

## LSND-AT

# Loaded DGT passive sampler for HPCPs, pharmaceuticals, EDCs and OPFRs in waters

These instructions are written for LSND-AT (organics in solution). The procedure for analysis is the same for LSND-AT (soils), but different deployment strategies are used as detailed in [soil deployments](#).

<b>Type:</b>	LSND-AT
<b>Measurable analytes:</b>	EDCs, HPCPs, OPFRs and pharmaceuticals (see details in the appendix)
<b>Holder:</b>	Standard DGT holder
<b>Filter membrane:</b>	PTFE membrane (thickness: 0.14 mm)
<b>Diffusive gel:</b>	0.8 mm agarose diffusive gel
<b>Binding layer:</b>	HLB

## Water types

Freshwater through to seawater.

## Conditions

**pH:** the recommended pH range is 5 to 9.

**Ionic strength:** tested in waters with IS between 1.0 mM – 0.5 M.

**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 analytes are low (less than a few micrograms per litre), as in a clean stream, and there is no indication of biofilm growth on the surface of the devices, longer deployment times may be appropriate.

## Storage

Store the units in a refrigerator (4°C). The DGT units provided are kept in the sealed clean plastic bags containing a few drops of 0.01M NaCl solution. Do not open them until immediately prior to deployment. Check the units occasionally to make sure they are not dried out. Add a few more drops of clean 0.01M NaCl solution if the solution inside the bag is evaporated.

## 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.

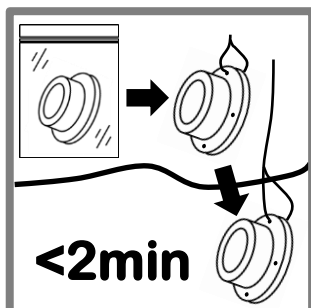
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## General deployment considerations

**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 two weeks. In pristine or deep waters, very long-term deployments (months extending to a year) have been unaffected by biofilms.

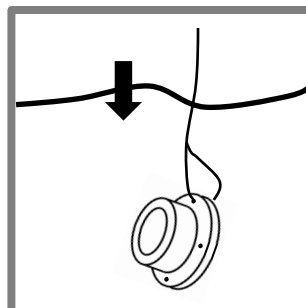
## Deploying DGT devices



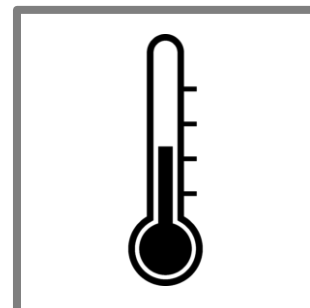
**1.** Having placed the DGT device in its deployment holder or simply attached it to any deployment device by tying it with a fishing line threaded through the hole on the rim of the unit, deploy the unit immediately (minutes).



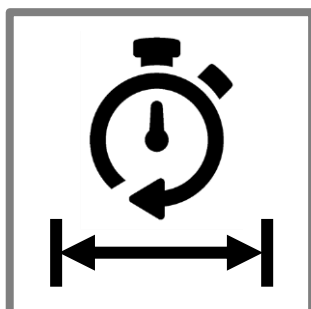
**2** Ensure the DGT device is deployed in flowing (or moving) water, but avoid excessive turbulence, particularly bubbles. Large open waters including lakes usually have sufficient natural flow through wave action.



**3.** Ensure that the white window 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 of 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).

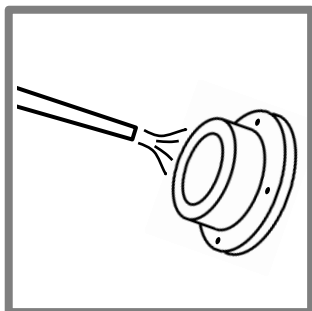


**5.** Provide an accurate record to the nearest minute of the deployment time

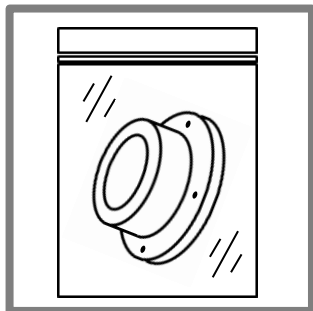
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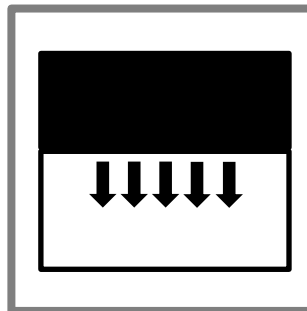
## DGT Recovery and Sample Treatment



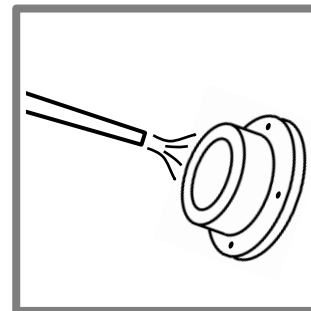
**1.** After retrieving the DGT device from the deployment environment thoroughly rinse it with ultrapure water.



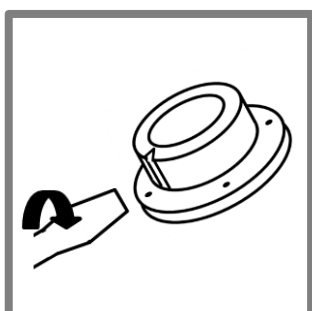
**2.** Place it in a clean plastic bag for storage and transportation back to the lab for sample treatment.



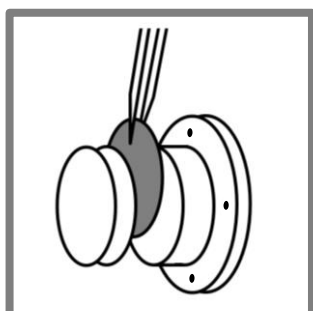
**3.** For analytes at trace concentrations, all sample treatment should be carried out in a laminar flow hood to avoid contamination.



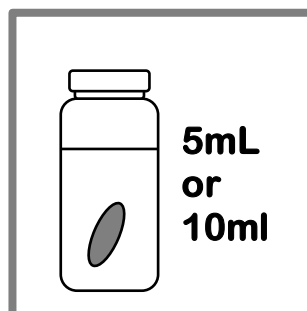
**4.** Remove from the plastic bag and thoroughly rinse the device with ultrapure water.



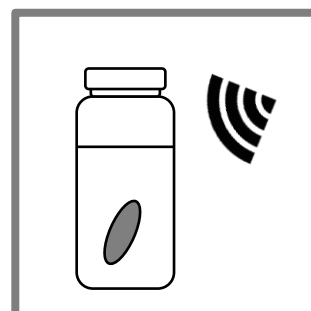
**5.** To retrieve the resin gel after deployment, insert a suitable screw driver into the groove in the cap and twist it. The cap will be broken at the weak point.



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

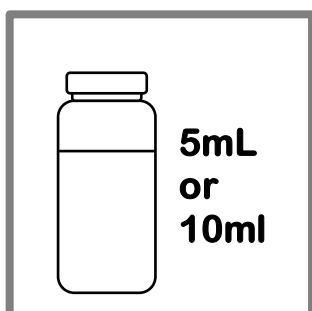


**7.** Place the resin gel in a clean amber glass vial. For HPCPs, EDCs and pharmaceuticals other than psychiatric drugs add 5mL acetonitrile. For OPFRs add 10 mL methanol. For psychiatric add 10mL methanol containing 5% ammonia water.

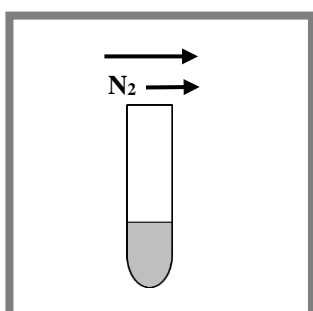


**8.** Fully immerse the resin gels in the organic solvents. Place them in ultrasonic bath for 30 minutes (for all chemicals other than psychiatric drugs) or 3 hours (for psychiatric drugs).

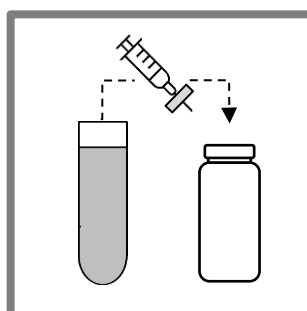
**Note for step 5:** If this fails, using clean tweezers break the white filter membrane and pull out the gels directly.



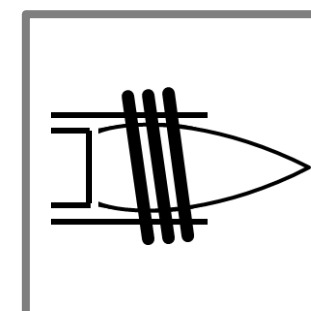
**9.** Remove resin gel from the elution solution.



**10.** Evaporate the eluant under a gentle stream of nitrogen to near dryness.



**11.** Re-dissolve with 1 mL methanol. Filter the solution with 0.22µm syringe filter to an amber vials.



**12.** Analyse as soon as possible, or store the solution at -20°C freezer prior to analysis.

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## Analysis

Typically, analysis of the eluate for this type of DGT is performed using HPLC-MS or LC-MS/MS or HPLC-UV.

## Method blanks 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. Field blanks are obtained from additional DGT devices, which are transported to the monitoring site, exposed briefly at the site when the devices are prepared for deployment (but no deployment is carried out), and transported back to the laboratory for treatment and analysis, the same procedures as for field samples. It is advisable to have at least one field blank for each test series.

## Calculations

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

$$C_{\text{DGT}} = \frac{M\Delta_g}{DA_p t}$$

$C_{\text{DGT}}$  (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 sample analysis (see below).

$\Delta_g$  (0.094 cm) is the total thickness of the materials in the diffusion layer (diffusive gel and filter membrane).

$D$  (cm<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient of analyte in the material diffusion layer at the temperature during deployment (obtained from the DGT web site).

$A_p$  (3.14 cm<sup>2</sup>) is the physical area of the exposed filter membrane or the window of the DGT device.

$t$  (s) is the deployment time.

Recommended units for each parameter to facilitate easy calculation are shown above. This calculation procedure should work well for most situations. For more accurate methods of calculation that incorporate estimates of the flow regime of the water, see FAQs on the web site.

The mass,  $M$ , of analyte on the binding layer, is calculated from the measured concentration of analyte,  $c_e$ , in the elution solution, of volume  $V_{re}$ , remembering to take into account any subsequent dilution or pre-concentration.

$$M = \frac{c_e V_{re}}{f_e}$$

## Elution efficiency, $f_e$

A fixed value of 1 has been found to apply well to this set up (for OPFRs and some pharmaceuticals), the  $f_e$  values of other compounds can be found in the Appendix. More detailed information on compounds have been measured can be found in the Appendix

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## Appendix

The compounds can be measured with LSND-AT device and their elution factor,  $f_e$ , values:

### EDCs:

Compound	$f_e$
17- $\alpha$ -ethynylestradiol	1
17- $\beta$ -estradiol	0.9
4-tert-octylphenol	0.8
Acetochlor	1
Diethylstilbestrol	0.7
Estriol	1
Estrone	0.7
Nonylphenol	0.8

### HPCPs:

Compound	$f_e$
4-hydroxybenzoic acid	0.75
Benzylparaben	1
Butylated hydroxyanisole	0.8
Butylated hydroxytoluene	0.6
Butylparaben	1
Heptylparaben	0.8
Isopropylparaben	1
Methylparaben	1
Ortho-phenylphenol	1
Propylparaben	1
Triclocarban	0.8
Triclosan	0.9

### OPFRs:

Compound	$f_e$
Tri-n-butyl-phosphate	1
Tri-n-propyl phosphate	1
Tris(1,3-dichloro-2-propyl)phosphate	1
Tris(2-butoxyethyl)phosphate	1
Tris(2-chloroethyl)phosphate	1
Tris(2-chloroisopropyl)phosphate	1

### Pharmaceuticals:

Compound	$f_e$
Atenolol	1
Clofibric acid	1
Diclofenac	1
Fenoprofen	1
Fluoxetine	1
Gemfibrozil	1
Ibuprofen	1
Ketoprofen	1
Metoprolol	1
Propranolol	1

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## Psychiatric Pharmaceuticals:

Compound	$f_e$
Alprazolam	0.75
Bupropion hydrochloride	0.95
Caffeine	0.95
Carbamazepine	1
Diazepam	0.85
Estazolam	0.9
Mirtazapine	0.85
Naproxen	1
Oxazepam	0.85
Paroxetine	1
Risperidone	0.9
Temazepam	0.85

## 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

### Elution procedures, efficiency data and other relevant information:

W. Chen, S. Pan, H. Cheng, A. J. Sweetman, H. Zhang, K. C. Jones, Diffusive gradients in thin-films (DGT) for in situ sampling of selected endocrine disrupting chemicals (EDCs) in waters. *Water Research*, 137: (2018), 211–219.

W. Chen, Y. Li, C-E. Chen, et al., DGT passive sampling for quantitative in situ measurements of compounds from household and personal care products in waters, *Environ. Sci. Technol.*, 51: (2017), 13274-13281.

Y-T. Zou, Z. Fang, Y. Li, R. Wang, H. Zhang, K. C. Jones, X-Y. Cui, X-Y. Shi, D. Yin, C. Li, Z-D. Liu, L. Q. Ma and J. Luo, Novel method for in situ monitoring of organophosphorus flame retardants in waters. *Anal. Chem.*, 90: (2018), 10016–10023.

J. K. Challis, M. L. Hanson, C. S. Wong, Development and calibration of an organic-diffusive gradients in thin films aquatic passive sampler for a diverse suite of polar organic contaminants. *Anal. Chem.* 88: (2016), 10583–10591.

Z. Fang, K. X. Li, Y. Li, H. Zhang, K. C. Jones, X. Y. Liu, S. Y. Liu, L. Q. Ma and J. Luo, Development and application of the diffusive gradients in thin-films Technique for measuring psychiatric pharmaceuticals in natural waters, *Environ. Sci. Technol.*, 53: (2019), 11223–11231.

### Reviews on DGT technique:

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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