DGT® Research
For measurements in waters, soils & sediments

Metals (cationic and oxyanionic) and P using a Chelex/Tioxide BL

These instructions are for LSNX-NP (metals and P in solution). The analysis procedure is the same for LSLX-NP (soils) and LSPX-NP (sediments), but different deployment strategies are used as detailed in soil deployments and sediment deployments. If only phosphate is required a simpler procedure can be used (DGT for phosphate)

Type:	LSNX-NP
Measurable analytes:	Al, Ca, Cd, Co, Cr(III), Cu, Fe, Mg, Mn, Ni, Pb, Zn, U, REEs, As(III), As(V), Mo(VI), P(V), Sb(V), Se?, V(V), W(VI), glyphosate
Holder:	Standard DGT holder
Filter :	Polyethersulphone membrane (thickness: 0.14 mm)
Diffusive gel:	0.8 mm APA diffusive gel
Binding layer:	Chelex (iminodiacetate) and TiO_2 (Metsorb) mixture

Water types and Limiting Conditions

Appropriate waters: Suitable for freshwater through to seawater. **pH:** recommended range is 5 to 8.5, but strong binding metals such as Pb and Cu are quantitative down to pH 2. **Ionic strength:** recommended range 1 to 700 mM. Can be used at lower ionic strengths, but as there is a possibility of gel charge affecting performance, control tests at low ionic strength 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 Mo in seawater is not recommended unless very short deployment times of <24 hours are used. 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 (Bennett et al, 2010).

Deployment time: Optimum deployment time depends on analyte concentrations as longer times increases sensitivity. Deployment times between 3 and 21 days are generally optimal, but shorter times of a day can be used (see FAQs). 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 to reach steady state accumulation does not affect the results.

Measured species: All species in solution for the specified oxidation states, within the given pH and ionic strength ranges. For P the dominant forms are the various protonation states of phosphate, which is considered to be the analyte measured in most cases. Total As in solution, that is As(III) + As(V), is measured by LSNX-NP. A separate DGT device with a different binding layer is available for the selective measurement of As(III) (LSNB-AP). DGT with a TiO_2 binding layer has been used successfully for measuring glyphosate. See the publication on this by Fauvelle et al (2015) for the methodology.

Storage

Store the DGTs in a refrigerator (4°C). Do not freeze. They 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 units about once a week to ensure they are moist. Add a few more drops of trace-metal-clean 0.01M $NaNO_3$ (or 0.01M NaCl) solution if it is necessary.

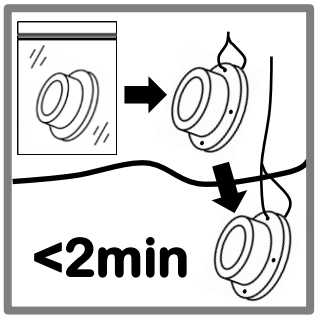
Handling

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.

General deployment considerations

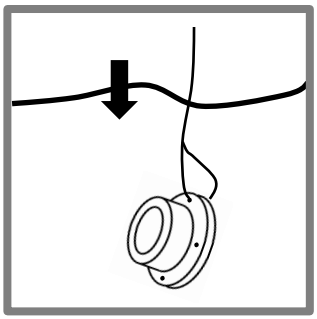
Biofouling: The extent of any biofouling is very dependent on local conditions, particularly light, temperature and productivity. Biofouling is not usually a problem for deployments less than one or two weeks. In pristine or deep waters, very long-term deployments (months extending to a year) have been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

Deploying DGT devices

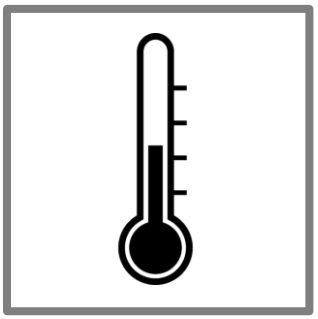


1. Having placed the DGT unit in its deployment holder or simply attached it to any deployment device by tying it with a fishing line threaded through the hole on the rim of the unit, deploy the unit immediately (minutes).

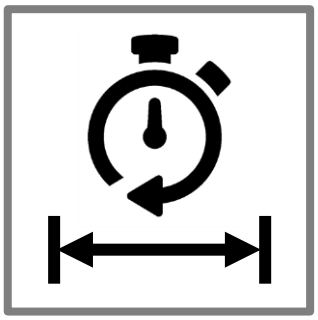
2 Ensure the DGT device is deployed in flowing (or moving) water, but avoid excessive turbulence, particularly bubbles. Large open waters including lakes usually have sufficient natural flow through wave action.



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).

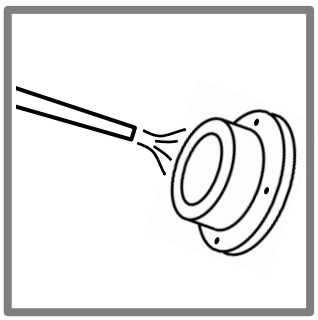


5.Provide an accurate record to the nearest minute of the deployment time

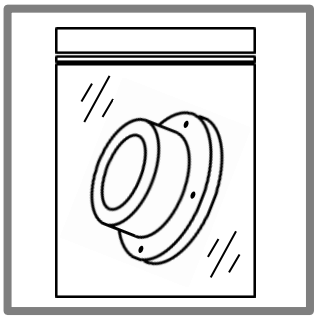
DGT Research Ltd
Skelmorlie, Bay Horse Rd, Quernmore, Lancaster, Lancashire, LA2 0QJ
Phone : +44 (1524) 593899, 2nd Phone : 01524 751451
Email : info@dgtresearch.com

Procedure for analyzing DGT samples

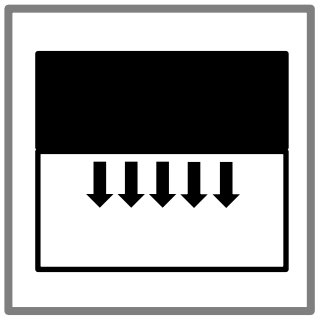
DGT Recovery and Sample Treatment



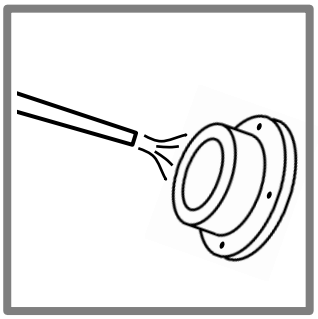
1. After retrieving the DGT device from the deployment environment thoroughly rinse the DGT device with ultrapure water.



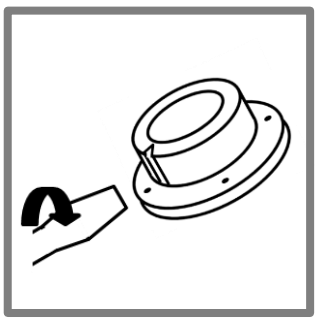
2. Place in a clean plastic bag for storage and transportation back to the lab for sample treatment.



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

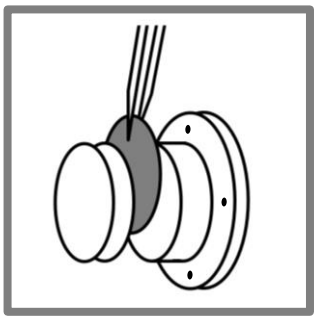


4. Remove from the plastic bag and thoroughly rinse the device with ultrapure water.

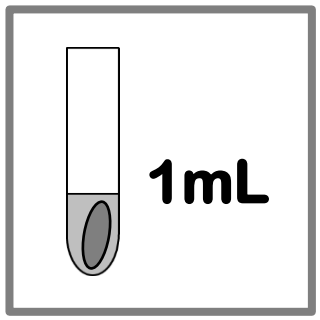


5. To retrieve the resin gel after deployment, insert a suitable screwdriver into the groove in the cap and twist. The cap will be broken at the weak point.

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



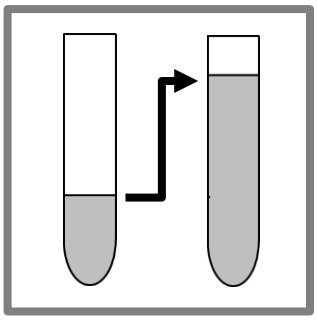
6. Remove the broken cap and then peel off the filter and diffusive gel layer to reveal the bottom binding-gel layer.



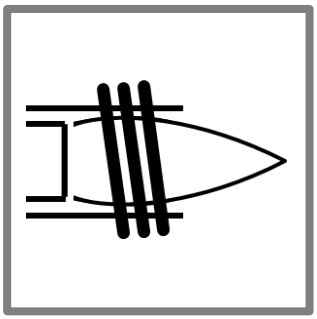
7. Place the binding gel in a clean sample tube and add 1 ml of 1.0 M high purity HNO_3 solution. Remove the binding gel after 24 h, wash with 10 ml of ultra-pure water, and immerse in 1 ml of 1.0 M high purity NaOH solution in a clean sample tube.

8. Make sure the binding gel is fully immersed in both the HNO_3 and NaOH solutions. Leave to stand for at least 24 hours in each one. Mix the nitric acid and sodium hydroxide eluents prior to analysis.

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

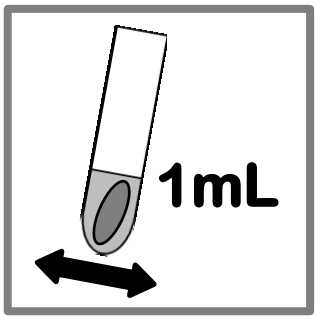


9. Dilute, as necessary for analysis using ultrapure water (18.2MOhms).

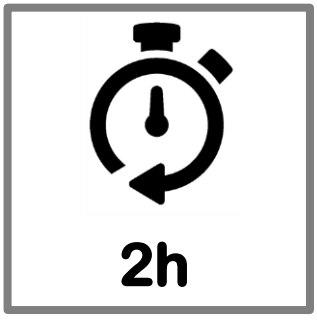


10. Analyse as soon as possible. To avoid clogging of the instrument's sampling introduction system, it is recommended to remove the resin gel from the solution.

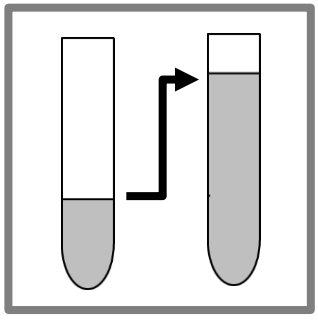
For urgent analysis



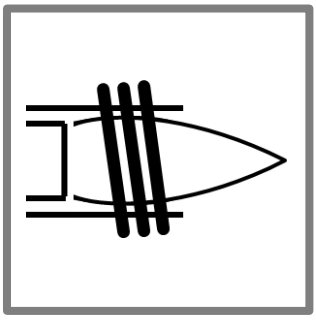
7a. For urgent analysis, agitate the sample tubes containing either nitric acid or sodium hydroxide on a shaker.



8a. Shake for at least 2 hours. Note that except for Cr Devillers et al (2017) obtained good recovery for cationic metals after 1 hour without shaking.



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 or ICP-OES or AAS. P as phosphate can be readily measured using the well-known colorimetric molybdenum blue method (Panther et al, 2010). If ICP-MS is used for analysis of P, elution with 1 M HNO_3 should be replaced with 1 M HCl to avoid N interferences. Total dissolved P is then obtained.

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 0.90 has been found to apply well for the cationic metals when using this set up. An exception is Cr where 0.8 is more appropriate. More detailed information on elution efficiencies, including values for each individual analyte have been published for this mixed binding layer by Panther et al (2014) and for Chelex by Devillers et al (2017). For the procedure described here and a 10x dilution of the eluent prior to analysis, appropriate elution efficiencies are 0.90 for Mo, W and P, 0.86 for V, and 0.80 for As (Panther et al, 2014). With this eluent scheme, the elution efficiency for Sb is less than 0.2. However, using a further eluent of 1 ml of 1M NaOH/1M H_2O_2 after the initial 2 step elution, neutralising this eluent with nitric acid, and then mixing the 3 eluents increases this to 0.89 for Sb while not affecting the elution of other analytes (Panther et al, 2014). Unfortunately H_2O_2 interferes with the molybenum blue method for P. If Sb and P are both required, P must be determined in the eluents prior to the third stage of adding 1 ml of 1M NaOH/1M H_2O_2 while all other analytes can be determined in the combined eluent fractions.

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 (diffusion coefficients).
A_p (3.14 cm^2) 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.

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.

$$M = \frac{c_{\mathrm{e}}\left(V^{\mathrm{bl}} + V_{\mathrm{e}}\right)}{f_{\mathrm{e}}}$$

For the usual set up where f_e = 0.9, M = 1.33c_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

Prime publications for these analytes:

W. W. Bennett, P. R. Teasdale, J. G. Panther, D. T. Welsh and D. F. Jolley, New diffusive gradients in a thin film technique for measuring inorganic arsenic and selenium (IV) using a titanium dioxide based adsorbent, *Anal Chem*, **82**: (2010), 7401-7407.
D. Devillers, R. Buzier, A Charriau and G Guibaud, Improving elution strategies for Chelex-DGT passive samplers, Anal. Bioanal. Chem. 409: (2017), 85-101.
V. Fauvelle, T. T. Nhu-Trang, T. Feret, K. Madarassou, J. Randon and N. Mazzella, Evaluation of titanium dioxide as a binding phase for the passive sampling of glyphosate and aminomethyl phosphonic acid in an aquatic environment, *Anal Chem*, **87**: (2015), 6004-6009.
J. G. Panther, P. R. Teasdale, W. W. Bennett, D. T. Welsh and H. Zhao, Titanium dioxide-based DGT technique for in situ measurement of dissolved reactive phosphorus in fresh and marine waters, *Environ Sci Technol*, **44**: (2010), 9419-9424.
J. G. Panther, R. R. Stewart, P. R. Teasdale, W. W. Bennett, D. T. Welsh and H. Zhao, Titanium dioxide-based DGT for measuring dissolved As(V), V(V), Sb(V), Mo(VI) and W(VI) in water, *Talanta*, **105**: (2013), 80-86.
J. G. Panther, W. W. Bennett, D. T. Welsh and P. R. Teasdale, Simultaneous measurement of trace metal and oxyanion concentrations in water using diffusive gradients in thin films with a chelex-metsorb mixed binding layer, *Anal Chem*, **86**: (2014), 427-434.
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), 1-1H.
H. Zhang and W. Davison, Use of DGT for studies of chemical speciation and bioavailability, *Environ. Chem.* **12**: (2015), 85-101.