

## Metals (oxyanionic) and P using DGT with a titanium oxide BL

These instructions are for LSNT-NP (oxyanions in solution). The analysis procedure is the same for LSLT-NP (oxyanions in soils) and LSPT-NP (oxyanions in sediment), 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](#)).

<b>Type:</b>	LSNT-NP
<b>Measurable analytes:</b>	As(III), As(V), Mo(VI), P(V), Sb(V), Se?, V(V), W(VI), glyphosate
<b>Holder:</b>	Standard DGT holder
<b>Filter :</b>	Polyethersulphone membrane (thickness: 0.14 mm)
<b>Diffusive gel:</b>	0.8 mm APA diffusive gel
<b>Binding layer:</b>	TiO <sub>2</sub> (Metsorb)

### Water types and Limiting Conditions

**Appropriate waters:** Suitable for freshwater through to seawater. **pH:** recommended range 5 to 8.5. **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 the same ionic strength as the field solution, are then advised.

**Binding limitations:** 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 the quantification limits of the analytical technique used to determine concentrations. 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.

**Measured species:** The oxidation states are specified in the measurable analytes above. All species that exist in solution for those oxidation states within the pH and ionic strength range given (freshwater to seawater) are measured. 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 this method. A separate DGT device with a different binding layer is available for the selective measurement of As(III) (LSNB-AP). LSNT-NP has been used successfully for measuring glyphosate. See the publication on this by Fauvelle et al (2015) for the appropriate methodology.

### Storage

Store the units in a refrigerator (4°C). Do not freeze. The DGT units provided are kept in the sealed clean plastic bags containing a few drops of 0.01M NaNO<sub>3</sub> (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<sub>3</sub> (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.

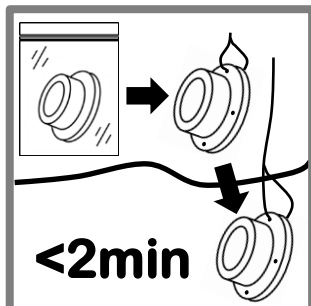
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## General deployment considerations

**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.

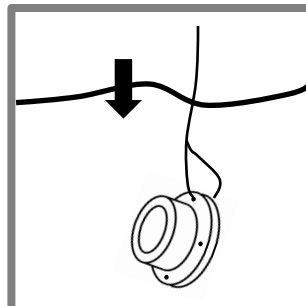
## Deploying DGT devices



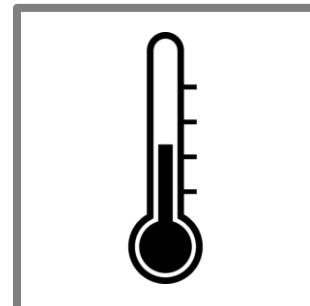
**1.** Having placed the DGT unit in its deployment holder or simply attached it to any deployment device by tying it with a fishing line threaded through the hole on the rim of the unit, deploy the unit immediately (<2 minutes).



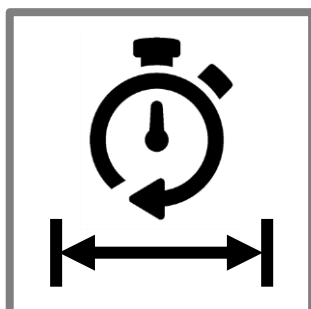
**2** Ensure the DGT device is deployed in flowing (or moving) water, but avoid excessive turbulence, particularly bubbles. Large open waters including lakes usually have sufficient natural flow through wave action.



**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  $\pm 2^{\circ}\text{C}$ , 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).



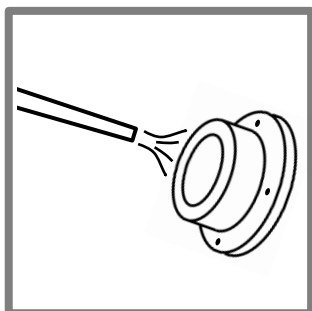
**5.** Provide an accurate record to the nearest minute of the deployment time

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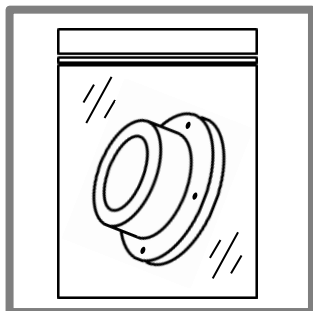
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## Procedure for analyzing DGT samples

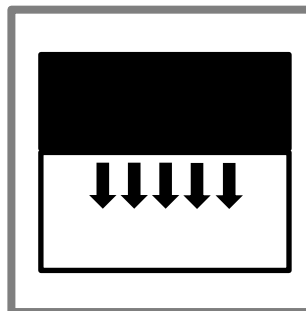
### DGT Recovery and Sample Treatment



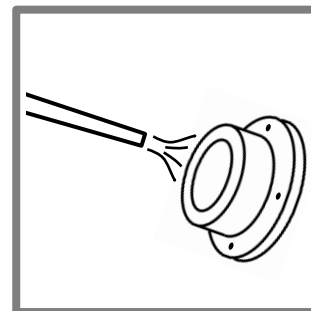
**1.** After retrieving the DGT device from the deployment environment thoroughly rinse the DGT device with ultrapure water.



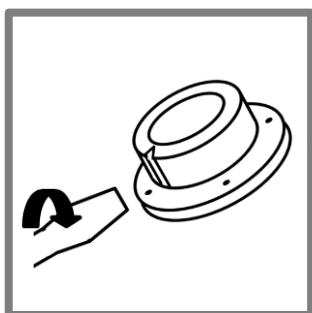
**2.** Place in a clean plastic bag for storage and transportation back to the lab for sample treatment.



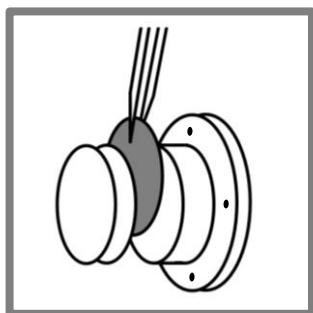
**3.** For analytes at trace concentrations, all sample treatment should be carried out in a laminar flow hood to avoid contaminating the sample.



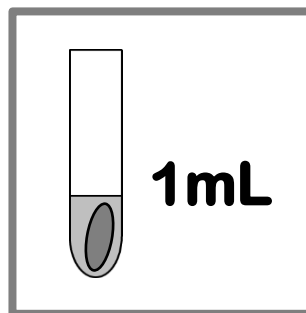
**4.** Remove from the plastic bag and thoroughly rinse the device with ultrapure water.



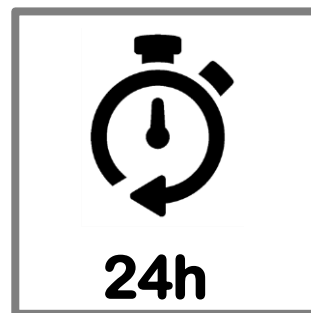
**5.** To retrieve the resin gel after deployment, insert a suitable screwdriver into the groove in the cap and twist it. The cap will be broken at the weak point.



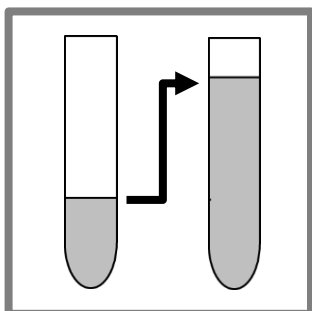
**6.** Remove the broken cap and then peel off the filter and diffusive gel layer to reveal the bottom binding-gel layer.



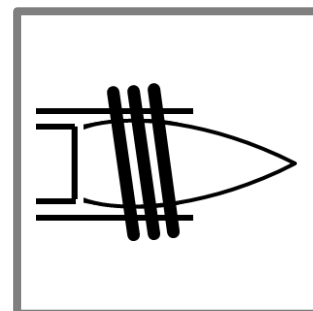
**7.** Place the binding layer in 5 ml of high purity water for 1 hour. Then place it in a clean sample tube and add 1 ml of 1.0 M high purity NaOH solution.



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



**9.** Neutralise the solution with high purity 1M HNO<sub>3</sub>. Dilute, as necessary for analysis using ultrapure water (18.2MΩms).



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

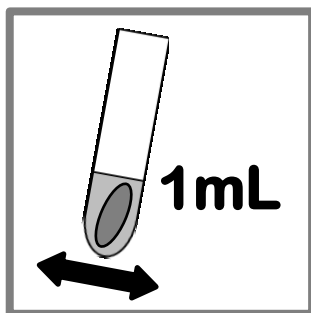
**Note for step 5:** If this fails, using clean tweezers break the white filter membrane and pull out the gels. The binding gel is the lower one.

**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

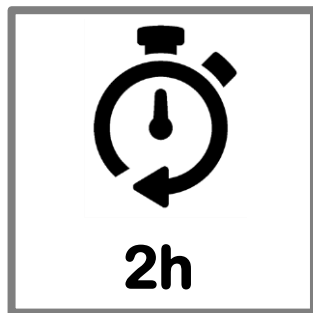
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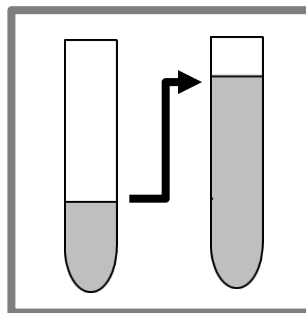
## For urgent analysis



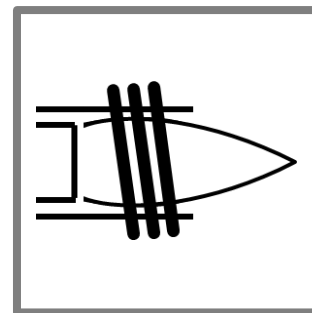
**7a.** For urgent analysis, agitate the tube containing the binding gel and 1 ml of 1.0 M NaOH on a shaker.



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



**9.** Neutralise the solution with high purity 1M HNO<sub>3</sub>. 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](#). If ICP-MS is used for analysis of P, elution with 1 M HNO<sub>3</sub> 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<sup>1</sup> and field blank<sup>2</sup> concentrations.

<sup>1</sup>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.

<sup>2</sup>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 0.88 for As, Mo, Se(IV) and V, 0.93 for P and 0.95 for W (Panther et al, 2004). With this eluent the elution efficiency for Sb is only 0.2. However, using 1 ml of 1M NaOH/1M H<sub>2</sub>O<sub>2</sub> as the eluent increases this to 0.91 for Sb while not affecting the elution of other analytes (Panther et al, 2013). Unfortunately H<sub>2</sub>O<sub>2</sub> interferes with the molybdenum blue method for P. If Sb and P are both required, a serial elution of 1M NaOH followed by 1M NaOH/1M H<sub>2</sub>O<sub>2</sub> can be used. P is determined in the first fraction 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.

$$C_{\text{DGT}} = \frac{M \Delta_g}{D_{\text{mdl}} A_p t}$$

$C_{\text{DGT}}$  (nmol mL<sup>-1</sup> or ng mL<sup>-1</sup>) 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)

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$\Delta_g$  (also known as  $\delta_g$ ) (0.094 cm) is the total thickness of the materials in the diffusion layer (diffusive gel and filter membrane).  $D^{mdl}$  ( $\text{cm}^2 \text{s}^{-1}$ ) is the diffusion coefficient of analyte in the material diffusion layer for the deployment temperature ([see diffusion coefficients](#)).

$A_p$  ( $3.14 \text{ cm}^2$ ) 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.

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

For the usual set up, if  $f_e = 0.9$ ,  $M = 1.33c_e$  (where  $c_e$  is in  $\text{nmol mL}^{-1}$  or  $\text{ng mL}^{-1}$ ,  $M$  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
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.
- 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), 1-13.
- H. Zhang and W. Davison, Use of DGT for studies of chemical speciation and bioavailability, *Environ. Chem.* **12**: (2015), 85-101.

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