DGT® Research
For measurements in waters, soils & sediments

Metals (cationic) using DGT with a Chelex binding layer

These instructions are written for LSNM-NP (cations in solution). The procedure for analysis is the same for LSLM-NP (soils) and LSPM-NP (sediments), but different deployment strategies are used as detailed in soil deployments and sediment deployments.

Type:	LSNM-NP
Measurable analytes:	Al, Ca, Cd, Co, Cr(III), Cu, Fe, Mg, Mn, Ni, Pb, Zn, U, REEs
Holder:	Standard DGT holder
Filter :	Polyethersulphone membrane (thickness: 0.14 mm)
Diffusive gel:	0.8 mm APA diffusive gel (0.4 – 2.0 mm available on request)
Binding layer:	Chelex (iminodiacetate)

Water types

Freshwater through to seawater

Limiting conditions (LSNM-NP (Chelex) Specific)

pH: the recommended pH range is 5 to 9, but strong binding metal such as Pb and Cu are quantitative down to pH 2.

Ionic strength: the recommended range is 1 to 700 mM. Control tests, where devices are deployed in known solutions with the same ionic strength as the field solution, should be performed for waters with ultra low ionic strengths (< 1 mmol L^{-1}).

Binding limitations: Weakly binding cations, such as Ca and Mg, can usually only be measured using short deployment times of a day. A TiO_2 binding agent gives better performance for determining U, but Chelex will work.

Deployment time: Optimum deployment time depends on the quantification limits of the analytical technique used to determine analyte concentrations. Deployment times between 3 and 21 days are generally optimal. If the concentrations of the metals are low (less than a few micrograms per litre), as in an offshore marine environment, and there is no indication of biofilm growth on the surface of the devices, longer deployment times may be appropriate.

Organic complexes: Care should be taken in waters with a high quantity of organic complexes to ensure the longer equilibrium time required to reach steady state accumulation does not affect the results. A deployment of 3 days or more will usually be OK.

Storage

Store the units in a refrigerator (4°C), but avoid freezing them as performance can be affected. The DGT units provided are kept in the sealed clean plastic bags containing a few drops of 0.01M $NaNO_3$ (or 0.01M 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 0.01M $NaNO_3$ (or 0.01M NaCl) 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.

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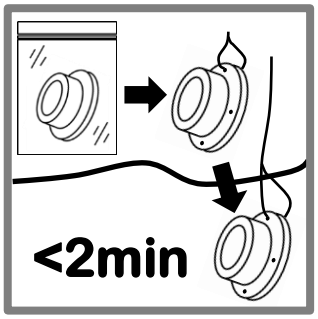
General deployment considerations

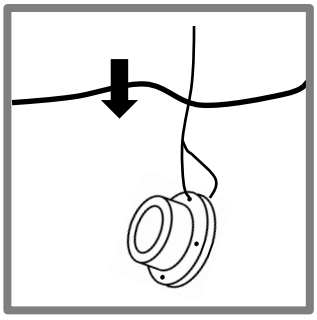
Biofouling: The extent of any biofouling is very dependent on local conditions, particularly light, temperature and productivity. Biofouling is not usually a problem for deployments less than one or two weeks. In pristine or deep waters, very long-term deployments (months extending to a year) have been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

Deploying DGT devices

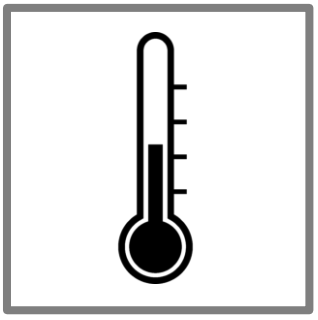


1. Having placed the DGT unit in its deployment holder or simply attached it to any deployment device by tying it with a fishing line threaded through the hole on the rim of the unit, deploy the unit immediately (minutes).

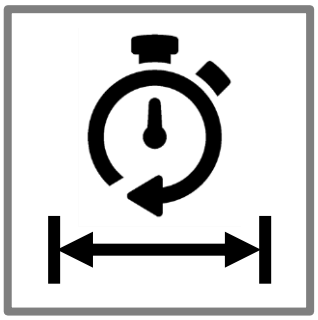
2 Ensure the DGT device is deployed in flowing (or moving) water, but avoid excessive turbulence, particularly bubbles. Large open waters including lakes usually have sufficient natural flow through wave action.



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 of a 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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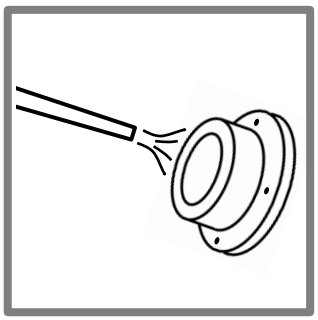
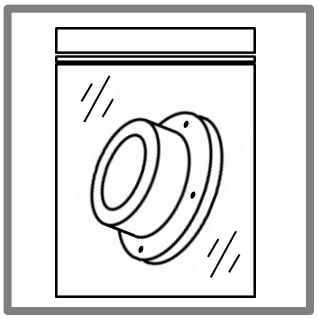
Procedure for analyzing DGT samples

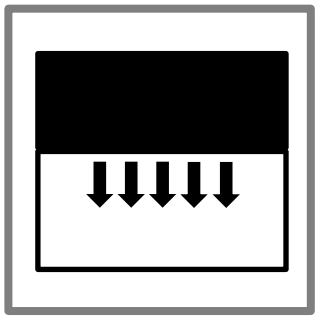
DGT Recovery and Sample Treatment



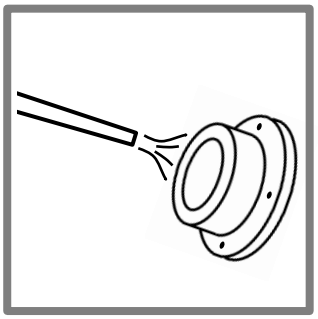
1. After retrieving the DGT device from the deployment environment thoroughly rinse the DGT device with ultrapure water.



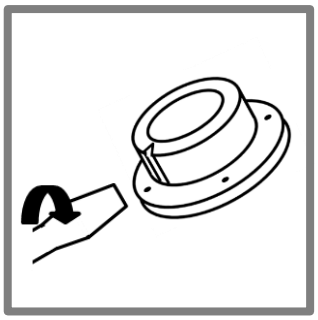
2. Place in a clean plastic bag for storage and transportation back to the lab for sample treatment.



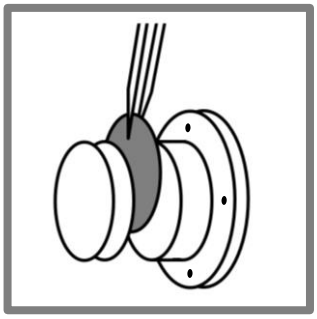
3. For analytes at trace concentrations, all sample treatment should be carried out in a laminar flow hood to avoid contamination.



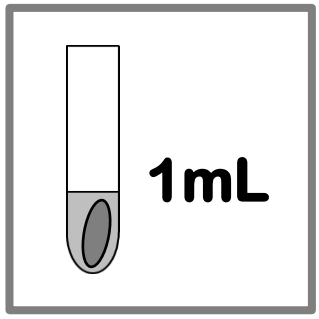
4. Remove from the plastic bag and thoroughly rinse the device with ultrapure water.



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.

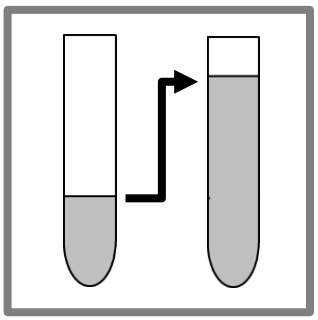


6. Remove the broken cap and then peel off the filter and diffusive gel layer to reveal the bottom resin-gel layer.

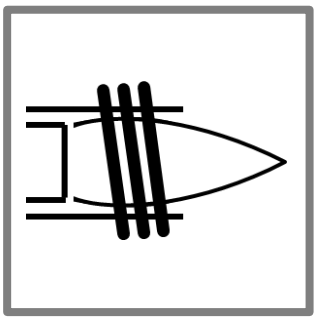


7. Place the resin gel in a clean sample tube and add 1 ml of 1.0 M high purity HNO_3 solution.

8. Make sure the resin gel is fully immersed in the HNO_3 solution. For the most commonly used elution procedure, 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 of the instrument's sampling introduction system, it is recommended 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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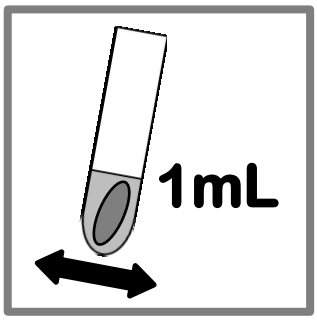
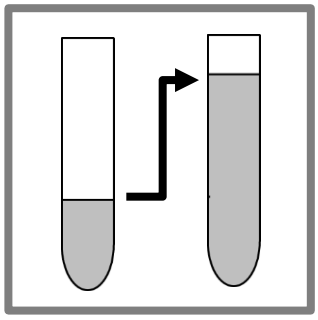
For urgent analysis



7a. Except for Cr, Devillers et al (2017) obtained good recovery after 1 hour without shaking. We recommend agitating the sample on a shaker for urgent analysis.

8a. Shake for 2 hours before analysis.



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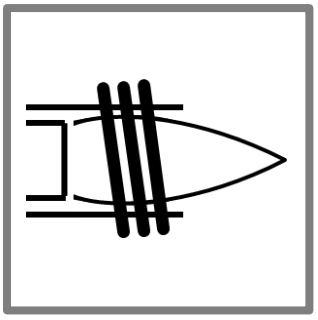

10. Analyse as soon as possible. To avoid clogging of the instrument's sampling introduction system it is recommended to remove the resin gel from the solution.

Analysis

Typically, analysis of the eluate for this type of DGT is performed using ICP-MS or ICP-OES or AAS.

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

A fixed value of 0.85 has been found to apply well to this set up. More detailed information on elution efficiencies, including values for each individual analyte have been published (see Devillers et al, 2017). An exception is Cr where 0.8 is more appropriate.

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). The 0.094 cm is based on a diffusive gel layer thickness of 0.080 cm. Other thickness (0.4 -2.0 cm) can be supplied on request.
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) is the physical area of the exposed filter membrane.
t (s) is the deployment time.

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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.

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, with $f_e = 0.85$, $M = 1.41c_e$ (where c_e is in nmol mL^{-1} or ng mL^{-1}, M is in nmol or ng.)

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

Elution procedures and efficiency data:
D. Devillers, R. Buzier, A Charriau and G Guibaud, Improving elution strategies for Chelex-DGT passive samplers, Anal. Bioanal. Chem. 409: (2017), 85-101.

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.