DGT® Research
For measurements in waters, soils & sediments

Metals and P using DGT with a Chelex/ferrihydrite BL

These instructions are written for LSNY-NP (cations and oxyanions in solution). The procedure for analysis is the same for LSLY-NP (soils) and LSPY-NP (sediments), but different deployment strategies are used as detailed in soil deployments and sediment deployments. Using ferrihydrite with Chelex in the binding layer simplifies elution and subsequent analysis.

Type:	LSPY-NP
Measurable analytes:	Al, Ca, Cd, Co, Cr(III), Cu, Mg, Mn, Ni, Pb, Zn, U, REEs, As(III), As(V), P(V), Sb(V), Se(V), V(V), W(VI)
Holder:	Standard DGT holder
Filter :	Polyethersulphone membrane (thickness: 0.14 mm)
Diffusive gel:	0.8 mm APA diffusive gel
Binding layer:	Chelex (iminodiacetate) and Ferrihydrite mixture

Water types and Limiting Conditions

Appropriate environment: Suitable for sediment and soil. **pH:** the recommended pH range is 5 to 8.5, but strong binding metals such as Pb and Cu are quantitative down to pH 2. **Ionic strength:** 1 – 700 mM. At extremely low ionic strengths (< 1 mmol L^{-1}) gel charge may affect performance. Control tests at the ionic strength of the deployment water are then advised.

Binding limitations: Weakly binding cations, such as Ca and Mg, can usually only be measured using short deployment times of a day. Measurement of Sb or W in seawater is not recommended. Measurement of Se is not straight forward: Se(IV) binds quantitatively, but Se(VI) binds inefficiently. Consequently total Se and Se(IV) cannot be estimated accurately unless the proportion of Se(VI) present in solution is low.

Deployment time: Optimum deployment time depends on analyte concentrations as longer times increases sensitivity. Deployment times of 1-4 days are generally optimal (see FAQs). If the concentrations of the metals are low (less than a few micrograms per litre), longer deployment times may be appropriate for the cationic trace metals and REEs.

Measured species: All species that exist in solution for the specified oxidation states, within the pH and ionic strength range given, are measured. For P the dominant forms are the various protonation states of phosphate, which is considered to be the analyte measured. Total As in solution, that is As(III) + As(V), is measured by this method. A separate DGT device with a different binding layer is available for the selective measurement of As(III) (LSPB-AP).

Storage

Store the DGT devices in a refrigerator (4°C). The DGT devices are provided in sealed clean plastic bags containing a few drops of 0.01M $NaNO_3$ (or 0.01M NaCl) solution. Do not open them prior to deployment. Check the devices about once a week to make sure they are under moist conditions. Add a few more drops of trace metal clean 0.01M $NaNO_3$ (or 0.01M NaCl) solution if it is necessary. Do not freeze the units, as performance could be affected.

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. Do not touch or contact the while filter membrane at the face of the device. In general, the highest quality reagents should be used and all equipment and laboratory apparatus cleaned appropriately.

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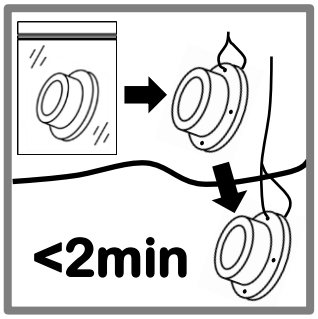
General deployment considerations

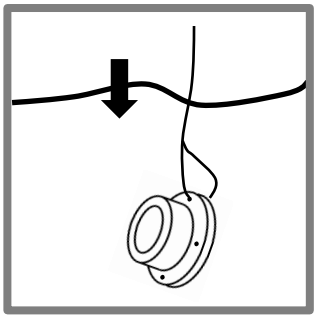
Biofouling: The extent of any biofouling is very dependent on local conditions, particularly light, temperature and productivity. Biofouling is not usually a problem for deployments less than one or two weeks. In pristine or deep waters, very long-term deployments (months extending to a year) have been unaffected by biofilms.

Deploying DGT devices

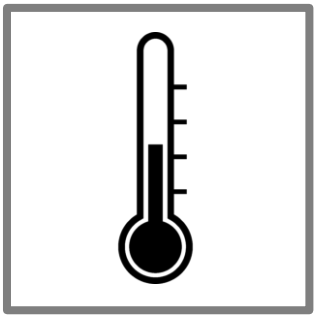


1. Having placed the DGT unit in its deployment holder or simply attached it to any deployment device by tying it with a fishing line threaded through the hole on the rim of the unit, deploy the unit immediately (minutes).

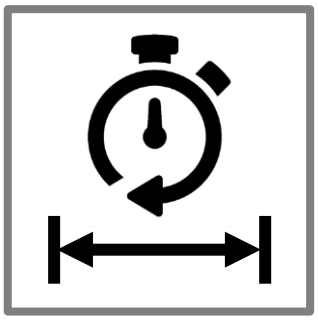
2 Ensure the DGT device is deployed in flowing (or moving) water, but avoid excessive turbulence, particularly bubbles. Large open waters including lakes usually have sufficient natural flow through wave action.



3. Ensure that the white face of the DGT unit is fully immersed during the deployment period.



4. Accurately record the temperature of the water 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

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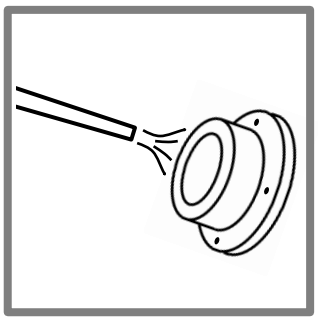
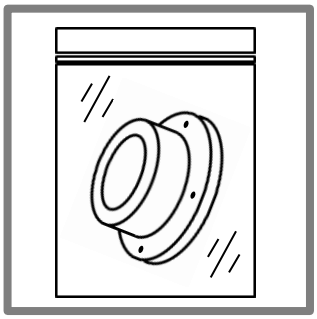
Procedure for analyzing DGT samples

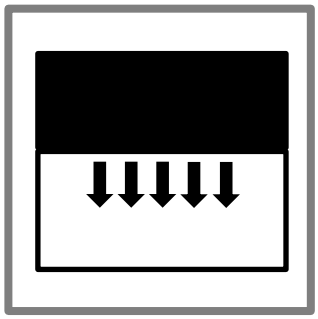
DGT Recovery and Sample Treatment



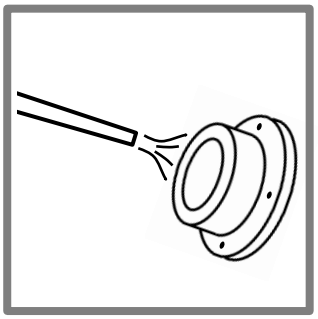
1. After retrieving the DGT device from the deployment environment thoroughly rinse the DGT device with ultrapure water from a wash bottle.



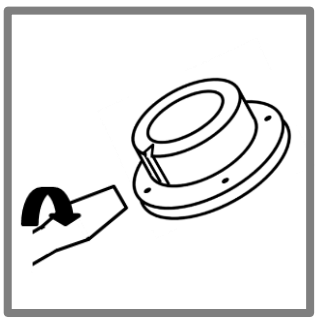
2. Place in a clean plastic bag for storage and transportation back to the lab for sample treatment.



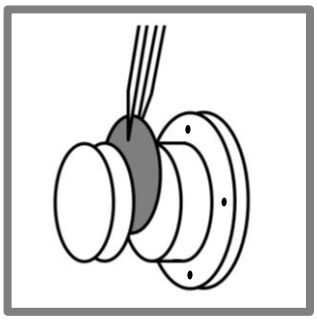
3. For analytes at trace concentrations, all sample treatment should be carried out in a laminar flow hood to avoid contaminating the sample.



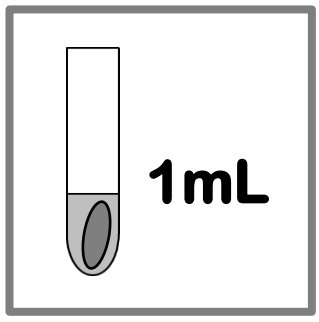
4. Remove from the plastic bag and thoroughly rinse the device with ultrapure water.



5. To retrieve the resin gel after deployment, insert a suitable screwdriver into the groove in the cap and twist it. The cap will be broken at the weak point.

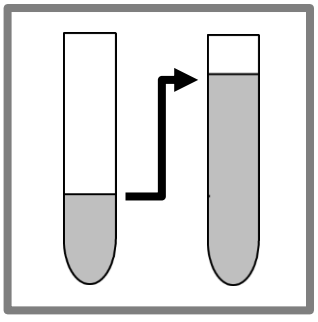


6. Remove the broken cap and then peel off the filter and diffusive gel layer to reveal the bottom binding-gel layer.

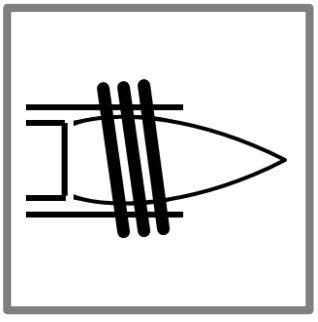


7. Place the binding layer (or sliced portion of it for sediment probes) in 5 ml of high purity water for 1 hour. Then place it in a clean sample tube and add 1 ml of 1.0 M high purity HCl.

8. Make sure the resin gel is fully immersed in the HCl solution. Leave to stand for at least 24 hours before analysis.



9. Dilute, as necessary for analysis using ultrapure water (18.2MOhms).



10. Analyse as soon as possible. To avoid clogging the instrument's sampling system, it is best to remove the resin gel from the solution.

Note for step 5: If this fails, using clean tweezers break the white filter membrane and pull out the gels. The binding gel is the lower one.

Note for step 9: To avoid any broken gel pieces or resin getting into the diluted solution, pipette an appropriate amount from the top of the sample tube and transfer it into a new clean tube and then add MQ water

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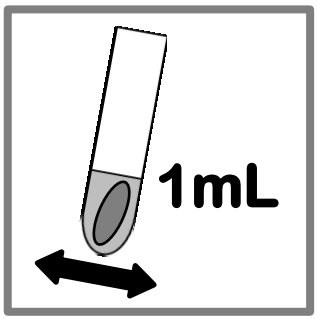
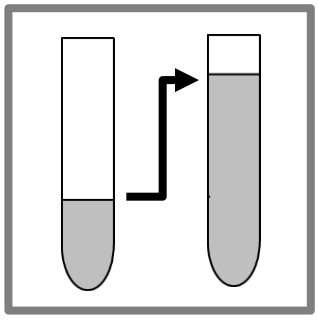
For urgent analysis

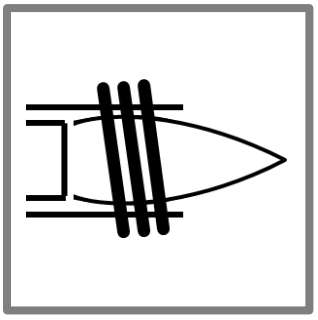


7a. For urgent analysis, agitate the tube containing the binding gel and 1 ml of 1.0 M HCl on a shaker.

8a. Shake for at least 2 hours before analysis.



9. Dilute, as necessary for analysis, using ultrapure water (18.2 MOhms).



10. Analyse as soon as possible. To avoid clogging of the instrument's sampling introduction system it is recommended to remove the resin gel from the solution.

Analysis

Typically, analysis of the eluate for this type of DGT is performed using ICP-MS. Following the work of Mason et al (2005), 1 M HCl has been chosen as the eluent because the molecular ions $^{14}N^{16}O^{1}H$ and $^{15}N^{16}O$ can interfere with the measurement of ^{31}P. For the measurement of phosphate alone, without the other oxyanions, we recommend elution with 0.25 M H_2SO_4 and colorimetric analysis using the molybdenum blue method, as detailed in a separate guide for phosphate. If a fraction of the HCl eluent used for general oxyanions is first neutralised, phosphate can be determined colorimetrically. If phosphate is not part of the suite of analytes 3 M HNO_3 could be used as an eluent instead of 1 M HCl, as reported in Price et al (2013).

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, the elution efficiency for all analytes is 0.92.

Calculation

In most situations where DGT is deployed in water that is flowing or subject to convection currents the standard DGT equation is appropriate.

$$c_{\mathrm{DGT}} = \frac{M\Delta_{\mathrm{g}}}{D^{\mathrm{mdl}}A_{\mathrm{p}}t}$$

C_{DGT} (nmol mL^{-1} or ng mL^{-1}) is the time-averaged concentration of analyte in the deployment medium measured by DGT.
M (nmol or ng) is the mass of analyte accumulated in the binding layer. It is obtained from the analysis (see below)
Δ_g (also known as δ_g) (0.094 cm) is the total thickness of the materials in the diffusion layer (diffusive gel and filter membrane).
D^{mdl} (cm^2 s^{-1}) is the diffusion coefficient of analyte in the material diffusion layer for the deployment temperature (see diffusion

coefficients).
A_p (3.14 cm^2 for the standard DGT solution holder, 2.54 cm^2 for soil devices) is the physical area of the exposed filter membrane.
t (s) is the deployment time.
Recommended units to facilitate easy calculation are shown. This calculation procedure should work well for most situations. For more accurate methods of calculation that incorporate estimates of the flow regime see FAQs on the web site.

The mass, M, of analyte on the binding layer, of volume, V^{bl} (usually 0.20 mL), is calculated from the measured concentration of analyte, c_e, in the acid eluent, of volume V_e (usually 1 mL), remembering to take into account any subsequent dilution.

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

For the usual set up for solution devices, if f_e = 0.92, $M = 1.3c_e$ (where c_e is in nmol mL^{-1} or ng mL^{-1}, M is in nmol or ng).

Using the same DGT equation for soils and sediment gives the mean concentration of analyte at the probe surface during the deployment time (see FAQs). For sediments, A_p is the area of the gel slice used. The mass calculation is the same for soil probes. For sediment probes the appropriate volume of the binding gel slice must be used.

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
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:
J. Luo, H. Zhang, J. Santner and W. Davison, Performance characteristics of diffusive gradients in thin films equipped with a binding gel layer containing precipitated ferrihydrite for measuring arsenic(V), selenium(VI), vanadium(V), and antimony(V), *Anal Chem*, **82**: (2010), 8903-8909.
S. Mason, R. Hamon, A. Nolan et al., Performance of a mixed binding layer for measuring anions and cations in a single assay using the diffusive gradients in thin films technique, *Anal. Chem.*, **77**: (2005), 6339-6346.
H. Österlund, S. Chlot, M. Faarinen and A. Widerlund, Simultaneous measurements of As, Mo, Sb, V and W using a ferrihydrite diffusive gradients in thin films (DGT) device, *Anal. Chim. Acta*, **682**: (2010), 59-65.
H. Zhang, W. Davison, R. Gadi, and T. Kobayashi, In situ measurement of dissolved phosphorus in natural waters using DGT, *Anal. Chim. Acta.* **370**: (1998), 29-38.
H. L. Price, P. R. Teasdale and D. F. Jolley, An evaluation of ferrihydrite- and Metsorb™-DGT techniques for measuring oxyanion species (As, Se, V, P): Effective capacity, competition and diffusion coefficients, *Anal Chim Acta*, **803**: (2013), 56-65.

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.