

Alabaster mass transfer sensor

Manual for use in freshwater 2018-10-22



Passive Sampling of Organic Compounds / PaSOC
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1. Introduction

This manual covers instructions for measuring mass transfer coefficients using alabaster plate dissolution rates in freshwater. These measurements may be useful in the study of uptake rates of organic and inorganic compounds by passive samplers, both in the lab and in the field. The scientific background is summarised below and is described in detail elsewhere (Booij et al., 2017).

2. Mounting

A typical configuration consists of an alabaster plate that is fitted within a protective ring (2-sides exposed) or protective housing (1-side exposed) as shown in the picture below.



The assembly is usually clamped in a passive sampler holder that is rigid. If so, it is important that the thickness of the passive sampler holder matches the thickness of the alabaster plate within 0.25 mm, in order to prevent excessive force on the plate assembly and to prevent gaps between the passive sampler holder and the plate assembly. Flexible spacers (e.g. silicone) can be put around or under the plate assembly to fill up empty space. Clamping bolts are typically fastened hand-tight + 1/8 turn. An example of the use of spacers is shown below for the case of POCIS.



3. Deployment

On first use: flush the alabaster surface with water (tap, deionized, or distilled) to remove dust.

Dry 10 min at 40 °C (not longer, not at higher temperature).

Allow to cool for 30 min in ambient air (no desiccator). Determine the mass of the alabaster plate in its protective ring, using a balance with precision of 0.1 mg (preferred) or 1 mg.

Mount the alabaster plate as described in the previous section.

Aim for a 200 mg mass loss during the exposure. This mass loss is based on the consideration that the mass loss can be determined with an accuracy of about 2 mg (~ error of 1%). A higher mass loss results in a smaller relative error, but decreases the number of measurements that can be made with one plate. Initially, the mass loss rate will be unknown. It is therefore suggested that a pilot experiment is done at moderate flow, with an exposure time of 0.5 h.

When tap water or river water is used: measure the conductivity and the concentrations of dissolved calcium and dissolved sulphate, or obtain these parameters from the local water authorities. Conductivity can be used to estimate ionic strength (I) using the Jurinak-Griffin relationship (Jurinak and Griffin, 1973)

$$I \text{ (mol/L)} = 0.0127 \kappa_{25} \text{ (mS/cm)} \quad (1)$$

where κ_{25} is the electrical conductivity at a reference temperature of 25 °C. This relationship is included in the calculation template.

Ionic strength and background concentrations of calcium and sulphate are needed to calculate the alabaster solubility. These values need not always be accurately known as long as they are small.

Sequential experiments (i.e., without changing the water between experiments) can be done, provided that an accurate record is kept of the total amount of alabaster that is dissolved. This allows to calculate the total ionic strength and the calcium and sulphate concentrations at the beginning of each new experiment. It is recommended to keep the concentrations of dissolved alabaster below 20% of its saturation value, however.

At the end of each experiment, take the alabaster plate assembly, pat dry with a paper tissue, and dry 15 min at 40 °C (not longer, not at higher temperature). Allow to cool for 30 min in ambient air (no desiccator), and determine the mass.

Check how much the alabaster surface has receded into the protective ring. Regenerate the sensor when this is more than 0.3 mm. This corresponds with ~70 mg per cm² exposed surface area. It is presently unknown if a surface recession > 0.3 mm significantly affects the k_w measurements, but 0.3 mm intuitively appears to be a safe value.

4. Sensor regeneration

The surface becomes increasingly shielded from the flow, as a result of the alabaster dissolution.



Remove the part of the protective ring that extends beyond the alabaster surface, using a lathe, a grinding machine, or half-round and flat files with decreasing coarseness, followed by sanding with coarse sandpaper. Illustrations are shown in the video (FacingPocisType1_2017-07-01.mp4).

Safety first:

- ☞ **protect yourself from dust (eyes, lungs, other)**
- ☞ **observe all safety instructions for the lathe, grinding machine, files, and all other tools that you might use. Only use the tools/machines for which you have the required skills.**

5. k_w of alabaster

Calculate the k_w of calcium sulphate using the calculation template for fresh water (river, lake, tap, deionized, etc.). This template is based on the calculation scheme as described by O'Brien et al. (2011).

Input parameters are

- Temperature
- Ionic strength of the exposure water at time = 0.
- Calcium and sulphate concentrations of the exposure water at time = 0.
- Exposed surface area of the plate
- Exposure time
- Observed mass loss
- Alabaster to calcium sulphate solubility ratio. (A default value of 1.028 typically suffices.)

The template yields the k_w of calcium sulphate in units of $\mu\text{m/s}$ and $\text{L}/(\text{dm}^2 \text{ d})$. Values of k_w typically range between 3 and 50 $\text{L dm}^{-2} \text{ d}^{-1}$ for nearly stagnant flows and very high flows (m/s range), respectively. Lower and higher values are suspect.

6. k_w of organic compounds

The k_w of organic compounds is usually smaller than the k_w of alabaster (calcium sulphate), because the diffusion coefficients of organic compounds are typically smaller.

$$k_{w,org} = k_{w,CaSO_4} \left(\frac{D_{w,org}}{D_{w,CaSO_4}} \right)^{2/3}$$

The D_w of calcium sulphate can be obtained from the calculation template. This estimate is based on the temperature dependency of salt diffusion coefficients from Li and Gregory (1974):

$$\log D_{w,CaSO_4} \left(10^{-10} \text{ m}^2 \text{ s}^{-1} \right) = 4.593 - \frac{1082}{T(K)}$$

where T is the temperature in K.

Diffusion coefficients at 25 °C are most conveniently obtained from Fig. 18.10 in Schwarzenbach et al. (2003), who correlated D_w with molecular weight of the non-electrolytes. Diffusion coefficients at other temperatures can be evaluated from the Hayduk-Laudie equation (Hayduk and Laudie, 1974), who showed that the D_w of non-electrolytes is inversely proportional to the dynamic viscosity of the solvent to the power 1.14. This method is applied in the calculation template.

7. References

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