



GMOS Standard Operational Procedure

Method for the determination of DGM in water

Foreword

The present Standard Operational Procedure (SOP) for the sampling and determination of dissolved gaseous mercury in water is intended for use within the GMOS project. No standard procedure for DGM measurements in water exist so far. There are several state of the art methods published in peer reviewed literature. The present SOP is based on several peer-reviewed publications on DGM measurements and USGS SOP for determination of DGM in water by purge and trap, and cold vapour atomic fluorescence spectrometry (CV AFS). The present version of this GMOS SOP can be used as quick reference guide when starting up DGM measurements. It also contains quality control protocols to be used in the field when performing DGM measurements.

The SOP is applicable for the measurement of DGM in fresh or sea water over 0.005 ng L^{-1} .

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1. Scope

This Standard Operational Procedure describes methods for sampling and determining dissolved gaseous mercury (DGM) in fresh or sea water using CVAFS detection or Zeeman CVAAS, respectively and should be followed regarding measurements DGM within GMOS project. Results are reported as the average mass DGM per volume of water, measured over a specified time period. The time should be reported as GMT time and concentrations should be reported as ng L^{-1} .

The ease of contaminating ambient water samples with mercury and interfering substances cannot be overemphasized. This method includes suggestions for improvements in facilities and analytical techniques that should minimize contamination and maximize the ability of the laboratory to make reliable THg determinations.

The detection limit and minimum level of quantisation in this method usually are dependent on the level of interferences rather than instrument limitations. The terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this method because they lack an exact definition. However, the information provided in this method is consistent with the summary guidance on clean and ultraclean techniques. This method is "performance based." The laboratory is permitted to modify the method to overcome interferences or lower the cost of measurements if all performance criteria are met.

This method should be used only by analysts experienced in the use of CVAFS (or CV AAS) techniques and who are trained thoroughly in the sample handling and instrument techniques described in this method. Each laboratory that uses this method must demonstrate the ability to generate acceptable results. This method uses either manual or automated systems for determination of DGM in water. Separate calibration, analysis, and calculation procedures are provided for manual and automated systems.

2. Abbreviations

Mercury Species:

Hg	Mercury
DGM	Dissolved Gaseous Mercury: the summary of gas phase species of mercury present in water that can be released from the sample by purging with inert gas (nitrogen or argon) or Hg free air
Hg ⁰	Elemental mercury
DMeHg	Dimethyl mercury - (CH ₃) ₂ Hg

Analytical Terms:

CVAFS	Cold Vapour Atomic Fluorescence Spectrometry
CVAAS	Cold Vapour Atomic Absorption Spectrometry
MFC	Mass flow controller
MFM	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)

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
ng L ⁻¹	nanograms per liter
°C	degrees Celsius
cm	centimeters
L	liters
lpm	liters per minute
V	volts

3. Gases, apparatus, reagents and standards

Gases

- Argon, of purity greater than 99.999 %, suitable for use as a carrier gas for CVAFS.
- Nitrogen, of purity greater than 99.999 %, suitable for use as a carrier gas for CVAAS.
- Air, of class 3.3.3 purity or better according to ISO 8573-1:2010.
- Elemental mercury, of purity 99.999 9 %, 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.

- Deionised water, resistivity greater or equal to 18 MΩ cm.
- Hydrochloric acid, diluted 1:49 with deionised water for cleaning of measurement device and sampling components.

WARNING — concentrated hydrochloric acid is corrosive and is an irritant. Avoid contact with the skin and eyes, or inhalation of the vapour. Use suitable personal protective equipment (including gloves, face shield or safety glasses, etc.) when working with hydrochloric acid. Handle open vessels containing concentrated hydrochloric acid in a fume hood. The vapour pressure of hydrochloric acid is high. Therefore, beware of pressure build-up in capped vessels when preparing dilute hydrochloric solutions.

Sampling equipment

- Sample collection bottles - teflon or glass, 125- to 1000-mL, with teflon or teflon-lined cap.

Cleaning

New bottles are cleaned by heating to 65–75 °C in 4 N HCl or concentrated HNO₃ for at least 48 h. The bottles are cooled, rinsed three times with deionised water, and filled with deionised water containing 1 % HCl. These bottles are capped and placed in a clean oven at 60-70°C overnight. After cooling, they are rinsed three more times with deionised water, filled with reagent water containing 0.4 % (v/v) HCl, and placed in a mercury free clean bench until the outside surfaces are dry. The bottles are tightly capped (with a wrench), doublebagged in new polyethylene zip-type bags until needed, and stored in wooden or

plastic boxes until use. The bottles may be shipped to the sampling site containing dilute HCl solution (e.g., 0.04%), containing reagent water, or empty.

Used bottles known not to have contained mercury at high (>100 ng/L) levels are cleaned as above, except for only 6–12 h in hot 4 N HCl.

To verify the effectiveness of the cleaning procedures, bottle blanks must be demonstrated to be free of mercury at the ML of this method.

As an alternative to cleaning by the laboratory, bottles may be purchased from a commercial supplier and each lot certified to be clean. Bottles from the lot must be tested as bottle blanks and demonstrated to be free of mercury at the ML of this method. If mercury is present above this level in any bottle, either the lot must be rejected or the bottles must be re-cleaned.

Equipment for bottle and glassware cleaning

- Vat, 100–200 L, high-density polyethylene (HDPE), half filled with 4 N HCl in reagent water.
- Panel immersion heater, 500-W, all-teflon coated

WARNING: *Read instructions carefully! The heater will maintain steady state, without temperature feedback control, of 60–75°C in a vat of the size described. However, the equilibrium temperature will be higher (up to boiling) in a smaller vat. Also, the heater plate MUST be maintained in a vertical position, completely submerged and away from the vat walls to avoid melting the vat or burning out!*

- Laboratory sink
- Clean bench
- Oven—stainless steel, capable of maintaining $\pm 5^\circ\text{C}$ in the 60–70°C temperature range.

Cold vapor atomic fluorescence spectrometer (CVAFS):

- The CVAFS system used may either be purchased from a supplier, or built in the laboratory from commercially available components.
- Commercially available CVAFS—Tekran (Toronto, ON) Series 2600 CVAFS, Brooks-Rand (Seattle, WA) Model III CVAFS, Leeman Labs Hydra AF Goldplus CVAFS, or equivalent
- Flowmeter—with needle valve capable of reproducibly keeping the carrier gas flow rate at 30 mL/min

Hg purging system

The system consists of the following:

- Flow meter/needle valve: capable of controlling and measuring gas flow rate to the purge vessel at 350 ± 50 mL/min.
- Teflon fittings: connections between components and columns are made of teflon tubing and teflon friction-fit or threaded tubing connectors.
- Acid fume pretrap: approximately 10 cm long x 0.9 cm ID teflon tube containing 2 – 3 g of reagent soda lime, packed between wads of silanized glass wool. This trap is cleaned of Hg by placing on the output of a clean cold vapor generator (bubbler) and purging for 1 h with N_2 at 350 mL/min.
- Cold vapor generator (bubbler): 200 mL borosilicate glass (15 cm high x 5.0 cm diameter), fitted with a sparging stopper having a coarse glass frit that extends to within 0.2 cm of the bubbler bottom (Frontier Geosciences, Inc. or equivalent).

The dual-trap Hg(0) preconcentrating system

- Gold-coated sand traps; 10-cm long x 6.5-mm OD x 4-mm ID quartz tubing. The tube is filled with gold-coated mesh quartz sand. The ends are plugged with quartz wool.
- Traps are fitted with teflon friction - fit sleeves for making connection to the system. When traps are not in use, teflon end plugs are inserted in trap ends to eliminate contamination.
- At least six traps are needed for efficient operation, one as the "analytical" trap, and the others to sequentially collect samples.
- Heating of gold-coated sand traps; To desorb Hg collected on a trap, heat for 2 min to 450–500 °C (a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24-gauge Nichrome wire at a potential of 10-14 VAC. Potential is applied and finely adjusted with an autotransformer.
- Timers; the heating interval is controlled by a timer, into which the heating coil autotransformer is plugged. Two timers are required, one each for the "sample" trap and the "analytical" trap.
- Air blowers; after heating, traps are cooled by blowing air from a small squirrel-cage blower positioned immediately above the trap. Two blowers are required, one each for the "sample" trap and the "analytical" trap.
- Recorder; any multi-range millivolt chart recorder, integrator, or computer with a range compatible with the CVAFS is acceptable.
- Pipettors; all-plastic pneumatic fixed-volume and variable pipettors in the range of 10 µL to 5.0 mL.
- Analytical balance capable of weighing to the nearest 0.01 g

4. Sample Collection and Storage

Samples are collected into rigorously cleaned teflon bottles with teflon or teflon-lined caps. It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads. Polyethylene sample bottles must not be used. Samples can be collected directly from sampler to bubblers using teflon tube to prevent mixing of the sample and consequently losses of DGM.

Samples to be analyzed may be shipped to the laboratory refrigerated if they are collected in glass bottles and capped tightly. Samples must be analyzed within 24 hours of collection.

Handling of the samples in the laboratory should be undertaken in a mercury-free clean bench, after rinsing the outside of the bottles with deionised water and drying in the clean air hood.

Sample bottles should be stored in clean (new) polyethylene bags in Hg free environment at 5 °C until sample analysis.

5. Principle of DGM measurements

Dissolved gaseous mercury is defined as sum of all mercury species present in the water in dissolved gaseous form. Hg⁰ is most dominating gaseous Hg species in natural waters and often constitutes more than 95 % of DGM. Dimethyl Hg is mostly present in deep sea waters in very low concentrations, but is readily lost from aquatic environment due to evaporation and photolytical degradation.

DGM measurements can be automated or manual. The commonly used manual method for DGM involves purging water samples with Hg-free gas (Ar, N₂, Hg free air), collection of the removed DGM on gold amalgamation traps, thermal desorption and detection by CV AFS or CV AAS. The principle of automated method is the same as manual. Most automated methods use Tekran 2537A ambient air Hg analyzer with installed gold amalgamation system.

Exactly determined water volume is placed from the sampling system (i.e. Go Flow-bottles, water pump) into a glass or Teflon bubbling system using a silicon or teflon tube. Due to volatile nature of DGM species, rapid mixing of sample and storage longer than 24 hours should be avoided, and analyzed immediately after collection.

The DGM is extracted by introducing a stream of Hg free gas via a frit in the bottom of the bubbler. The gaseous mercury extracted is then collected on an Au trap connected to an outlet of the bubbler. To avoid condensation of water vapour, the Au-trap is heated to ~50 °C. Each water sample is purged between 5 and 90 min, depending on Hg free gas flow rate and volume of the bubbler. Most methods use gas flow rate between 0.06 and 1 L min⁻¹. The mercury is then thermally desorbed as gaseous elemental mercury - GEM (Hg⁰) at approximately 500 °C and detected by CVAFS or by CV AAS. The mass of Hg⁰ as function of the detector response is obtained by calibration using known amounts of Hg⁰ vapour. The accuracy of the measurement depends on the accuracy of the calibration and the water volume measurements. Normally volumetric flask or weighting is used to determine the water volume. The DGM concentration is presented as ng Hg⁰ per L. The CVAFS instruments are more sensitive in comparison to CVAAS, but require pure Ar or He gas during the desorption and detection step, whereas CVAAS instruments use mercury free air or nitrogen. Both CVAFS and CVAAS instruments detect mercury as GEM by UV radiation at 253.7 nm.

Concentration of DGM in the sample is calculated as a function of sample volume, sample and standard detector signal and known amount of injected standard (Equation 1).

$$C_{s\text{amp}} = \frac{P_{s\text{amp}} \cdot m_{\text{std}}}{P_{\text{std}} \cdot V_{s\text{amp}}} \quad (\text{Equation 1})$$

where:

$C_{s\text{amp}}$ = DGM concentration in sample (in ng L⁻¹)

$P_{s\text{amp}}$ = detector response for sample

P_{std} = detector response for standard

m_{std} = mass of injected standard (in ng)

$V_{s\text{amp}}$ = volume of the sample (in L)

6. General requirements regarding DGM measurements

Measurements of DGM using a manual or automated method can be performed on board the vessel or in the laboratory immediately after sampling. Purging, amalgamation and detection steps requires dry, sheltered, mercury free and temperature controlled environment.

Power requirements for are specific for each system. For instance Tekran 2537A requires 100/120 V, 50-60 Hz and 250 VA max, 100 VA average. Power requirements for the Lumex RA 915+ are 220-240 V, 50-60 Hz and 120 VA max.

The water should be sampled by acid cleaned Niskin (or similar) sampling bottles or by vacuum pump using acid cleaned teflon or silicon tubes and connectors. Sample should be pour into bubbler very carefully, using acid cleaned teflon tube to avoid rapid mixing and bubbling of the water. During all sampling and sample handling steps powder free gloves should be wear.

Bubbler, tubing and connectors should be make of teflon, borosilicate glass and quartz, and acid cleaned before use. The mercury detector should be installed and connected to the purging and/or amalgamation line according to the descriptions given in the user manual provided with the instrument.

7. Manual procedure

Sample Preparation

Pour a 500 mL aliquot from a sampling bottle or directly from sampler, into a teflon or glass bubbler.

Hg reduction and purging

NOTE: Purging of free halogens onto the gold trap will result in damage to the trap and low or irreproducible results.

Connect a fresh trap to the bubbler, pour the sample into the bubbler and purge the sample onto a gold trap with N₂ or Hg free air at 350 ± 50 mL/min for 10 - 20 min.

Desorption of Hg from the gold trap

Remove the sample trap from the bubbler, place the Nichrome wire coil around the trap and connect the trap into the analyzer train between the incoming Hg-free argon or air and the second gold-coated (analytical) sand trap. Pass argon through the sample and analytical traps at a flow rate of approximately 50 mL/min for approximately 2 min to drive off condensed water vapour. Apply power to the coil around the sample trap for 3 minutes to thermally desorb the Hg (as Hg(0)) from the sample trap onto the analytical trap.

After the 3 min desorption time, turn off the power to the Nichrome coil, and cool the sample trap using the cooling fan. Turn on the chart recorder or other data acquisition device to start data collection, and apply power to the Nichrome wire coil around the analytical trap. Heat the analytical trap for 3 min (1 min beyond the point at which the peak returns to baseline). Stop data collection, turn off the power to the Nichrome coil, and cool the analytical trap to room temperature using the cooling fan.

Place the next sample trap in line and proceed with analysis of the next sample.

NOTE: Do not heat a sample trap while the analytical trap is still warm; otherwise, the analyte may be lost by passing through the analytical trap.

Peaks generated using this technique should be very sharp and almost symmetrical. Mercury elutes at approximately 1 minute and has a width at half-height of about 5 seconds. Broad or asymmetrical peaks indicate a problem with the desorption train, such as improper gas flow rate, water vapour on the trap(s), or an analytical trap damaged by chemical fumes

or overheating. Damage to an analytical trap is also indicated by a sharp peak, followed by a small, broad peak.

If the analytical trap has been damaged, the trap and the teflon tubing downstream from it should be discarded because of the possibility of gold migration onto downstream surfaces. Gold-coated sand traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded.

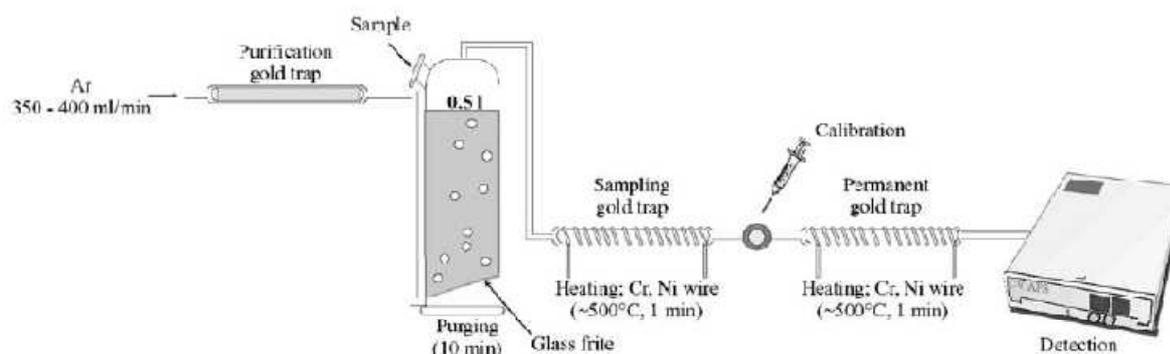


Fig. 1. Schematic presentation of manual DGM determination procedure (Horvat et al. 2003)

Calculations for the bubbler system

Calculate the mean peak height or area for Hg in the bubbler blanks measured during system calibration or with the analytical batch (ABB; n = 3 minimum). Calculate the concentration of Hg in ng/L (parts-per-trillion; ppt) in each sample according to the following equation:

$$[Hg] \text{ (ng/L)} = \frac{A_s - \bar{A}_{BB}}{CF_m \times V}$$

where:

A_s = peak height (or area) for Hg in sample

\bar{A}_{BB} = peak height (or area) for Hg in bubbler blank

CF_m = mean calibration factor (Section 10.2.2.5)

V = Volume of sample (L)

Determine the mean concentration of DGM in the method blanks associated with the analytical batch (a minimum of three). The concentration of DGM in the corresponding method blank may be subtracted from the concentration of Hg in the sample.

Reporting

Report results for Hg in ng/L, to three significant figures. Report results for Hg in samples below the ML as <0.005 ng/L.

Report results for Hg in samples, method blanks and field blanks separately.

6.1 Bubbler blanks

A bubbler blank is prepared by adding of analytical volume of deionised water to a bubbler following the procedure as for regular sample. Blanks are critical to the reliable determination of Hg at low levels. Frequent analysis of bubbler blanks is required to demonstrate freedom of system contamination and the absence of carry over from one sample to the next.

No bubbler blank must contain more than 10 pg of Hg. If a bubbler blank is found to contain more than 10 pg Hg, at the beginning of the day, another set of bubbler blanks should be run to ensure the entire system has been purged and that the value is true. If this second set of blanks is also out of control the analyst must isolate and correct the problem before continuing. If a bubbler blank is found to contain more than 10 pg Hg, during the course of the day is analysed, the system is out of control and data produced on that bubbler should be rerun or carefully evaluated and flagged as being suspect.

6.2 Interferences

Free halogens: The destruction of the gold traps exists if they are exposed to free halogens resulting in low mercury values. This can be avoided with the addition of a soda lime trap directly upstream of the sample traps during purging.

Water vapour: Water vapour may collect on the gold traps during the purging step. If water vapour is present on the traps, this will give a false peak during analysis. This can be avoided with the addition of a soda lime directly upstream of the sample traps during purging.

6.3 Calibration

Manual or automated DGM determination systems are calibrated by

- manual injection of known amounts of mercury vapour obtained from a thermostated mercury vapour source.
- or by utilising known amounts of mercury vapour from an internal permeation source.

DGM instruments may be calibrated by exposing to air containing Hg^0 , generated from a constant mercury source, or using cells with saturated Hg^0 vapour, as with the Lumex RA 915 AM monitor. This instrument may also be calibrated by injection. The performance of the instruments should regularly be checked and calibration should be performed according to recommendations in the instrument manuals. Information on the characteristics of the mercury vapour source and how it should be used to calibrate is presented in Annex A.

Prepare and analyze a minimum of 3 system blanks and tabulate the peak heights or areas. Calculate the mean peak area or height for the system blanks. For each calibration point, subtract the mean peak height or area of the system blanks from the peak height or area for each standard. Calculate the calibration factor (CF_x) for Hg in each of the five standards using the mean reagent-blank-subtracted peak height or area and the following equation:

$$CF_x = \frac{(A_x) - (\bar{A}_{SB})}{(C_x)}$$

Where:

- A_x = peak height or area for Hg in standard
- \bar{A}_{SB} = mean peak height or area for Hg in calibration blanks
- C_x = concentration of standard analyzed (ng/L)

This method may be calibrated to a range 0.005 to 100 ng, provided that the following requirements are met:

- There must be a minimum of five non-zero calibration points.
- The difference between successive calibration points must be no greater than a factor of 10 and no less than a factor of 2 and should be approximately evenly spaced on a logarithmic scale over the calibration range.
- The relative standard deviation (RSD) of the calibration factors for all calibration points must be less than 15%.
- The calibration factor for any calibration point at a concentration greater than 100 ng/L must be within $\pm 15\%$ of the average calibration factor for the points at or below 100 ng/L.
- The calibration factor for any point < 0.5 ng/L must be within 25% of the average calibration factor for all points.
- If calibration is to a higher range and this Method is used for regulatory compliance, the ML must be less than one-third the regulatory compliance limit

8. Automated (continued) procedure

Reference: N.J. O'Driscoll*, S.D. Siciliano, D.R.S. Lean, 2003: Continuous analysis of dissolved gaseous mercury in freshwater lakes, *The Science of the Total Environment*, 304, (2003) 285–294

The analysis system consists of a Hydrolab Sonde 4a in series with a sparger and Tekran air analysis unit. The 1 L glass volumetric sparger and Tekran 2537A is set to measure DGM in the water every 5 min. The Hydrolab is modified to serve as a flow through sample chamber by installing Teflon inlet and outlet connectors into the cup portion of the unit.

The analysis system can be used to measure DGM in 1 L water samples (discrete mode) or continuously from a water reservoir (continuous mode). When analyzing a discrete sample the peristaltic pump was turned off and a 1 L sample was bubbled for 30 min using mercury free air. The volatile mercury was then measured by gold amalgamation and atomic fluorescence spectrometry. This type of analysis is similar to the analysis methods used for previously published work on DGM (Lindberg et al., 2000; Amyot et al., 2000).

When in continuous mode, water is pumped from the Hydrolab to the bottom of a 1 L graduated glass sparger with water exiting at the 1 L volume mark. The water flow rate is 50 ml min^{-1} , which means that 1 L of lake water passes through the analyzer every 20 min. Therefore, every 5 min, DGM levels in 250 ml of lake water are recorded.

A Tekran 1100 zero air generator is used to supply mercury-free air to the glass sparger at a rate of 1 L min^{-1} . This was chosen instead of argon due to its mobility and its ease of use with the Tekran mass flow controller (that is set to measure ambient air volumes). The zero air pump uses ambient air and removes the mercury by passing it through a series of particulate and mercury removal filters. The mercury free air enter the water sample through a coarse glass dispersion tube that is placed at the bottom of the glass sparger (close to the lake water inlet). The DGM is carried with the analysis air from the sparger to the sample inlet of the Tekran 2537A (using 1.4 inch Teflon tubing). Once in the Tekran, the DGM is amalgamated onto one of two gold sand traps arranged in parallel. The gold traps collect DGM for 5 min continuously, after which they are thermally desorbed and the released mercury is measured by atomic fluorescence spectrometry.

The Tekran 2537A is calibrated prior to analysis using the internal mercury permeation calibration source, which is further checked for accuracy with standard air injection of elemental mercury using a gas tide syringe and a Tekran 2505 mercury vapour calibration unit. The analysis system allows warming up and stabilizing for a minimum of 2 h before readings are recorded for interpretation.

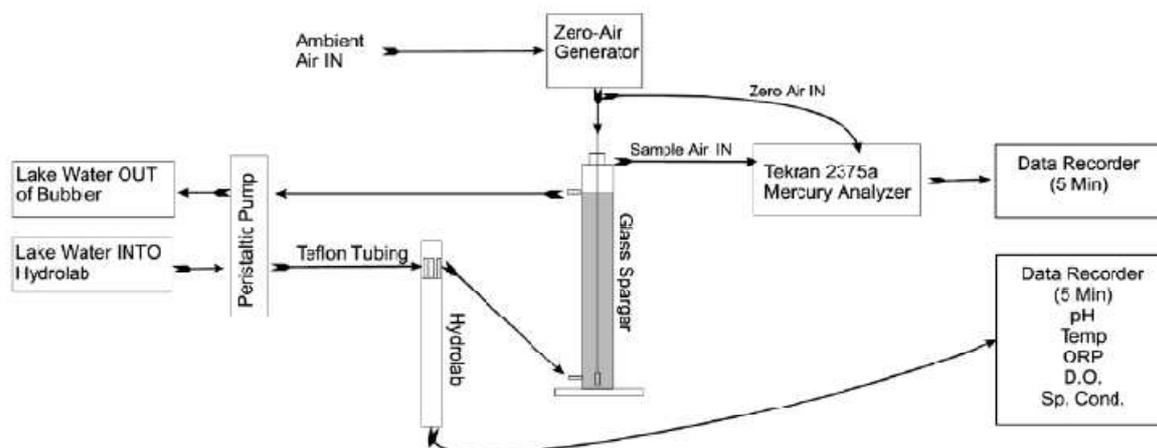


Fig 2. Schematic presentation of automated DGM determination procedure (O'Driscoll et al., 2003).

9. *In situ* automated procedure

Reference: Katarina Gårdfeldt, Milena Horvat, Jonas Sommar, Joze Kotnik, Vesna Fajon, Ingvar Wängberg Oliver Lindqvist, 2002. Comparison of procedures for measurements of dissolved gaseous mercury in seawater performed on a Mediterranean cruise. *Anal Bioanal Chem* (2002) 374 :1002–1008.

The system consists of a funnel situated at the water surface, under which a glass frit leads pressurised air into the water column. Using this set-up the mercury in the seawater is extracted by air, which was collected by the funnel and led via FEP tubing to a Tekran 2537A analyser to determine the mercury vapour concentration.

The air flow is regulated by a mass flow controller and depending on the weather conditions the flow rate varies between 3 and 6 L min⁻¹. In this flow rate range, the water is renewed underneath the funnel, i.e. no depletion was seen. This is tested by changing the gas flow, while keeping other parameters constant.

The Tekran air sampling rate is 0.5 L min⁻¹ and the excess air was led out via a three way connector. The mercury concentration in the outcoming air is in equilibrium with DGM in the water phase.

Hence, the DGM concentration can be obtained from the equilibrium equation:

$$\text{DGM} = \text{Hg}_{\text{extr}}/H'$$

where H' is the dimensionless Henry's Law coefficient and Hg_{extr} is the obtained equilibrium mercury concentration in the air used to extract the seawater. Prior to the cruises, the Henry's Law coefficient was determined for salinities and temperatures corresponding to the Mediterranean Sea:

$$H' = e^{-2708.4/T+15.151}$$

This coefficient was preferred, because determination is based on experiments, which were made with water with the same salinity as in the Mediterranean Sea. Using the two measured parameters, TGM and Hg_{extr} the degree of DGM saturation (S) in the seawater can be calculated according to:

$$S = Hg_{extr}/TGM$$

At equilibrium this ratio is equal to 1. If it is greater than 1 the water is supersaturated with respect to mercury and evasion of elemental mercury will occur.

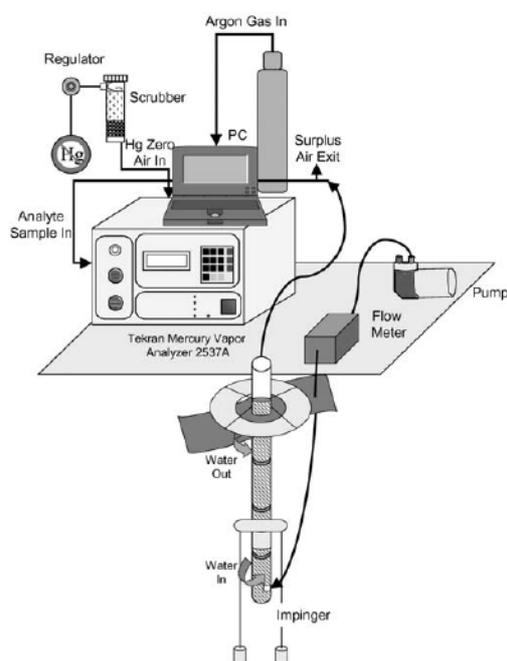


Fig. 3. Schematic presentation of *In situ* automated procedure for DGM determination (Gårdfeldt et al. 2002).

10. Measurements of DGM in bow water

Reference: Maria E. Andersson, Katarina Gårdfeldt, Ingvar Wängberg, Francesca Sprovieri, Nicola Pirrone, Oliver Lindqvist. Seasonal and daily variation of mercury evasion at coastal and off shore sites from the Mediterranean Sea. *Marine Chemistry* 104 (2007) 214–226.

The bow water system is based on the same principle as the *in situ* method. The air is equilibrated with the water phase with respect to DGM, and the mercury concentration in the air is measured with a Tekran 2537A instrument. In the system, the water was coming from the ship's bow water inlet and was constantly flowing through a specially designed impinger, which consists of a jacketed Plexiglas cylinder with a water inlet at the top and a gas inlet at the bottom. In order to establish equilibrium, the air and the water flow were adjusted accordingly, using the opposite flow principle. The DGM concentration was calculated in the same way as the *in situ* technique.

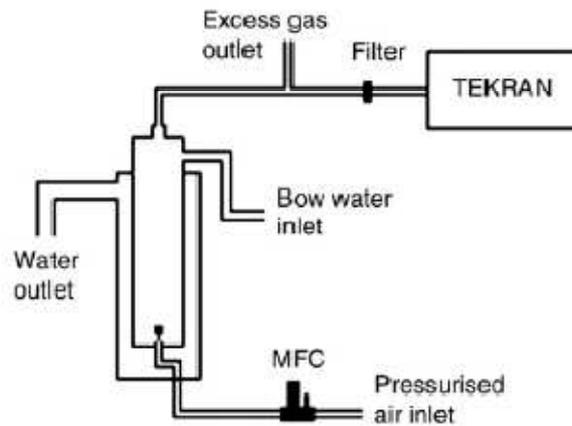


Fig. 4. Schematic presentation of automated procedure for DGM determination in bow water (Andersson et al. 2007).

11. Quality control and quality assurance

Each analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This includes the ability to reproduce standards, establish acceptable daily detection limits (DDL), produce acceptable relative percent differences between replicates, that meet acceptance criteria.

Working with detection limits in the picogram range, protecting these samples from contamination cannot be over emphasized. The greatest difficulty in low level mercury analysis is preventing the samples from becoming contaminated. Extreme caution must be used throughout collection and analysis procedures to avoid contamination.

It is very important that the laboratory air be low in both particulate and gaseous Hg. The mercury in the air can be reduced with the use of gold-coated cloth at the intakes of the laminar flow hoods.

12. Calculation of Hg exchange between water and atmosphere (Gas exchange model)

Reference: Maria E. Andersson, Katarina Gårdfeldt, Ingvar Wängberg, Francesca Sprovieri, Nicola Pirrone, Oliver Lindqvist. Seasonal and daily variation of mercury evasion at coastal and off shore sites from the Mediterranean Sea. *Marine Chemistry* 104 (2007) 214–226.

The gas exchange model developed by Nightingale et al. (2000) is used in order to calculate the mercury evasion from the sea surface. The model requires measurements of DGM, TGM, water temperature (T_w), and wind speed (u_{10}), the mercury evasion can then be calculated according to:

$$\text{Hg}_{\text{evasion}} = k \times (\text{DGM} - \text{TGM}/H')$$

where H' is the dimensionless Henry's law coefficient at the desired temperature. In the model by Nightingale et al. (2000) the gas-transfer velocity, k , is calculated according to the equation:

$$k = (0.22 \times u_{10}^2 + 0.333 \times u_{10}) \times (Sc_{Hg}/660)$$

u_{10} is the wind speed normalised to 10 m above sea surface according to:

$$u_{10} = (10.4u_z)/(\ln(z) + 8.1)$$

where z is the height where the wind speed was measured. The Schmidt number (Sc) is the ratio between the kinematic viscosity of the water and the aqueous diffusivity of mercury. The Sc_{Hg} was calculated using the Wilke–Chang method described in Reid et al. (1987) and corrected for seawater according to Wanninkhof (1992) and references therein. The temperature and salinity dependence of viscosity and diffusivity was calculated for each case.

13. References

C. M. Tseng, C. Lamborg, W. F. Fitzgerald, And D. R. Engstrom, 2004: Cycling of dissolved elemental mercury in Arctic Alaskan lakes, *Geochimica et Cosmochimica Acta*, Vol. 68, No. 6, pp. 1173–1184,

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Annex A

Characteristics of the mercury vapour source

A small amount of liquid elemental mercury is kept in a closed thermostatted container, according to Figure A. The mercury concentration in the source is determined by the mercury vapour pressure (P_{Hg}) over the liquid mercury phase. Since P_{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 ± 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.

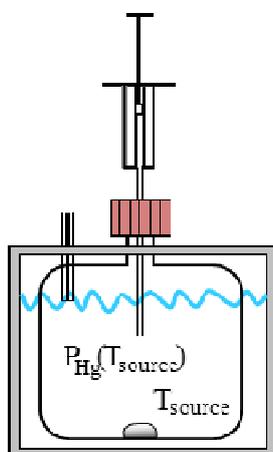


Figure A.1. A saturated mercury vapour source consisting of pure liquid mercury housed in a thermostatted water bath.

Figure A.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_{Hg} , can be calculated by help of the Ideal Gas Law according to,

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

where A_{Hg} , R and T_{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_{source} is the temperature in K [1].

It should be noted that the mercury concentration in the syringe will only be equal C_{Hg} when the temperature of the syringe is equal to T_{source} . Hence, if the temperature of the syringe happens to be lower than T_{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,

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

To use equation A.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.

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

T_{syringe} is the temperature of the syringe in Kelvin;
 T_{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 A.3 shall be used to calculate the mass concentration of mercury vapour samples collected from a mercury vapour source using a syringe.

Equation A.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 A.3 takes account of two different temperatures – the temperature of the mercury source and that of the syringe.
- Equation A.3 is only valid for situations where T_{syringe} is equal to or higher than the temperature of the mercury source (T_{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_{source} as mentioned above. This is because the vapour pressure of mercury is exponentially dependent on temperature. Therefore, T_{source} appears in the exponential term of Equation A.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 ± 1 °C.

References

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Annex B

Cleaning of gold traps

Cleaning procedure of gold traps is intended to use with Tekran 2537, but is also applicable to other systems

A gold traps, i.e. glass tubes containing a large gold surface, is used in the Tekran 2537A mercury analyser to trap gaseous mercury from ambient air. The two cartridges continuously undergo adsorption/desorption cycles during the measurements. After some use deactivation may occur and cleaning of the cartridges is necessary. For quality control a monthly standard cleaning procedure is recommended.

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 (HNO₃) 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 detergent¹. 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:

- 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 with 5 min sampling cycles at a sampling rate of 1.5 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 ± 5 when compared to each other and should also not differ more than 5 % in comparison to the reference cartridges.

¹Labosol-U-Ultraschall-Reiniger. This detergent is provided by the German company neoLab (www.neolab.de).

Annex C

Cleaning of equipment used for DGM measurements

All parts that are in contact with the sample shall be cleaned extensively before use. Plastic gloves shall be used during all steps of the cleaning procedure.

A suitable cleaning procedure is given below.

- 1) Wash with an alkaline detergent. Rinse thoroughly with ultrapure water
- 2) Leach with 2 % HCl (3.7) for at least 48 h. This can be done in a polyethylene tank.
- 3) Rinse thoroughly with ultrapure water (3.5) and dry in a clean hood.

Store the cleaned equipment in double plastic bags.

Annex D

Methods for DGM determination

Reference: N.J. O'Driscoll*, S.D. Siciliano, D.R.S. Lean, 2003: Continuous analysis of dissolved gaseous mercury in freshwater lakes, *The Science of the Total Environment*, 304, (2003) 285–294:

The analysis system (Fig.1) consisted of a Hydrolab Sonde 4a in series with a sparger and Tekran air analysis unit. The 1-L glass volumetric sparger and Tekran 2537A were set to measure DGM in the water every 5 min. The Hydrolab was modified to serve as a flow through sample chamber by installing Teflon inlet and outlet connectors into the cup portion of the unit.

The analysis system can be used to measure DGM in 1 L water samples (discrete mode) or continuously from a water reservoir (continuous mode). When analyzing a discrete sample the peristaltic pump was turned off and a 1 L sample was bubbled for 30 min using mercury free air. The volatile mercury was then measured by gold amalgamation and atomic fluorescence spectrometry. This type of analysis is similar to the analysis methods used for previously published work on DGM (Lindberg et al., 2000; Amyot et al., 2000).

When in continuous mode, water was pumped from the Hydrolab to the bottom of a 1-L graduated glass sparger with water exiting at the 1-L volume mark. The water flow rate was 50 ml min^{-1} , which means that 1 L of lake water was passed through the analyzer every 20 min. Therefore, every 5 min, DGM levels in 250 ml of lake water were recorded. A Tekran 1100 zero air generator was used to supply mercury-free air to the glass sparger at a rate of 1.0 L min^{-1} . This was chosen instead of argon due to its mobility and its ease of use with the Tekran mass flow controller (that is set to measure ambient air volumes). The zero air pump uses ambient air and removes the mercury by passing it through a series of particulate and mercury removal filters. The mercury free air entered the water sample through a coarse glass dispersion tube that was placed at the bottom of the glass sparger (close to the lake water inlet). The DGM is carried with the analysis air from the sparger to the sample inlet of the Tekran 2537A (using 1.4 inch Teflon tubing). Once in the Tekran, the DGM is amalgamated onto one of two gold sand traps arranged in parallel. The gold traps collect DGM for 5 min continuously, after which they are thermally desorbed and the released mercury is measured by atomic fluorescence spectrometry.

The Tekran 2537A was calibrated prior to this analysis using the internal mercury permeation calibration source which was further checked for accuracy through the use of standard air injection of elemental mercury using a Hamilton digital syringe and a Tekran 2505 mercury vapour calibration unit. The analysis system was allowed to warm up and stabilize for a minimum of 2 h before readings were recorded for interpretation. Stripping efficiency was tested by filling the sample with water from Big Dam West Lake and bubbling until a stable baseline of DGM concentration was achieved. This stable base line value was subtracted from the subsequent sample analysis when in near-continuous mode. After bubbling for 60 min, the sample was poured back into the sample container and then back into the sparger to test for sources of contamination from the sampling routine.

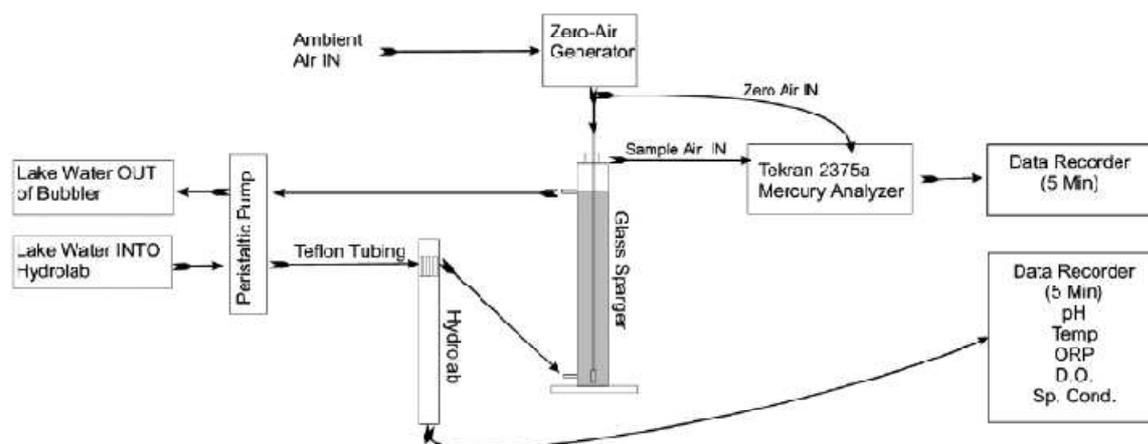


Fig. 1. Schematic diagram of continuous DGM analysis instrumentation.

Reference: Lanzillotta, E. and Ferrara, R. 2001: Daily trend of dissolved gaseous mercury concentration in the Mediterranean Sea, *Chemosphere*, 45.

Surface water samples were taken a few metres from the coast where the water was 3–4 m deep. 1 l of sea-water was collected in a 1.5 l pre-cleaned cylindrical glass bottle (internal diameter 6 cm) using a PVC rod and analysed for DGM immediately after collection. In agreement with Lindberg et al. (2000b), samples' storage was avoided considering the volatile nature of these forms of mercury. The transparent bottle is supplied with a glass bubbler, so as to allow the determination of DGM concentration without decanting the water into a second measuring bottle. A scheme of the measuring device is reported in Fig. 1. The volatile mercury compounds were trapped on a concentrating gold trap bubbling mercury-free air for 10 min with a flow of 0.3 l/min in dark conditions. A modified version of the Gardis-IA Mercury Analyser with a detection limit of 0.5 pg of mercury was used (Ferrara and Mazzolai, 1998). The instrument is an atomic absorption spectrometer using a two-stage gold trap analysis technique. The concentrating gold trap was placed outside the instrument and kept at a temperature of 50°C in order to avoid moisture condensation in the trap itself. During the measuring time the purging air passes through the concentrating gold trap and returns to the atmosphere without entering the optical cell of the spectrophotometer. At the end of this step the concentrating gold trap is

automatically connected to the spectrophotometer by means of a pinch solenoid valve. Mercury is thermally desorbed from the concentrating trap and re-collected on the analytical one. A second thermal desorption process releases mercury from the analytical trap and allows its determination by the atomic absorption spectrometer. Freshly acid-cleaned Teflon tubing was used to connect the glass bottle to the measuring device. Consecutive cycles of mercury determinations were performed on the same water sample until a constant value was reached (3 cycles) to allow the extraction of more than 95% of the DGM and to determine the blank value. Polyethylene gloves were worn at all times.

The spectrometer was calibrated by injection of mercury saturated air via a gas-tight microsyringe. A portable cooled (4°C) mercury vapour generator (Ferrara et al., 2000a) was used.

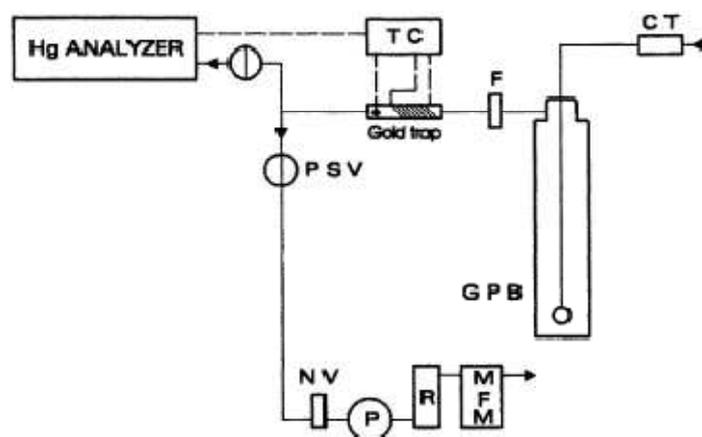


Fig. 1. Scheme of the measuring device used to determine the DGM concentration in seawater. TC: temperature control; PSV: pinch solenoid valve; F: quartz wool filter; CT: carbon trap; NV: needle valve; P: pump; R: rotameter; MFM: mass flow meter; GPB: glass purging bottle.

S.E. Lindberg; A.F. Vette, C. Miles, F. Schaedlich, 2000: Mercury speciation in natural waters: Measurement of dissolved gaseous mercury with a field analyzer, *Biogeochemistry* 48: 237–259.

We developed the Tekran Automated Purging System (TAPS) to alleviate the need for extended storage, and to allow for the relatively “rapid” (<1 h) analysis of sequential samples needed for diel studies, and studies of the effects of solar radiation and precipitation events on DGM production in surface waters. By providing “near-real-time” concentration data (<1 h for sample plus blank), the TAPS method also affords the important advantages of in-field blank determinations, and immediate feedback on the vacuum integrity of the purging apparatus. With the vacuum-based TAPS method, a leak in the purging vessel is quickly detectable in the instrument readout by the presence of elevated Hg introduced into the sample from ambient air (while this works well in low-DGM systems such as those studied here, it may be less useful where the DGM and ambient air signals are comparable; however, leaks will always be immediately apparent in the purge blanks). The ability to quantify field blanks can also preclude the loss of data from contaminated purging and sampling vessels which might otherwise remain undetected until a later time during analysis. The Tekran Mercury Vapor Analyzer was introduced in 1993 and has gained wide use as a field and laboratory monitoring device (e.g., Schroeder et al. 1995). The device uses now-routine gold-trap and cold-vapor atomic fluorescence spectroscopic (CVAFS) analytical methods to analyze Hg vapor in ambient air, providing continuous sequential analyses of samples collected over periods of 5 min. The advantages of applying the Tekran to more sophisticated studies has become clear, and several groups have published such approaches for direct measurement of Hg_g fluxes over surfaces (e.g., Poissant & Casimir 1998; Lindberg & Price 1999). To our knowledge, this paper is the first published application of the Tekran to aquatic speciation analyses such as DGM.

The purging apparatus initially used with both approaches consisted of a 2.2 L bottle with a cover with two, 1/4" ID transfer port fittings (illustrated in Figure 1a) and was completely constructed of PFA Teflon. A gas dispersion tube with a coarse glass frit was attached to

Teflon tubing (the MI apparatus used Teflon tubing with pin-holes in place of the glass frit). The tubing was sealed in the inlet transfer port such that the frit was near the bottom of the bottle and a short portion extended above the fitting to attach to the Hg-free purge gas (N₂ or air). An iodated, activated carbon trap (e.g., Lindberg 1981) was attached to the inlet port to supply Hg-free air in TAPS mode, while a gold coated sand or bead trap was used to supply Hg-free N₂ in the manual purge mode. Teflon tubing extended through the outlet port fitting for attachment either to the Tekran or to a gold sampling trap. The bottle was sealed by hand-tightening followed by clamping with a high-pressure, stainless steel clamp. We have since determined using the Tekran to “sniff” the sample that the bottle cover can be sealed positively by hand tightening (this holds for vacuum purging with TAPS only). For purging with the *Tekran Automated Purge System (TAPS)*, the inlet line to the Tekran analyzer was connected directly to the outlet line from the purge bottle (Figure 1(a)) at the beginning of a discrete air sampling sequence. The Tekran mercury vapor analyzer was operated in the normal 5-min sample collection mode (see below). For the Florida samples eight, 5 min purge samples at a flow rate of 1.5 L/min were collected for a total 40 min run time (20 min sample, 20 min blank for a total of 60 L gas flow, yielding a purge gas/water volume ratio 30). Longer purge times were necessary for the samples collected in Michigan for which the DGM levels were much higher than those collected in Florida. Twelve, 5 min. purge samples were collected for a total 60 min. run time or 90 L total gas (40-min. sample, 20- min. blank, gas/water volume ratio 45). The iodated activated carbon trap connected to the purge bottle inlet supplied clean ambient air for purging (the blank value is readily tested prior to sampling by purging the dry sample bottle into the Tekran; the values are often below detection, \sim 0.5 pg, and generally <2 pg, e.g., see Figure 3 below). The TAPS method was also used in Michigan to evaluate an all glass sampling and analysis design. The apparatus shown in Figure 1b included a 2 L glass bottle and impinger with ground glass joints. Samples were purged with Hg-free N₂ supplied through a 0.5 psi regulator (part of the Tekran zero gas supply). A glass impinger with a 4-way Teflon stopcock and long glass tube was attached to the bottle with the tube 1 cm from the bottom. The stopcock allowed N₂ to flow to the Tekran inlet in either sample purge mode or tubing flush mode. In sample purge mode (Figure 1(b)) Hg-free N₂ flowed into the sample through the top of the stopcock and down the long glass tube. The DGM was removed from solution by N₂, and flushed through the bottom of the stopcock into the Tekran. In tubing flush mode Hg-free N₂ flowed through the stopcock directly into the Tekran bypassing the sample (indicated in Figure 1(b) by a dashed line). This flushing of the inlet tubing eliminated the signal from ambient air before a sample was purged. This mode also provided a quantitative leak check before sampling, yielding generally lower system blanks than other approaches. For purging with the *manual pressure method*, nitrogen gas was supplied through silicone tubing into the Teflon or glass bottle through a gold-coated sand/bead trap. A gold-coated sand/bead trap was connected to the outlet with Teflon tubing to collect the purged DGM. In Florida, samples were purged onto gold-coated traps at 0.75 L N₂/min for 40 min followed by another 40 min for a blank sample (60 L total gas). Samples from Lake Michigan were purged onto gold-coated bead traps at 0.5 L N₂/min for 90 min followed by another 90 min for blanks (90 L total gas). In the manual method, the reusable gold-coated quartz sand or bead traps (a quartz tube with Teflon tubing on both ends) were pre-blanked by heating to 450 °C prior to use and sealed with Teflon plugs. The traps efficiently collect known forms of gaseous mercury by amalgamation and adsorption on the gold coating. After return to our primary laboratory (usually within 5 d) the gold traps were analyzed for Hg₀ by dual-amalgamation cold vapor atomic fluorescence spectrometry (CVAFS) using methods modified for the ORNL lab (Lindberg et al. 1995). The CVAFS system was calibrated using a gas-tight microsyringe to inject Hg₀-saturated air from a constant temperature bath onto a gold trap. This procedure yielded very high precision ($<0.5\%$ relative standard error based on 6 replicate injections over 6h, using peak-area integration). The absolute detection limit for Hg₀ (three times the instrumental noise) is 0.2 pg, and the working limit in our lab based on gold trap blanks is 1–2 pg (compared to typical DGM sample signals of 10–100 pg). All handling and analysis of gold traps in our laboratory

was done in class 100 laminar flow clean air benches (particulate Hg <0.001 ng/m³, Hg 5–8 ng/m³).

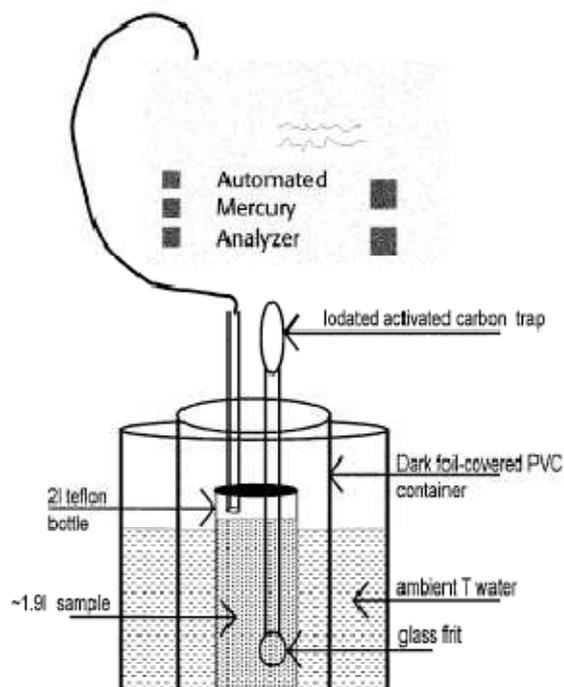


Figure 1. (a) Schematic of the Tekran Automated Purge System (TAPS) developed for in-field determination of mercury speciation in water. Operation is described in the text. The dimensions of the teflon purging vessel are 10×24 cm.

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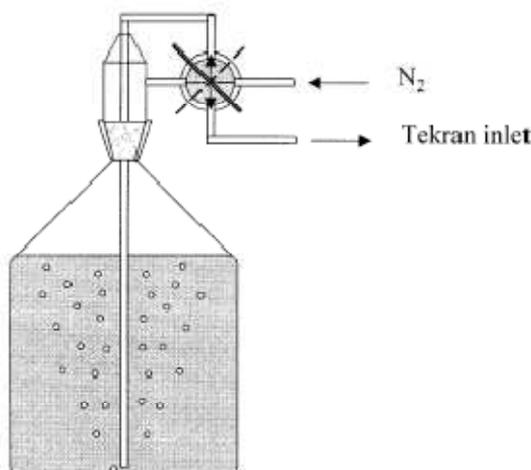


Figure 1. (b) Glass purging apparatus used with the TAPS shown in sample purge mode. The dashed line indicates the position of the stopcock in tubing flush mode.

C. M. Tseng, C. Lamborg, W. F. Fitzgerald, And D. R. Engstrom, 2004: Cycling of dissolved elemental mercury in Arctic Alaskan lakes, *Geochimica et Cosmochimica Acta*, Vol. 68, No. 6, pp. 1173–1184,

DGM is defined operationally as the Hg⁰ collected on a gold (Au) trap after purging an unamended sample with N₂ gas (Vandal et al., 1991; Mason et al., 1993a,b). Briefly, a 2-L sample is purged with Hg-free N₂ in a 2.5-L borosilicate bubbler and the Hg is amalgamated onto a gold-coated trap. Analyses are conducted by pyrolysis in a two-stage Au amal-

gamation gas train with detection by atomic fluorescence spectroscopy (AFS; Fitzgerald and Gill, 1979; Bloom and Fitzgerald, 1988).

In this study, we used a novel semiautomatic in-line purge-and-trap system, coupling the two-stage Au-amalgamation and flow-injection techniques with AFS (Tseng et al., 2003). This analytical framework provides simple, rapid, precise, and accurate analyses. Complete trapping of DGM for a 2-L water sample can be achieved with a 30-min purge at a 1 L min^{-1} N_2 flow rate. Instrument calibration was performed by injection of known masses of a Hg^0 gas standard into both the Ar gas stream (before sample or analytical traps) and the bubbler. Hg^0 averaged 15 ± 2 pg in procedural blanks (mean ± 1 SD, $n = 10$) during the 3-week measurement period. Method detection limit (MDL) for DGM analysis, defined as 3σ of procedural blanks, was ~ 30 fM. The relative standard deviation of replicate DGM samples, a measure of overall precision, was less than 10% ($n = 3$). Recovery from analytical spikes averaged $100 \pm 5\%$ ($n = 30$).

Edenise Garcia, Alexandre J. Poulain, Marc Amyot a, Parisa A. Ariya, 2004: Diel variations in photoinduced oxidation of Hg^0 in freshwater. *Chemosphere* 2004.

Approximately 500 ml of water was slowly decanted into 1-l glass bubblers and purged for 15 min with Hg-free air with a Tekran 1100 zero air generator. The volatile Hg compounds were trapped on a gold-coated sand column. The trap was dried for 3 min in an argon air stream and Hg was subsequently desorbed by pyrolysis at a flow rate of 60 ml min^{-1} , using the double amalgamation technique. Hg was quantified by gas-phase atomic fluorescence spectrometry with Tekran Hg analyzer model 2500. In this study, simultaneous analyses of replicates were possible due to the use of two analytical lines, each one consisting of two bubblers coupled to one Hg-free air generator and one Hg detector. Quality control was achieved through the intercalibration of the two lines, as well as by processing 3 or 4 system blank checks before the beginning of the analysis. For the intercalibration, water from Lake Croche was collected 4 h after sunset in order to minimize the influence of photoreductants or photooxidants.

Ingvar Wangberg, Stefan Schmolke, Peter Schager, John Munthe, Ralf Ebinghaus, Ake Iverfeldt, 2001: Estimates of air-sea exchange of mercury in the Baltic Sea. *Atmospheric Environment* 35 (2001) 5477–5484

All DGM samples were immediately analysed in the laboratory on board the ship. A 2.0 l volume of the sample was poured into an acid cleaned Teflon impinger. The impinger consisted of a tube of 1.80 m length and 4.1 cm inner diameter as shown in Fig. 2. The sample was extracted by introducing a stream of pre-purified nitrogen via a glass frit in the bottom of the impinger. The gaseous mercury extracted was collected on an Au trap connected to an outlet at the top of the impinger. To avoid condensation of water vapour, the Au-trap was heated to $45 \text{ }^\circ\text{C}$. Each water sample was extracted during 90 min, with a nitrogen flow-rate of 0.31 l min^{-1} . The Au-traps were analysed using the standard dual amalgamation and CVAFS detection technique (Brosset, 1987; Bloom and Fitzgerald, 1988). Between samples, the Teflon impinger was kept clean by purging with Hg-free nitrogen. The procedural blanks were 3.02 ng m^{-3} , from which a detection limit of 1.1 ng m^{-3} was calculated. Prior to the cruises, known DGM amounts were analysed to test the efficiency and reproducibility of the extraction method. From these experiments, it was concluded that DGM concentrations in the range of $15\text{--}20 \text{ ng m}^{-3}$ could be determined with a precision of 76%.

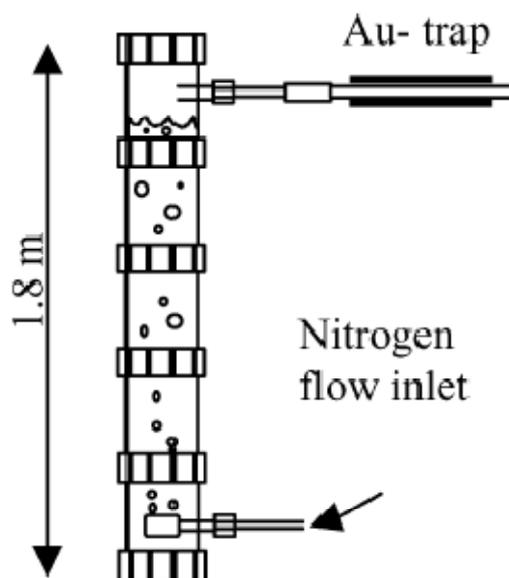


Fig. 2. 2.0 L volume DGM extractor. The extractor was fed by pre-purified nitrogen (by means of a freshly desorbed Au-trap). Hg vapour evolved was trapped on an Au-trap maintained at 45°C at the outlet in the top.

R. Ferrara, C. Ceccarini, E. Lanzillotta, K. Gardfeldt, J. Sommar, M. Horvat, M. Logar, V. Fajon, J. Kotnik, 2003. Profiles of dissolved gaseous mercury concentration in the Mediterranean seawater. *Atmospheric Environment* 37 Supplement No. 1 (2003) S85–S92

Immediately after sampling, 1 l of seawater was transferred from the Go-Flo directly into a 1.5-l purging bottle made of pyrex glass, supplied with a suitable lightshield so as to perform DGM analysis in dark conditions. All handling was performed using clean techniques. The purging bottle and Teflon tubing were precleaned in the laboratory by acid washing and tested on board by several subsequent DGM extractions of the same sample. After extended purging, typical and reproducible data were obtained. The purging bottle was stored with purged on-site water between consecutive sampling stations. A schematic view of the measuring device is reported in Fig. 1. The DGM was stripped from seawater by bubbling the sample with ambient air sucked by a membrane pump at a flow rate of 200 ml min⁻¹ for 10 min. An iodated activated carbon trap was attached to the impinger to supply Hg-free air. The end of the impinger consists of a pyrex frit 1 cm from the bottom. The glass frit with pore size between 16 and 40 mm ensures a high efficiency of extraction even with a low value of the purging flow rate. The volatile mercury compounds are trapped on a concentrating gold trap, placed externally to a Gardis- 1A Atomic Absorption Spectrometer (detection limit 0.003 pM). A washing bottle containing 10 ml of distilled water is inserted between the purging bottle and the concentrating gold trap to retain the salts present in the seawater; this ensures constant efficiency of the gold trap for a long time, even for a large number of determinations. The trap is kept at a temperature of 50 °C in order to avoid moisture condensation in the trap itself. During the stripping time the purging air passes through the preconcentrating gold trap and returns to the atmosphere without entering the optical cell of the spectrometer. Then the external trap is automatically connected to the internal analytical gold trap. Mercury thermally desorbed from the concentrating trap is collected again on the analytical one. A new thermal desorption step allows mercury determination by the atomic absorption spectrometer. Consecutive cycles of DGM determination were performed on the same sample until a

constant value was reached (3 cycles) to allow the extraction of more than 95% of the DGM and to determine the blank value. The blank of all the measuring device is significantly correlated with sample signals and results to be about 30% of the signal itself. The instrument was calibrated using a 50 ml Hamilton gas-tight micro-syringe to inject elemental mercury saturated air from a mercury vapour generator kept at a constant temperature (4 °C) onto the concentrating gold trap. This procedure yields very high reproducibility (2%, number of replicates=7).

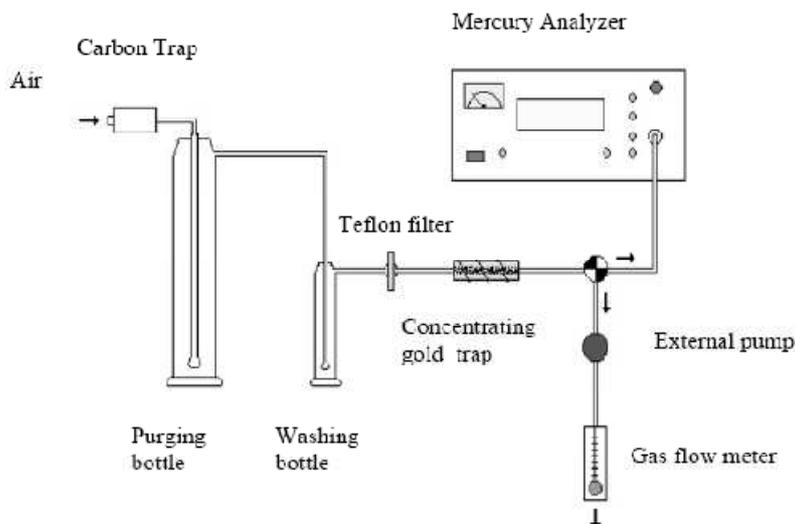


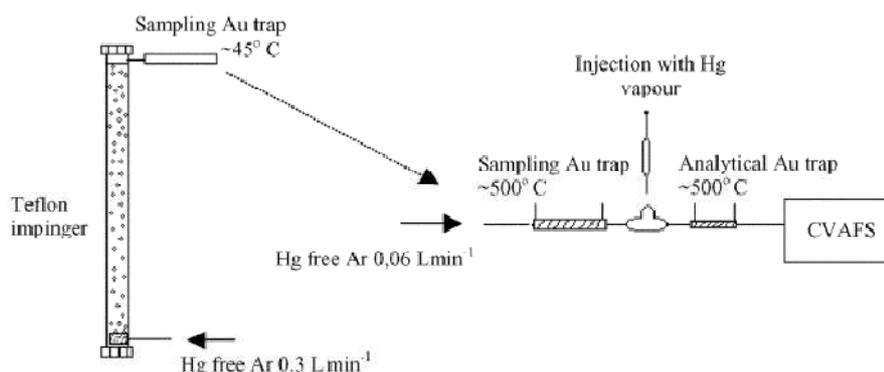
Fig. 1. Schematic view of the measuring device used to determine the DGM concentration in the seawater deployed by the CNR-IB.

Katarina Gårdfeldt, Milena Horvat, Jonas Sommar, Joze Kotnik, Vesna Fajon, Ingvar Wängberg Oliver Lindqvist, 2002. Comparison of procedures for measurements of dissolved gaseous mercury in seawater performed on a Mediterranean cruise. *Anal Bioanal Chem* (2002) 374 :1002–1008.

Manual method

A schematic presentation of the GU system for determination of DGM is given in Fig. 3. A 2-L sample was carefully transferred from one of the Go-Flo samplers directly to a PFA Teflon impinger. The impinger consisted of Savillex parts making up a tube of 1.80-m length and 4.1-cm inner diameter. The impinger is constructed to act as a sampler itself and the open GU analytical system allows it to be transferred and directly filled by immersing into the sea or filled from Go-Flo bottles on deck. The impinger was rinsed three times with sample water before it was filled for the measurement. The sample was purged for 90 min at a flow rate of 300 mL min⁻¹ by a stream of pre-purified inert gas via a glass frit in the bottom of the impinger. DGM purged from the sample was collected on a gold trap positioned at the outlet. This trap was heated to approximately 45 °C to avoid condensation of water vapour. Subsequently it was transferred to an analytical line where it was analysed by standard dual amalgamation and cold vapour atomic fluorescence spectrophotometric (CVAFS) detection techniques. To avoid contamination of the impinger between analyses, a pre-analysed sample was kept in the impinger with a low flow of argon gas. The method has been used previously and its statistical reproducibility is reported to be ±6% ($2\sigma n^{-1}$) when determining DGM concentrations in the range 15–20 µg L⁻¹. The blank of the impinger was checked on board ship by purging MQ water with mercury-free Ar gas with subsequent analysis of the sampling gold trap (three times). A detection limit of approximately 2.7 µg L⁻¹ (calculated as 3 times the standard deviation of total blanks) was obtained during this work.

Fig.3 Schematic set-up of the GU system for the determination of dissolved gaseous mercury



Automated *in situ* method

The principle of the automated *in situ* procedure is shown in Fig. 4. Ambient air was equilibrated with the seawater in a PFA Teflon impinger under the seawater surface. The flow of ambient air was introduced through a glass frit positioned at the bottom of the impinger. The impinger (assembled of interchangeable components from Saville) was designed to allow the seawater to be continuously replaced by the purging air flow (2 L min^{-1}).

An important feature of the *in situ* approach involves the attainment of the phase equilibrium independent of whether the carrier gas is ambient air or mercury-free inert gas. However, in our study ambient air was used. The impinger was maintained in a vertical position by weights fastened in a ring construction on the impinger as shown in Fig. 4. The equilibrated exhaust air was continuously fed to an automated mercury analyser, Tekran Model 2357A. Excess air from the *in situ* purging system (0.5 L min^{-1}) was released via a three-way connector attached to the sampling line before the Tekran inlet (Fig. 4).

The DGM *in situ* measurements were calibrated with the internal source of the Tekran instrument.

The internal source of the Tekran instrument was intermittently verified with the calibration procedure described later. The detection limit of the Tekran instrument was approximately 0.3 ng m^{-3} under the operation conditions (flow rate 1.5 L min^{-1} and 5 min time resolution). The DGM concentration of the water was calculated assuming Henry's law equilibrium between the mercury concentration in the equilibrated air (Hg_{air}) and the water (DGM), according to Eq. (1):

$$\text{DGM} = \frac{\text{Hg}_{\text{air}}}{H}$$

The Henry's law coefficient (H) refers solely to Hg^0 . Other volatile Hg species present in the water were below the detection limit in surface samples and solely represented a few percent of the DGM under the thermocline. The partitioning coefficient H is a function of temperature and was calculated according to the following expression:

$$H = \frac{M_w (10^{-1078/T+6.250})}{R \rho_w T}$$

where M_w is the molar weight of water $18.01 \times 10^{-3} \text{ (kg mol}^{-1}\text{)}$, R is the gas constant $8.2058 \times 10^{-2} \text{ atm L K}^{-1} \text{ mol}^{-1}$, ρ_w is the density of seawater (kg L^{-1}) and T (K) is the temperature of the seawater.

In the work by Sanemasa solubilities of mercury vapour in pure water and seawater were investigated at 5–30 °C. By using the data from Sanemasa the solubility of mercury vapour was estimated to be 12% less in seawater at 25 °C than in pure water. As the Henry's law

coefficient is inversely proportional to the solubility of mercury vapour, it was increased by a factor 1/0.88 (i.e. 13.6%) to be representative for seawater media.

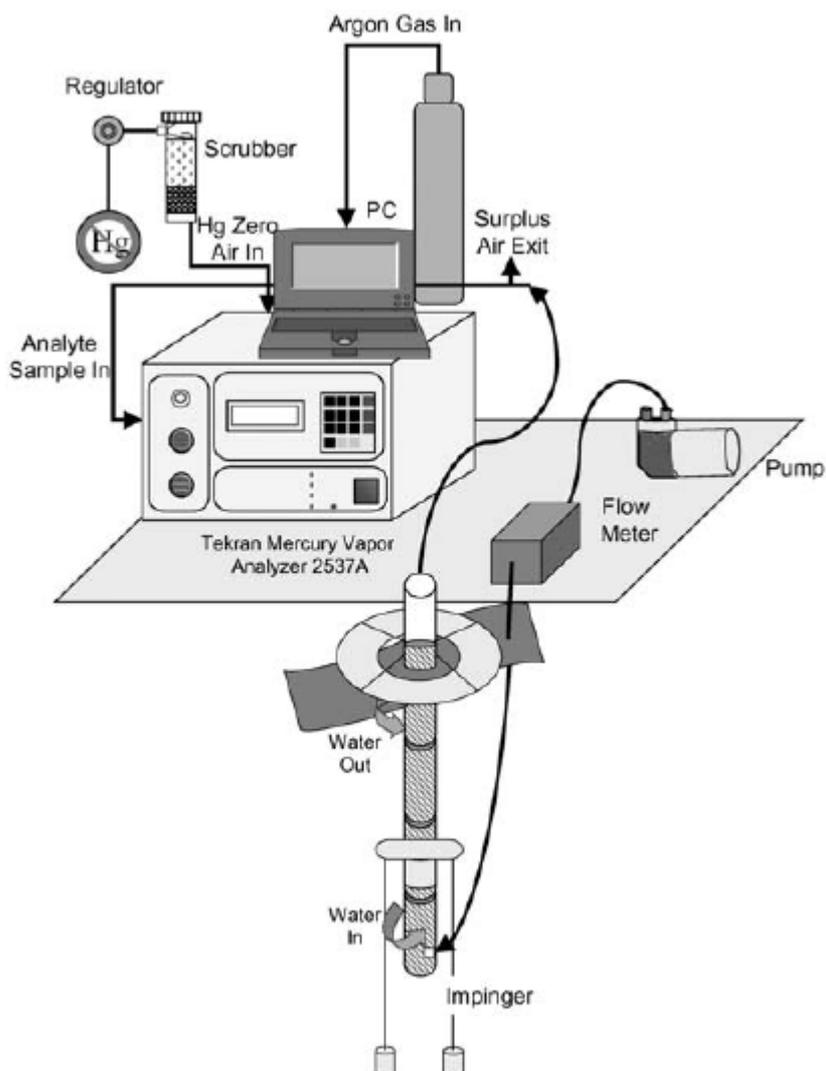


Fig.4 The automated GU in situ analytical prototype for DGM analysis

Milena Horvat, Jože Kotnik, Martina Logar, Vesna Fajon, Tomislav Zvonaric, Nicola Pirrone, 2003: Speciation of mercury in surface and deep-sea waters in the Mediterranean Sea. Atmospheric Environment 37 Supplement No. 1 (2003) S93–S108

A schematic presentation of the system for determination of DGM is shown in Fig. 2. In the purging step an aliquot of 0.5 l of seawater sample was transferred to a glass bubbler immediately after sampling. The carrier gas flow was 300 ml/min and entered the glass bubbler through a glass frit sealed at the bottom of the bubbler. This guaranteed the most efficient purging of the water samples, and allowed for quantitative removal of volatile Hg species in a short period of time (e.g. 8–10 min). Volatile mercury species were purged for 10 min and collected onto a sampling gold-coated silica trap kept at room temperature with Hg-free argon (or nitrogen). In the measurement step, the sampling gold trap was immediately transferred to a double amalgamation CV AFS analyser system. The sampling

gold trap was heated for 1 min (ramp heating to a maximum of 500 °C) and mercury collected on this trap was released and purged with a flow of argon onto a permanent analytical gold trap kept at room temperature. After heating the analytical gold column the trapped Hg was thermally desorbed (ramp heating to a maximum of 500 °C) into an argon stream that carried the released Hg vapour into the cell of a cold vapour atomic fluorescence spectrometer (Tekran 2500) for detection. The system was calibrated with a gas phase Hg (Hg^0) kept at 4 °C. An aliquot of 10–15 ml was transferred with gas-tight syringe into the measurement train through a septum. The amount of Hg injected was calculated from a gas law (i.e. taken from the mercury/temperature-dependent curve) and corrections for the difference in temperature of the gas phase and the syringe were also applied (Gardfeldt et al., 2002). The detection limit of the procedure was 5 pg/l calculated on the basis of the three standard deviations of the blank. The repeatability of the method was about 4%.

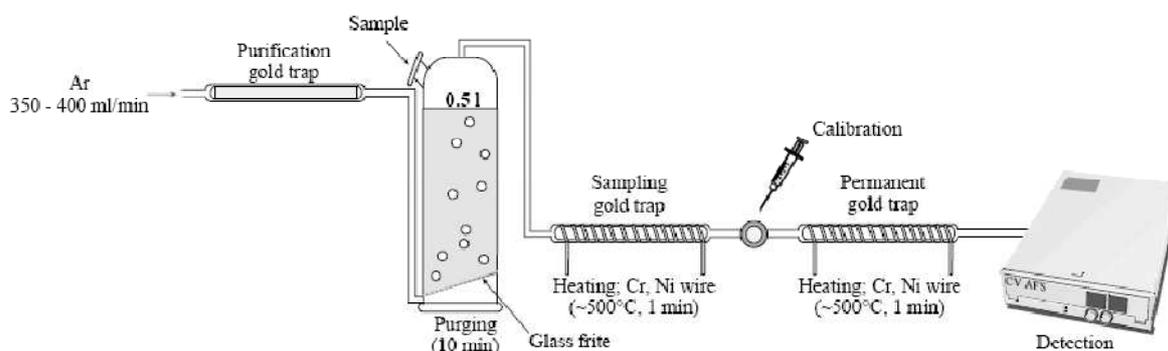


Fig. 2. Schematic presentation of the system for the determination of DMHg.

Table D1. Comparison of methods used for DGM determination.

Reference		Location		Purging step					Amalgamation	Detection		Calibration
Author	Year	Location	Type	Single/Continuous measurement	Gas	Gas flow rate (L/min)	Amount of water (L)	Duration (min)		Resolution	Detector	
O'Driscoll et al.	2003	two lakes in Kejimikujik Park, Nova Scotia	freshwater lake	continuous	zero air	1	1	5	single inside the detector	5 min	Tekran 3375a	saturated Hg vapours
Lanzillotta and Ferrara	2001	Mediterranean Sea	sea water	single	zero air	0.3	1.5	10	single outside the detector		Gardis IA	saturated Hg vapours
Lindberg et al.	2000	North American Lakes	freshwater	continuous	air or N ₂	1.5	2.2	5	single inside the detector	5 min	Tekran Mercury Vapor Analyzer	saturated Hg vapours
Tseng et al.	2004	Arctic Alaska	freshwater	single	N ₂	1	2	30	double			saturated Hg vapours
Garcia et al.	2004	Canadian Shield lake, Lake Croche	freshwater	single	zero air	0.06	0.5	15	single		Tekran, Model 2500	saturated Hg vapours
Wangeberg et al.	2001	Baltic Sea	sea water	single	N ₂	0.3	2	90	double		Tekran model 2537	saturated Hg vapours
Ferrara et al.	2003	Mediterranean Sea	sea water	single	zero air	0.2	1	10	single		Gardis IA	saturated Hg vapours
Gardfeldt et al. MANUAL METHOD	2002	Mediterranean Sea	sea water	single	Ar	0.3	2	90	double		Tekran model 2537	saturated Hg vapours
Gardfeldt et al. AUTOMATED METHOD	2002	Mediterranean Sea	sea water	continuous	zero air/Ar	2		on time	none	5 min	Tekran 3375a	saturated Hg vapours
Horvat et al.	2003	Mediterranean Sea	sea water	s	N ₂	0.3	0.5	10	double		Tekran 3375a	saturated Hg vapours