DGT® Research
For measurements in waters, soils & sediments

LSPB - AP Loaded DGT device for mercury and monomethylmercury in sediment

Type:	LSPB-AP
Measurable analytes:	As(III), Hg^{2+} and MeHg
Holder:	Standard DGT sediment probe
Filter :	Polyethersulphone membrane (thickness: 0.14 mm)
Diffusive gel:	0.8 mm agarose diffusive gel
Binding layer:	3-mercaptopropyl functionalized silica gel

General considerations

Suitable for sediment and saturated soil. **pH:** the recommended pH range is 3 to 8.5. (Gao et al., 2014)

Ionic strength: recommended range 0.001 M- 0.7 M. Can be used at lower ionic strengths, but as there is a possibility of gel charge affecting performance, control tests at the same ionic strength as the field solution, are then advised.

Binding limitations: resin gel can effectively accumulated MeHg in a pH range of 3 – 9. At pH outside of this range, competition between H^+ and MeHg and formation of stable MeHg hydroxide complexes prevents these species from being effectively absorbed by the resin. (Clarisse and Hintelmann, 2006)

Deployment time: After a maximum reached within a few hours, the flux to a DGT device deployed in a soil or sediment will progressively decline as the analyte adjacent to the device is consumed. Normal deployment time is 1 day. Longer deployment times up to three days may, however, be appropriate in some circumstances. For example, if trace metals are strongly complexed by humic substances, the slower diffusion of these complexes delays the time to maximum flux. Deployment of 3 days will ensure that this slower approach to a pseudo steady state negligibly affects the measurement. When probes are inserted into sediments there will inevitably be a small temporary disturbance of the spatial distribution of analyte. This spatial structure is rapidly restored through the strong redox buffering mechanisms. However, if there is a desire to measure metals at high spatial resolution in sediments or soils, leaving the probes in place for longer than 1 day will allow better establishment of the structure and minimise the effect of the initial disturbance on the time-averaged measured flux.

Storage

Store the units in a refrigerator (4°C). The DGT units provided are kept in the heat-sealed clean plastic bags containing a few drops of 0.03 M NaCl solution. Do not open them until immediately prior to deployment. Check the units about once a week to make sure they are under moist conditions. Add a few more drops of trace metal clean 0.03 M NaCl (or NaNO3 for marine sediment) solution if it is necessary.

Handling

The main consideration when using DGT devices is to prevent contamination of the sample. Clean handling procedures should be adopted during deployment and recovery of the DGT devices and all subsequent handling during the sample treatment step. In general, the highest quality reagents should be used and all equipment and laboratory apparatus cleaned appropriately.

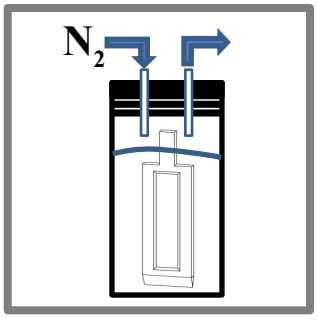
DGT Research Ltd
Skelmorlie, Bay Horse Rd, Quernmore, Lancaster, Lancashire, LA2 0QJ
Phone : +44 (1524) 593899, 2nd Phone : 01524 751451
Email : info@dgtresearch.com

General deployment considerations

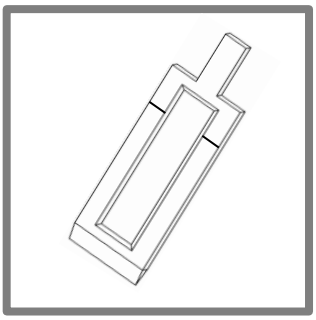
Deoxygenation: Deoxygenation of the DGT probes is not so straightforward because it will only be effective if the transfer of the DGT probes from their deoxygenation solution to the sediment can be done within no more than a few 10s of seconds. Exposure of the probe to the air for longer times will quickly replenish the oxygen, as demonstrated in Davison et al (1994). However, whether it will be necessary will depend on individual circumstances. Because the DGT assembly is thin it does not contain a lot of oxygen and, within a short period of time, (say 30 minutes) the oxygen diffusing out into the sediment and electron donors diffusing into the gels will consume the oxygen within the DGT gels. Clearly this will compromise the DGT measurement of redox sensitive and secondary affected components (e. g. trace metals) within this 30 minute time period of initial accumulation. However, DGT is usually deployed for times in excess of a day. Therefore, this initial period where the presence of oxygen can have an effect on the DGT accumulation will only represent at most about 2% of the total accumulation time. Consequently the effect on the DGT measurement is likely to be negligible. There is an urgent need for work to be done to verify experimentally the effect of preliminary deoxygenation on DGT measurements and whether it is necessary.

Biofouling: Biofouling is not a problem for deployments in sediments, but could affect the part of the probe in the overlying water. The extent of any biofouling is very dependent on local conditions, particularly light, temperature and productivity. Biofouling is not usually a problem for deployments less than a week.

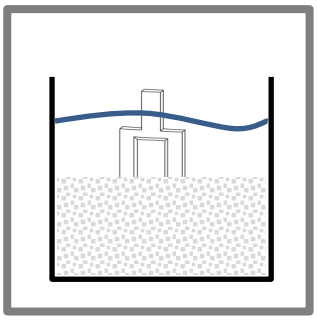
Deploying DGT devices



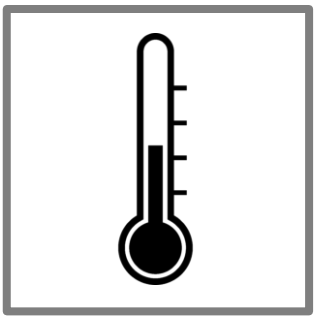
1. If probes are to be deoxygenated include this step, otherwise proceed directly to step 2. Immerse the DGT probe for 24 h in a clean container filled with 0.03 M NaCl solution through which N2 is steadily bubbled. Seal this container to maintain it oxygen-free for transportation to the deployment site (ideally no more than a few hours).



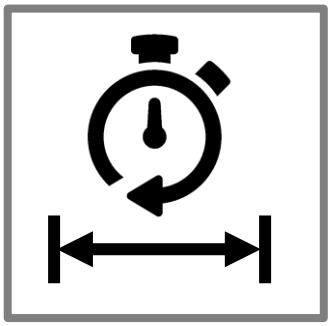
2. Remove the probe from either the oxygen-free container or its supplied plastic bag. Quickly mark the plastic body of the probe (permanent marker) at the intended depth for the sediment-water interface.



3. As soon as possible (within seconds) of removing the probe from its oxygen-free environment, smoothly push it into the sediment until the mark is in line with the sediment-water interface. Keep the probe as vertical as possible during the insertion.



4. Accurately record the temperature during the deployment period. If the variation is within ± 2°C a mean (or start and end temperature) will suffice. If the variation is greater, ideally the mean temperature should be obtained from an integrated record of temperature (data logger).

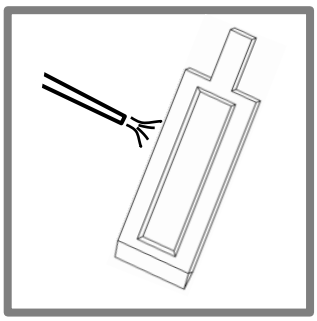


5. Provide an accurate record to the nearest minute of the deployment time

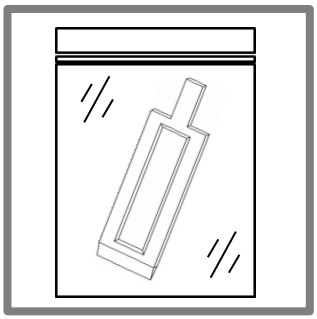
DGT Research Ltd
Skelmorlie, Bay Horse Rd, Quernmore, Lancaster, Lancashire, LA2 0QJ
Phone : +44 (1524) 593899, 2nd Phone : 01524 751451
Email : info@dgtresearch.com

Procedure for analyzing DGT samples

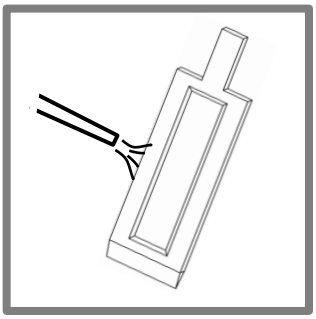
DGT Recovery and Sample Treatment for Total Hg



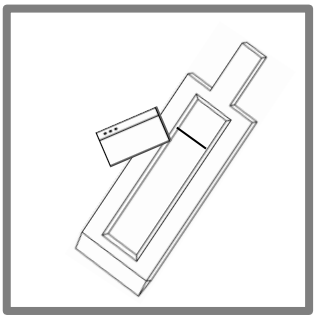
1. After retrieving the DGT probe from the sediment, thoroughly rinse the probe with MQ water jet from a wash bottle



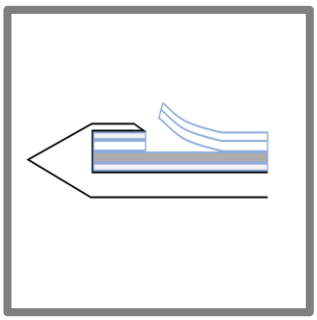
2. Place the probe in a clean plastic bag for storage and transportation.



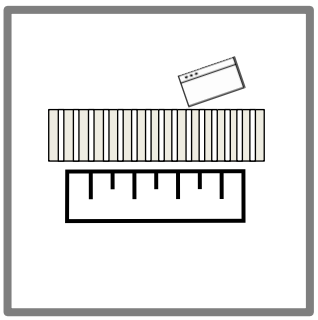
3. Remove from the plastic bag and thoroughly rinse the probe again with MQ water. For analytes at trace concentrations, all sample treatment should be carried out in a laminar flow hood to avoid contamination.



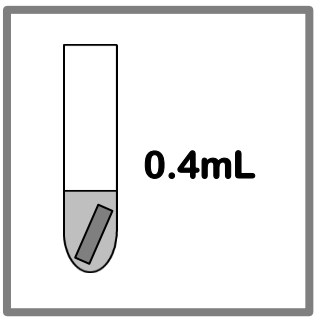
4. Make a cut at the sediment/water interface mark using a Teflon coated blade. Then, cut the gels and the filter membranes along the window edges without disassembling the probe.



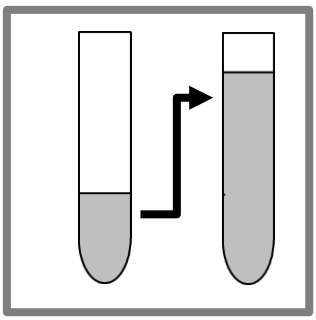
5. Remove the top filter membrane and the diffusive gel first.



6. Carefully lift the resin gels together with the bottom filter membranes out of the window and lay them alongside an acid cleaned plastic ruler on an acid cleaned Perspex board. Cut the resin gel at the resolution required (no less than 1 mm).



7. Place each gel strip into a clean micro tube. For Total Hg, place the 18mm x 5mm x 0.5mm binding layer in a glass vial/ or Teflon vial/ or High-Density Polyethylene vial containing 0.4 ml of Hg-free aqua regia and shake overnight. Or analyse directly with AMA-254 (Advance Mercury Analyser-254)



8. Remove the binding layer from the tube, squeezing out any residual liquid. Then dilute the eluate by adding 3.6 mL of MilliQ water (depending on the concentration levels of Hg) prior to analysis using Cold-Vapor AFS or ICPMS.

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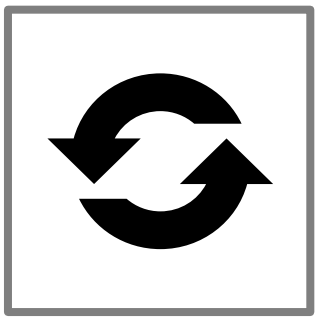
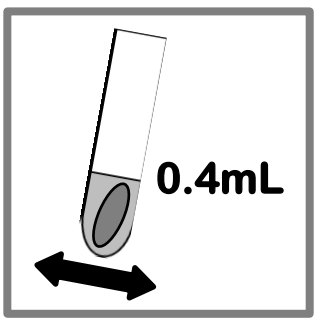
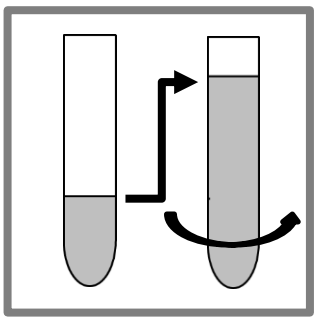
DGT Recovery and Sample Treatment for MeHg



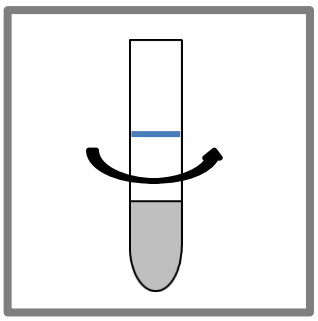
1a. Repeat the above steps 1 – 6 again.



2. Extracte the resin gel with 0.4 mL 6 M HNO3 in a glass vial for 6 hours at 70 °C.



9. After cooling down to room temperature, add 3.6 mL of MilliQ water.



10. Centrifuge the eluate at 3000 rpm for 10 min, then keep the supernatant for further analysis using for example GC-AFS (in this case, ethylation of the supernatant is necessary).

Analysis for total Hg

Typically, analysis of the total Hg for this type of DGT can be performed by Advanced Mercury Analyzer-254 (AMA-254) with direct combustion of resin gels (no elution needed) or by inductively coupled plasma mass spectrometer (ICP-MS) after acid extraction as outlined above (aqua regia is recommended, however other strong acid extractions can work too). To control the quality of the analysis, NIST 2704 reference should be used for total Hg.

Analysis for MeHg

Analysis of Methylmercury (MeHg) is highly depended on availability of instruments. If the lab is equipped with HPLC-ICP-MS, different Hg species can be extracted (acid extraction) from the resin gels and Hg speciation can be carried out with HPLC-ICP-MS. Or if the lab is equipped with a specific MeHg analyzer, then the DGT user is recommended to use their own extraction protocols for MeHg (for example, extraction of MeHg from sediment sample, extraction of MeHg from biological sample), which will normally work for the extraction of MeHg from our DGT resin gels. Then the analysis can be carried out with their own MeHg analyzer.

Method and field blanks

To ensure accurate results it is recommended to determine DGT laboratory[1] and field blank[2] concentrations.

[1]The laboratory blank is an unexposed DGT device carried through all steps of the measurement process (from extraction through analysis). A laboratory blank is typically analyzed with each sample batch.

[2]The field blank is designed to identify levels of contamination from DGT devices exposed in the field as the field. In summary, field blanks consist of additional DGT devices, which are transported to the monitoring site, exposed briefly at the site when the samples are exposed (but no deployment is carried out), and transported back to the laboratory for analysis, similar to a field sample. It is advisable to have at least one field blank for each test series.

Elution efficiency, f_e

For the procedure described here and a 10x dilution of the eluent prior to analysis, there is some agreement that appropriate elution efficiencies are 1.0 for total Hg and MeHg for the elution method with analysis by ICP-MS.

Calculation

The mass, M, of analyte accumulated on the binding layer, of volume, V^{bl}, is calculated from the measured concentration of analyte, c_e, in the eluent, of initial volume V_e, remembering to take into account any subsequent dilution. f_e is the elution efficiency.

$$M = \frac{c_e(V^{bl} + V_e)}{f_e}$$

Where c_e is in nmol mL^{-1} or ng mL^{-1}, and V^{bl} and V_e are in mL, M is in nmol or ng. For 5mm resolution (or 5 mm gel strip), the binding gel volume is 0.045 mL (1.8cm x 0.5cm x 0.05cm).

This mass can be used to calculate the mean flux from the sediment through the window of the DGT probe, of area A_p, for the deployment time, t (in sec). The window width of the probe is 1.8 cm. For 5 mm resolution, A_p is 0.09 cm^2 (which is 0.05 cm x 1.8cm)

$$F = M/ A_p t$$

The DGT equation can be used to calculate the mean concentration at the surface of the probe during the deployment time.

$$c_{DGT} = \frac{M\Delta_g}{DA_p t}$$

Δ_g (usually 0.094 cm) is the total thickness of the materials in the diffusion layer (diffusive gel and filter membrane).
D (cm^2 s^{-1}) is the diffusion coefficient of analyte in the diffusion layer at the deployment temperature (see Diffusion Coefficients provided under What DGT Does). Use recommended units to facilitate easy calculation as shown above.

Note:

A key consideration is the meaning of C_{DGT}. Because DGT continually removes analyte, its concentration at the surface of the DGT device may be lowered during the course of the deployment. In some sediments the analyte may be continually resupplied to solution from the solid phase. When this effective buffering is substantial, the measured C_{DGT} is close to the concentration in the porewaters, C_{pw}, at the same location. Comparison of C_{DGT} with C_{pw} can provide information on the dynamics of analyte exchange between porewater and solid phase. A detailed account of the dynamic processes existing when DGT is deployed in sediments can be found in Chapter 7 of the DGT book (see reference below). Note that spatially resolved concentration maxima in porewater concentrations are faithfully represented by DGT (Sochaczewski et al, 2009).

References

Diffusive Gradients in Thin-Films for Environmental Measurements, Ed. W. Davison, Cambridge University Press, 2016, Cambridge.
Chapters in this book, which are particularly relevant are:

1. Introduction to DGT (covers the basic principles)
   William Davison and Hao Zhang
2. Principles of measurements in simple solutions (explains procedures for calculations)
   William Davison and Hao Zhang
3. Diffusion layer properties (provides and critiques diffusion coefficients)
   William Davison and Hao Zhang
4. Binding layer properties (provides properties including elution efficiencies for a range of binding agents and analytes)
   William W. Bennett, Maja Arsic, Jared G. Panther, David T. Welsh, and Peter R. Teasdale
6. Applications in natural waters (gives some case studies)
   Heléne Osterlund, Anders Widerlund and Johan Ingri
10. Practicalities of working with DGT (practical issues such as deployment, quality control and sensitivity)
    Dianne F. Jolley, Sean Mason, Yue Gao and Hao Zhang

Prime publications for these analytes:

Y. Gao, S. D. Craemer and W. Baeyens, A novel method for the determiniation of dissovled methylmercury concentrations using diffusive gradients in thin films technique, *Talanta*, **120**: (2014), 470-474.

O. Clarisse and H. Hintelmann, Measurement of dissolved methylmercury in natural waters using diffusive gradients in thin film (DGT), *J. Environ. Monit.*, **8**: (2006), 1242-1247.

A. Bratkic, K. Klun, Y. Gao, Mercury speciation in various aquatic systems using passive sampling technique of diffusive gradients in thin-film, *Science of the Total Environment,* **663**: (2019), 297-306.

M. Reichstadter, P. Divis, E. Abdulhur-Alfakhoury, Y. Gao, Simultaneous determination of mercury, cadmium and lead in fish sauce using Diffusive Gradients in Thin-Films technique, , *Talanta*, **217**: (2020), 121059.

Relevant reviews:

W. Davison and H. Zhang, Progress in understanding the use of diffusive gradients in thin-films – back to basics, *Environ. Chem*. **9**: (2012), 1-13.

H. Zhang and W. Davison, Use of DGT for studies of chemical speciation and bioavailability, *Environ. Chem*. **12**: (2015), 85-101.