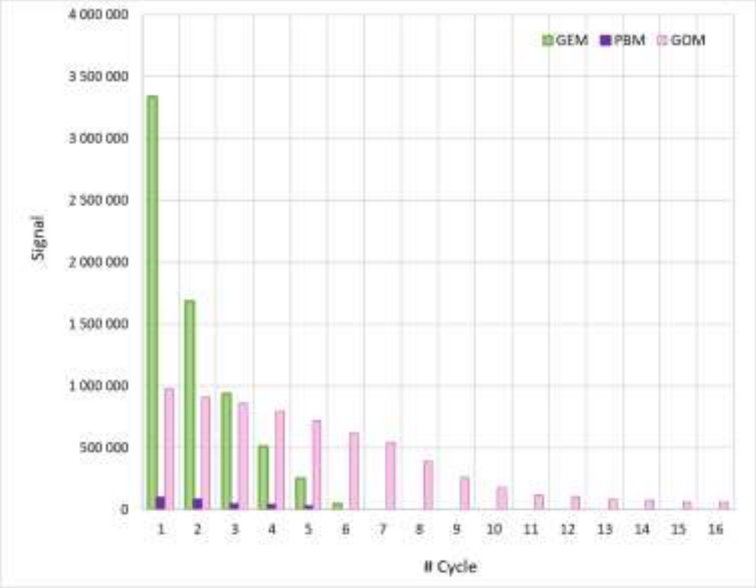

Figure 5. Plot of the GEM, GOM, and PBM area values as obtained from the $HgCl_2$ solution by the Tekran Integrated System

3.2 Calibration by non-thermal plasma gas generator

Instrumental calibration for GOM measurements on the Tekran speciation unit using non-thermal plasma gas generator was carried out by mounting KCl-coated denuders, loaded in the laboratory with 115 pg of Hg(II) on average, into the Tekran integrated system. These denuders were then desorbed at 500°C under a zero-air flow, within the typical desorption cycle of the Tekran , which also included GEM and PBM detection. The obtained corresponding peak area was then converted into the mass of Hg(II) based on the internal calibration of the instrument. The results were always corrected for the corresponding procedural blank. The results of nine experiments are reported in Table 2.

Table 2. Results of the desorption tests of the denuders loaded by non-thermal plasma oxidation of GEM

Run #	Loaded GOM (pg)	GOM by Tekran (pg)	GOM+PBM+GEM by Tekran (pg)	Denuder Recovery (%)	GOM+PBM+GEM Recovery (%)
1	115.3	69.4	105.1	53.8	91.2
2	114.2	59.2	108.3	45.3	94.9
3	115.9	54.4	111.5	40.5	96.2
4	117.3	52.2	109.5	38.1	93.4
5	115.8	58	99.4	43.7	85.8
6	118.6	77	105.9	58.7	89.3
7	121.8	75.5	114.3	56	93.9
8	117.2	64.2	105	48.5	89.6
9	118.4	67.8	86.6	51	73.1

The comparison of the Hg(II) masses measured by the desorption of the denuders and the masses loaded using the gas generator showed that only a small percentage, on average 48.4 ± 7.1%, of the loaded Hg(II) is adsorbed and/or detected by the denuder. However, during desorption unexpected non-zero values of GEM and PBM were also detected, thus suggesting that the mercury loaded on the denuders was detected during the entire desorption cycle. In the common desorption cycle of the procedural blanks, GEM and PBM usually have zero value. Indeed, the sum of the areas related to GEM, PBM, GOM, cleaning and flush cycles converted into Hg mass led to a much higher ratio compared to the Hg mass initially loaded, which was up to 92.6 ± 2.7% (if runs 5 and 9 are not considered). This indicates that Hg(II) loaded on denuders using non-thermal plasma is practically being immediately released from the denuder and contaminates other parts of the Tekran system under these experimental conditions. This might explain the observation that Tekran speciation unit commonly underestimates atmospheric GOM concentrations; it seems that denuders are not able to retain all sampled GOM until the GOM desorption and measurements cycle commence.

3.3 Calibration by Bell-jar and NIST SRM 3133 of the Tekran analyzer

Calibrations of the Tekran Speciation unit was performed via manual injection using Tekran 2505 Calibration unit but also via desorption of the sorbent trap loaded with NIST SRM 3133. In particular, three different systems were tested for the introduction of the known amount of Hg, which are showed in Figure 6. In detail, calibration was first performed via injection of Hg through the inlet of the 1130 Tekran unit, without the use of a zero-air filter upstream. In this case, a flow of 12 sL/min was measured. The second configuration was quite similar, with the addition of a zero-air canister and a mercury scrubber upstream, configuration that slightly reduced the flow rate at 11 sL/min. In the third configuration, mercury was injected through the sample port of the Tekran 2537X unit, where the sample flow is at 1 sL/min. In each case, calibration of both A and B traps was performed, and both of them were considered together for the calibration line calculation.

Figure 6. Inlet configurations used for the introduction of the known amount of Hg

In the first type of calibration, that is without the zero-air canister upstream, NIST SRM 3133 calibration was performed at four levels (Figure 7).

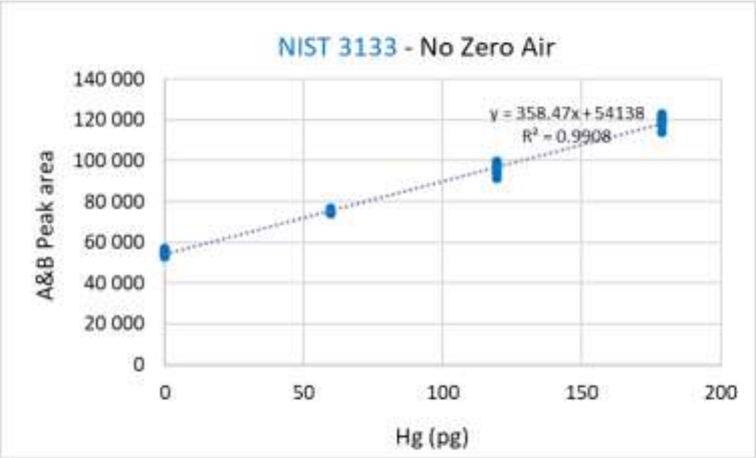

Figure 7. NIST 3133 calibration line on the Tekran Speciation unit without zero air canister at the inlet

Considering that both cartridges are reported, which although brand-new and matched can experience some differences, a good linearity was obtained, with a determination coefficient R^2 of 0.9908, and a slope of 358.47 counts/pg. The addition of a zero-air filter upstream in the second configuration for NIST SRM 3133 calibration led to a quite different calibration line, which is reported in Figure 8.

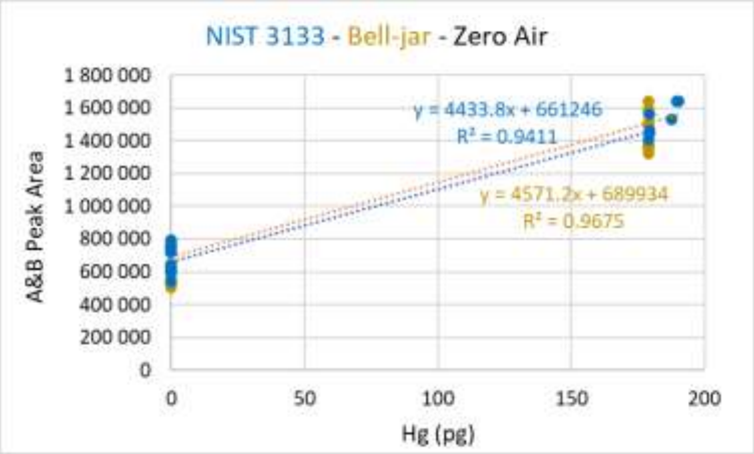

Figure 8. NIST SRM 3133 calibration line on the Tekran Speciation unit with zero air canister at the inlet

Indeed, though two levels were tested, a worse linearity was obtained, with a coefficient R^2 of 0.9411, and a significantly different slope value was obtained, being more than 12 times higher than the corresponding calibration without zero air filter. This difference was not explained with the different flowrates between the two configurations. Further study is required to elucidate the exact reasons for these observations.

In the same figure, also calibration with Bell-jar injection at two levels into the Tekran inlet with the zero-air filter is reported. These two calibrations were comparable each other, both in terms of linearity and sensitivity. Indeed, the slope of the calibration line was of the same order of magnitude than for NIST calibration, with a value of 4571.2 counts/pg that deviated from the NIST slope by 3%.

Calibration using the injection port (Figure 9) showed a good linearity, with R^2 being 0.9985, and was also comparable with the Tekran internal calibration using permeation source, which is also plotted in the figure. However, compared to NIST calibration through the sample port with zero air filter, this resulted in a still higher slope, which was 6059.2 counts/pg, and led to a deviation of 36%. Losses in the sampling speciation module could probably explain this difference and the higher slope value for the calibration through the injection port.

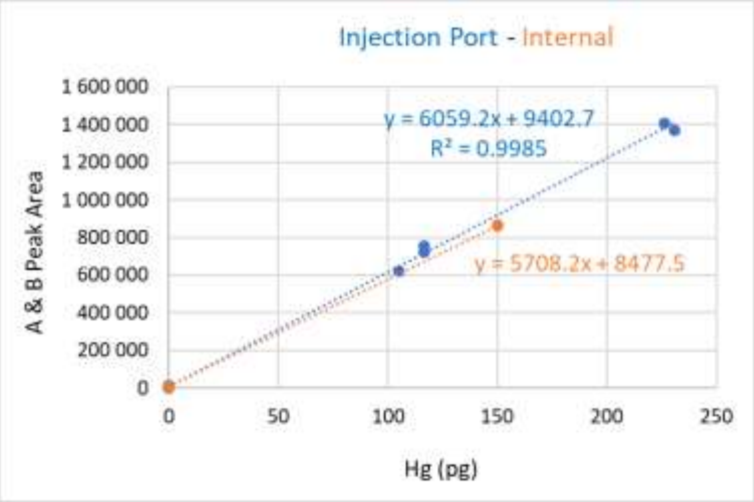

Figure 9. Bell-jar calibration via the injection port of the 2537X unit

3.4 Calibration by Bell-jar and NIST SRM 3133 of the Sir Galahad II analyzer

Bell-jar and NIST SRM 3133 calibrations were also performed on the SGII analyzer (Figure 10), which was set to sample ambient air at 0.5 sL/min. Also in this case, calibration was performed both through the sampling port and the injection port, with a zero-air filter upstream in the case of sample port injections.

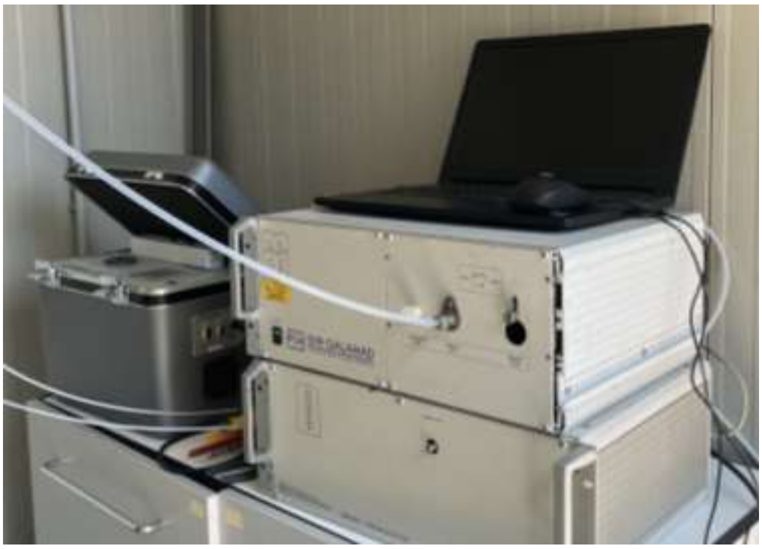

Figure 10. Sir Galahad II analyzer for TGM

For each calibration exercise a good precision among the injection replicates was obtained (Figure 11), and also good linearity resulted from the two calibrations through the sample port. However, since the two calibrations were performed with a similar setup, the corresponding slopes should have resulted in the same value, but this was not achieved. Bell-jar injections led to a higher slope value, which deviated by 36% from the NIST calibration with the similar setup.

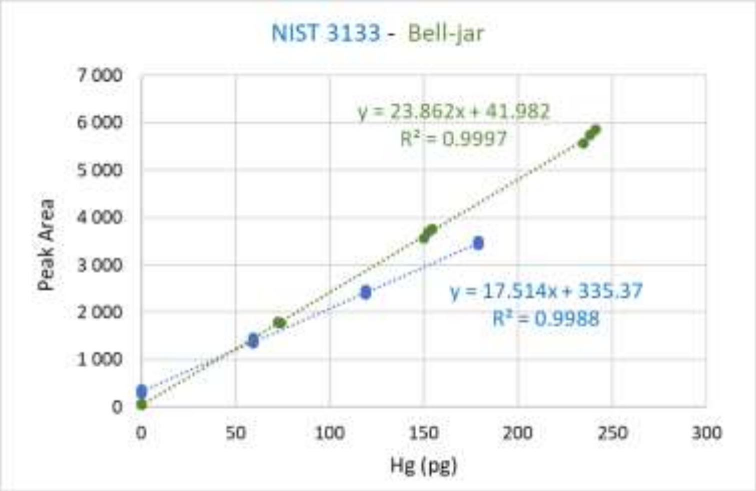

Figure 11. NIST SRM 3133 and Bell-jar calibration lines through the instrument sample port

Calibration using the injection port on the front panel of the instrument also provided slightly different slope values, which in this case may be related to the different instrumental setup compared to calibration with NIST SRM 3133 through the sample port. In this case, the deviation from the NIST slope was even greater, specifically 44% (Figure 12).

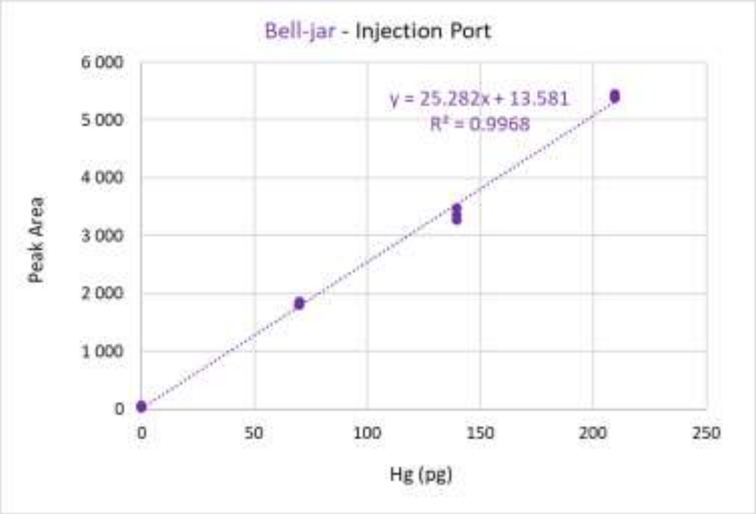

Figure 12. Bell-jar calibration line through the instrument injection port

3.5 Calibration by Bell-jar and NIST SRM 3133 of the UT-3000 analyzer

NIST SRM 3133 and Bell-jar Calibration were also performed on the UT-3000 TGM analyzer (Figure 13). These calibrations were carried out both using the sampling port, with a zero-air filter upstream, and the injection port provided on the front panel of the instrument. The analyzer was set to work at a sample flow rate 0.67 L/min.

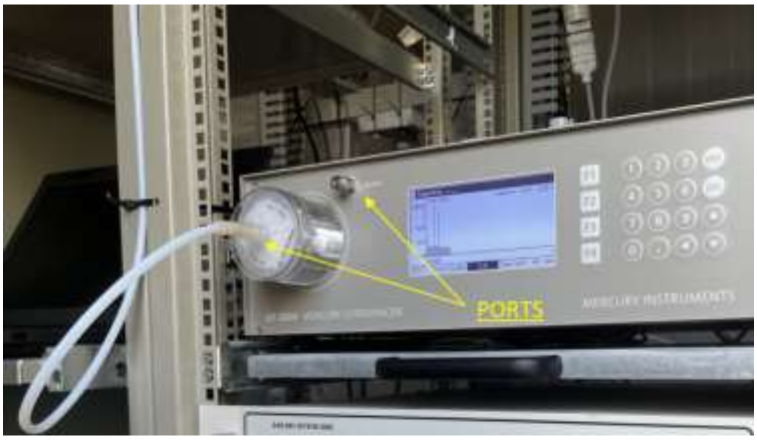

Figure 13. UT-3000 sample line and injection port used for calibrations

The three different calibration tests that were carried out on the UT are summarized in Figure 14 and Figure 15.

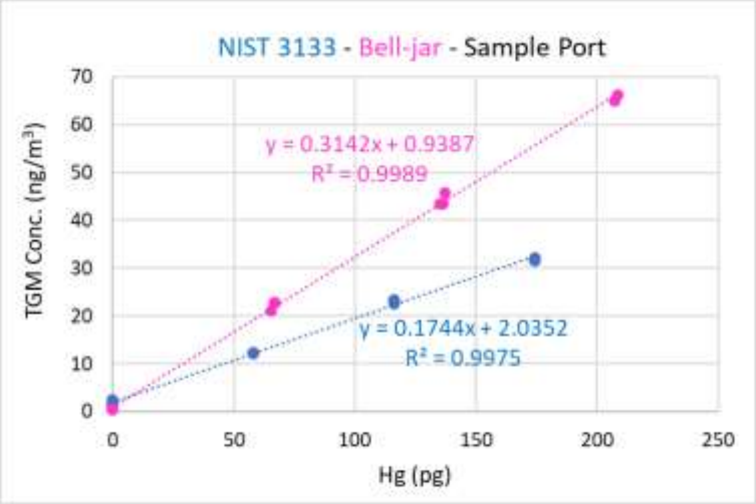

Figure 14. NIST SRM 3133 and Bell-jar calibration lines on UT-3000 through the sample port Hg introduction

Calibration using the sample port, also in this case provided low values of the calibration slopes, which were also significantly different from each other. While the NIST calibration resulted in a slope value of 0.1744 ng/m^3 per pg Hg injected, Bell-jar injection showed about twice this value. Besides not being able to explain such a difference, the slope value showed that the UT-3000 was, of all the analyzers involved in the campaign, the least sensitive, with a very low slope value, which caused the measurements resulting from the analyzer being almost constantly zero for the duration of the campaign. In fact, the calibration by injection port also provided a very low slope value, confirming the result already obtained with the NIST calibration. Consequently, the deviation from NIST was 180 % for the calibration through the sample port and 46 % for that through the injection port.

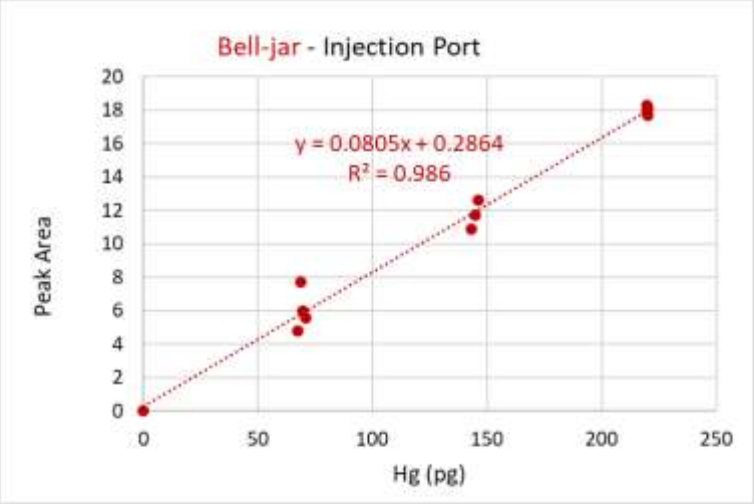

Figure 15. Bell-jar calibration line on UT-3000 through the injection port

3.6 Calibration by Bell-jar gas standard of the Lumex analyzer

Multiple injections at different levels were conducted using the bell-jar generators into the sample port of the Lumex analyzer using a gas-tight syringe equipped with the bevel tip needle for gas locking. The plot refers to the peak obtained from one of the manual injections as an example (Figure 16).

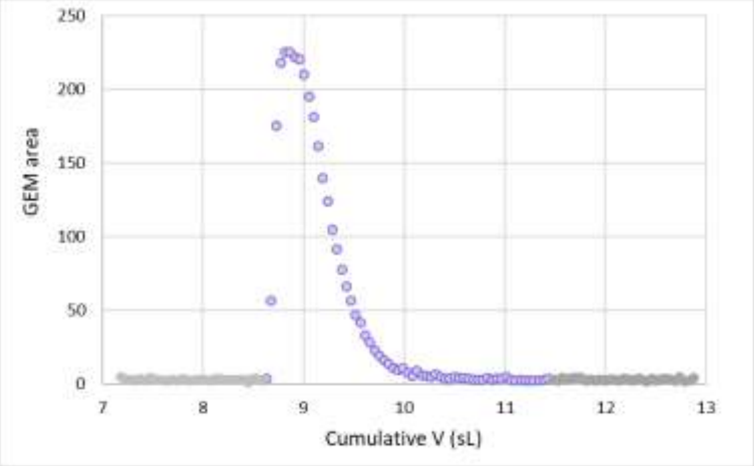

Figure 16. Example of the peak obtained from a manual injection into the Lumex sample port

The amount of mercury (in pg; calculated as the area under the curve) released into the sampling inlet using a micro-syringe was calculated by summing all products of GEM concentrations at 1-second interval and corresponding volumes of sampled air (Σ ci × ΔVi). This amount was corrected for the background values by subtracting the corresponding area obtained before and after the injection. The results of the manual injection and the sorbent trap desorption are summarized in Table 3.

Table 3. Results of the calibration of the Lumex analyzer using Bell-jar injections and sorbent tube desorption

Run #	Hg by Lumex (pg)	Hg via gas standard (pg)	Ratio (%)
1	138	182	75.8
2	140	183	76.7
3	138	183	75.1
4	137	184	74.8
5	417	558	74.7
6	421	560	75.2
7	710	938	75.7
8	700	941	74.4
9	708	944	75.1
10	717	947	75.8

On average, a good precision was obtained from the manual injections with a relative standard deviation of only 0.90%. All the manual injections provided values that were about 75% of those obtained from the gas standard. These results seem to agree with previous laboratory tests (Andron at al., submitted to the Atmospheric Measurement Techniques), which also demonstrated that Lumex RA-915M used at low ambient air levels underestimated GEM concentrations, with a calibration slope from bell-jar manual injections of about 70%, which found confirmations from the results of our campaign.

3.7 Sorbent tube sampling

Besides the active analyzers, also remote tubes were included in the field campaign with the aim to assess their accuracy compared to the concentration obtained from the active analyzers. Ambient air sampling of remote tubes started on 24th July and ended on 2nd August. These Amasil traps were deployed inside a transparent cylindrical holder, useful to protect them from the meteorological conditions, and connected to pumps for air sampling (Figure 17). In particular, two remote tubes (G3 and G4 traps) were connected to pumps powered by solar panel, whereas two remote tubes (G5 and G6 traps) were connected to a pump powered by mains voltage, passing through a mass flow controller.

Before deployment, all the traps were blanked using the remote port heater of the SGII analyzer, which permitted to remove any potential contamination before sampling. After deployment, SGII was also used to analyze the Hg mass trapped by each cartridge, which was then converted into Hg concentration considering the total volume sampled during the deployment time. Volumetric flow through each trap and the flowrate of the solar powered pump were not measured onsite. The device comes with a data logger to monitor the input voltage to the micropump however this was not activated at the start of the sampling, thus the information about the sorbed Hg mass will be only discussed.

Figure 17. Deployment of the remote tube samplers on the rooftop of the monitoring station

The results of the thermal desorption are summarized in Table 4.

Table 4. Results of the remote tube analyses

Sampler ID	Hg in Blank (ng)	Hg mass (ng)	Average ± SD (ng)	RSD (%)
G3	0.85	4.03	3.72 ± 0.43	11.6
G4	0.96	3.42		
G5	0.28	4.26	3.59 ± 0.95	26.4
G6	0.81	2.92		

The Hg mass values obtained from the blanks analysis were high and variable, so these will be neglected for calculations. The mass sorbed during the exposure period averaged 3.65 ± 0.61 ng, and precision among the replicates was 11.6 and 26.4 % for G3-G4 and G5-G5 samplers, respectively (Figure 18).

Figure 18. Plot of the Hg mass (ng) sorbed by each Amasil trap

4. Conclusions

HovaCAL SP system demonstrated bias when calibrating Tekran speciation unit, together with a quite long stabilization time of the gas generator; nevertheless, our results indicate a promising calibrator unit for further studies of low-level calibrations. Calibration of Tekran denuders using non-thermal plasma oxidation of elemental mercury revealed that GOM can be readily desorbed from the denuder during the full sampling/measurement cycle of the Tekran unit. This confirms previous findings of Tekran's underestimation of GOM concentrations in ambient air.

All calibration curves obtained in the intercalibration campaign showed good linearity, including those performed through the whole sampling system, which is a requirement of the EN 14181:2014 standard: 6.2.3 Linearity test (Linearity tests shall be performed by passing gaseous reference materials through the entire automated measuring systems). However, the observed differences in the calibration slopes were not successfully explained; therefore, further tests are required to address these issues and to explain the observations. The best alignment of calibration slopes is obtained using bell-jar and NIST SRM 3133 calibration under same experimental conditions (through the Tekran speciation unit's sampling inlet).

Offline samplers were also involved in the field campaign, providing information on the sorbed mass of atmospheric Hg with an acceptable standard deviation between individual samplers. More data about the average flow of ambient air passing through each sampler could have provided information on the time-integrated Hg concentrations, thus more work has to be done to compare these results and those obtained by active Hg measurements.

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