

Alabaster mass transfer sensor

Guidance for use in freshwater or seawater

2023-03-02



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1. Introduction

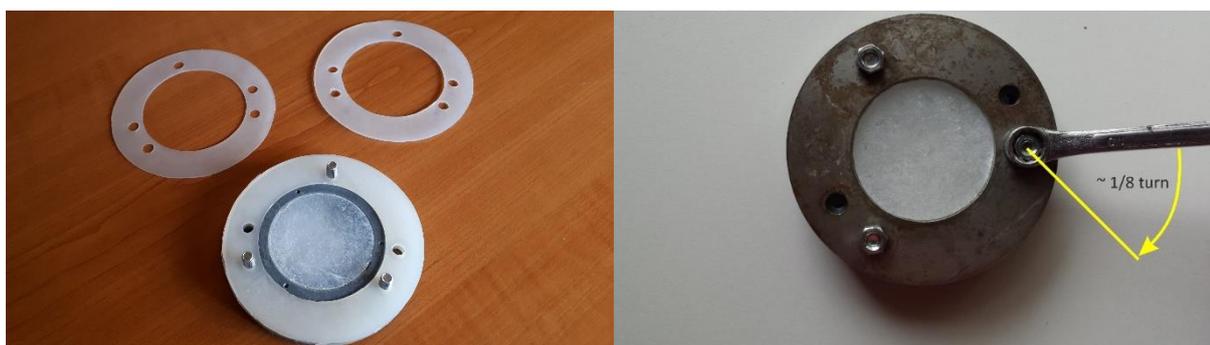
This document gives guidance for measuring mass transfer coefficients using alabaster plate dissolution rates in freshwater and seawater. These measurements may be useful for the study of uptake rates of organic and inorganic compounds by passive samplers, and for the bottom shear stress measurements in the lab and in the field. The scientific background is summarised below and is described in detail elsewhere (Booij et al., 2017; O'Brien et al., 2011; Opdyke et al., 1987).

2. Mounting

The alabaster plates are fitted in a PVC holder or ring that is to be mounted in a passive sampler housing. The alabaster surface should be in the exact position of the exchange surface that is to be evaluated. The plate assembly is robust, but excessive force is to be avoided when mounting. Hand-tight is tight enough.



For mounting in POCIS holders, the assembly is clamped between two stainless steel washers. The following procedure will do. The distance between the washers should match the thickness of the alabaster plate within ~ 0.3 mm, to prevent excessive force on the plate assembly and to prevent gaps between the passive sampler holder and the plate assembly. Flexible silicone spacers can be put around or under the plate assembly to fill up empty space. Clamping bolts are 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, or after prolonged storage: briefly flush the alabaster surface with water (tap, deionized, or distilled), and dry 15 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 plate, using a balance with precision of 0.1 mg (preferred) or 1 mg.

Mount the plate as described in the previous section.

Aim for a mass loss of approximately 20 mg per cm² surface area, but more than 200 mg is usually not needed. These recommended mass losses are based on the consideration that mass loss can be determined within a few tenths of a mg for small plates (~1 cm²), and a few mg for large plates (13 cm² and larger). A higher mass loss results in a smaller relative error, but decreases the number of measurements that can be made with one plate. Mass loss rates will initially be unknown, and a pilot experiment is useful to gain experience. An initial guess of 60 min exposure time for fresh water at moderate flow rates (~ 10 cm/s) usually works fine. For seawater an initial guess of 45 min is fair.

Calcium sulfate solubilities are larger at higher ionic strength and are smaller when background concentrations of calcium and sulfate are higher. Laboratory experiments are therefore best carried out with deionized water or artificial seawater, because ionic strength and background concentrations are well known in these cases. For field exposures the background concentrations of calcium and sulfate are preferably measured, or obtained from local water authorities. Ionic strength of seawater and estuarine waters can be obtained from salinity, as outlined in the calculation template. Ionic strength of freshwater may be estimated from conductivity, using the Jurinak-Griffin relationship (Jurinak and Griffin, 1973)

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

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

After deployment, alabaster plates are patted dry with paper tissue, followed by drying 15 min at 40 °C (not longer, not at higher temperature) in a stove. 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. For regeneration methods see section 7.

It is useful to make one or more deployments in stagnant water, to identify the smallest k_w that can be obtained with a particular plate size, water type, and temperature. At very low flow velocities the dissolution process generates a free convection flow, because the saturated calcium sulfate solution near the surface has a slightly higher density than bulk water. This denser solution sinks downwards, or spreads sideways, and thereby draws exposure water over the alabaster surface. Modelling of this effect requires lengthy calculations (Booij et al., 2017, section S5), but its experimental determination is straightforward. Experimental k_w values that are 1.5 to 2 times higher than the free convection value can be considered to be reliable.

4. Use of the template

The template for calculating k_w has separate worksheets for freshwater and for seawater. The reason for this is that freshwater chemists usually express concentrations in amount per volume, whereas seawater chemists typically use amount per unit mass of solution. The template automatically takes these differences in concentration units into account.

For both worksheets alabaster solubility is modelled according to O'Brien et al. (2011), which yields solubility in units of mol per kg water. Solubility of alabaster appears to be 1.028 times higher than solubility of CaSO₄·2H₂O (Booij et al., 2017), which is minor but measurable. Calculation of k_w for exposures in limited and infinite water volumes is done according to Booij et al. (2017).

4.1. Freshwater template

39	Solubility calculation		
40	Temperature	20	°C
41	Ca ²⁺ background	0.00037	mol/kg H ₂ O
42	SO ₄ ²⁻ background	0.00012	mol/kg H ₂ O
43	I _{background}	0.00790	mol/kg H ₂ O
44	water density	0.998	kg/L
45	alabaster/CaSO ₄ ·2H ₂ O solubility ratio	1.028	
46			
47	solubility	0.01571	mol/kg H ₂ O
48	solubility	2.70	g/L
49	iteration error (%)	0.00	
50			
51	k_w of calcium sulphate		
52	Exposed area	0.126	dm ²
53	Exposure time	90	min
54	mass loss	0.2531	g
55	water volume (value or "infinite")	5.0	L
56			
57	k _{w,CaSO₄}	12.0	L/(dm ² d)
58	k _{w,CaSO₄}	13.9	µm/s

Cells with green background require careful inspection by the user, and updating if needed. Results of the calculations are shown in cells with amber background. The upper block of cells deals with the calculation of solubility. For freshwater, background concentrations in mol per kg water are practically equal to concentrations in mol/L. Density of air-saturated pure water is used in the calculations (Jones and Harris, 1992). The lower block deals with the calculation of k_w . For field exposures specify water volume = infinite.

At the right hand side of the worksheet two calculation blocks are given for the convenience of the user.

Estimation of ionic strength and Total Dissolved Solids from electrical conductivity		
k ₂₅	0.62	mS/cm
I	0.0079	mol/L
TDS	0.4	g/L

Contribution of accumulated alabaster to calcium and sulphate concentrations and ionic strength		
Water volume	5.0	L
Dissolved alabaster	0.7521	g
ΔCa ²⁺	0.000874	mol/L
ΔSO ₄ ²⁻	0.000874	mol/L
ΔI	0.003495	mol/L

The upper block yields estimates of ionic strength and total dissolved solids, using correlations with electrical conductivity for freshwater. The lower block may be useful for sequential exposures without water replacement. Alabaster that has dissolved during previous exposures results in elevated ionic strength and elevated calcium and sulfate concentrations at the start of new exposures. Results of these calculations are not automatically linked to the k_w calculation in column B, but must be manually copied and pasted as values..

4.2. Seawater template

39	Solubility calculation		
40	Temperature	20	°C
41	Absolute salinity, S_A	18	g/kg solution
42	Ca^{2+} background	0.0054	mol/kg H ₂ O
43	SO_4^{2-} background	0.0147	mol/kg H ₂ O
44	I	0.3633	mol/kg H ₂ O
45	water density	1.012	kg/L
46	alabaster/ $CaSO_4 \cdot 2H_2O$ solubility ratio	1.028	
47			
48	solubility	0.02148	mol/kg H ₂ O
49	solubility	0.02109	mol/kg solution
50	solubility	3.67	g/L
51	iteration error (%)	0.00	
52			
53	k_w of calcium sulphate		
54	Exposed area	0.126	dm ²
55	Exposure time	60	min
56	mass loss	0.1824	g
57	water volume (value or "infinite")	10	L
58			
59	$k_{w,CaSO_4}$	9.5	L/(dm ² d)
60	$k_{w,CaSO_4}$	11.0	µm/s

Cells with green background require careful inspection by the user, and updating if needed. Results of the calculations are shown in cells with amber background. The upper block of cells deals with the calculation of solubility. Absolute salinity (S_A in units of g/kg solution) is used instead of practical salinity (S_P , dimensionless, but PSU is often used as a unit).

The following conversion of concentration units applies for seawater:

$$1 \text{ mol /kg H}_2\text{O} = 1/(1-S_A/1000) \text{ mol/kg solution}$$

$$1 \text{ mol/kg solution} = 1 \times \text{density mol/L}$$

Density of seawater is calculated from Millero and Huang (2009).

The lower block deals with the calculation of k_w . For field exposures choose water volume = infinite.

At the right hand side of the worksheet two calculation blocks are given for the convenience of the user.

Ionic strength and calcium and sulphate concentrations for dilutions of standard seawater		
S_A	18	g/kg
Ca^{2+}	0.0054	mol/kg H ₂ O
SO_4^{2-}	0.0147	mol/kg H ₂ O
I	0.3633	mol/kg H ₂ O
Contribution of accumulated alabaster to calcium and sulphate concentrations and ionic strength		
S_A	18	g/kg
Water volume	3.0	L
Dissolved alabaster	0.1521	g
ΔCa^{2+}	0.00030	mol/kg H ₂ O
ΔSO_4^{2-}	0.00030	mol/kg H ₂ O
ΔI	0.00119	mol/kg H ₂ O

The upper block yields estimates of ionic strength and background concentrations of calcium and sulfate for dilutions of standard seawater, based on values listed by Millero and Sohn (1992).

The lower block may be useful for sequential exposures without water replacement. Alabaster that has dissolved during previous exposures results in elevated ionic strength and elevated calcium and sulfate concentrations at the start of new exposures. Results of these calculations are not automatically linked to the k_w calculation in column B, but must be manually copied and pasted as values.

5. Sequential deployments

Alabaster plates may be sequentially exposed without refreshing the water in laboratory experiments, provided that a record is kept of the amount of alabaster that has dissolved during previous exposures. This allows to calculate the total ionic strength and the calcium and sulfate background concentrations at the beginning of each new experiment. Concentrations of dissolved alabaster should be kept below 20% of its saturation value. The effect of previously dissolved alabaster may be ignored when this is less than 1% of the solubility, for example. Accounting for previously dissolved alabaster requires calculation of changes in ionic strength and background concentrations of calcium and sulfate. This can be done using the lower block of cells at the right hand side of the template (see sections 4.1 and 4.2).

Calculation example for freshwater:

Water volume: 10.0 L

Temperature: 20 °C

Background concentrations in the source water:

calcium: 0.00037 mol/L

sulfate: 0.00012 mol/L

ionic strength: 0.0079 mol/L

Alabaster that has dissolved during previous experiments: 0.2354 g (0.02354 g/L)

Increase in calcium concentration: $0.2354 \text{ g} \div 172.172 \text{ g/mol} \div 10.0 \text{ L} = 0.00014 \text{ mol/L}$

Increase in sulfate concentration is also 0.00014 mol/L

Increase in ionic strength is $\frac{1}{2} (2^2 \cdot 0.00014 + 2^2 \cdot 0.00014) = 0.00056 \text{ mol/L}$

Background concentrations at the start of the new exposure:

calcium: $0.00037 + 0.00014 = 0.00051 \text{ mol/L}$

sulfate: $0.00012 + 0.00014 = 0.00026 \text{ mol/L}$

ionic strength: $0.00790 + 0.00056 = 0.00846 \text{ mol/L}$

Alabaster solubility: 2.67 g/L

Ignoring the effect of previously dissolved alabaster yields a solubility of 2.70 g/L

6. Parallel deployments

Exposing multiple plates at the same time can be considered to reduce workload. For field exposures no change in calculation methods is required, because the water volume is infinite anyway, but for smaller water volumes the fluxes from multiple plates are coupled, because calcium sulfate from one plate reduces the dissolution rate of the other plates. This reduction can be ignored if the calcium sulfate concentrations at the end of the exposure are much smaller than the solubility. In that case the water volume is essentially infinite, and dissolution rates of individual plates are not coupled. In other cases the exact k_w of individual plates is obtained in two steps. First, the average k_w ($k_{w,avg}$) is calculated from the template, using the total mass loss (m_{total}) and the total surface area of all plates (A_{total}) as input parameters.

The k_w for an individual plate is then obtained from

$$k_{w,i} = k_{w,avg} \frac{\Delta m_i}{\Delta m_{avg}}$$

where Δm_{avg} is the average mass loss over all plates. Here it is assumed that all plates have the same surface area.

Calculation example for freshwater:

Three plates of 20.0 mm diameter are exposed in 2.0 L deionized water for 120 min at 18°C.

Mass losses are 0.1033, 0.1254, and 0.0833 g. Average mass loss = 0.1040 g

Total area = $3 \times 3.14 = 9.42 \text{ cm}^2 = 0.0942 \text{ dm}^2$

The template for freshwater yields a solubility of 2.59 g/L and $k_{w,avg} = 18.3 \text{ } \mu\text{m/s}$

The k_w of individual plates are

$$k_{w,1} = 18.3 \times 0.1033/0.1040 = 18.2 \text{ um/s}$$

$$k_{w,2} = 18.3 \times 0.1254/0.1040 = 22.1 \text{ um/s}$$

$$k_{w,3} = 18.3 \times 0.0833/0.1040 = 14.7 \text{ um/s}$$

Values of k_w that are calculated directly from the template, using the individual mass losses and surface areas are ~ 2% lower in this case. The increase in concentrations during the exposure (0.3120 g / 2.0 L = 0.156 g/L) is 6% of the solubility.

7. 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. Using a lathe is easiest. Illustrations are shown here:

<https://www.youtube.com/watch?v=W XKQWO77sNY&t=34s>.

PaSOC can do it for you.

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.

8. Some notes on the use of calcium sulfate k_w in further modelling

Calcium sulfate k_w is often a starting point for further modelling. This can be the estimation of friction velocities, or estimation of the water boundary layer resistance of target analytes in passive sampling. In these applications it should be considered that k_w is not only determined by flow intensity, but also by the diffusion coefficient, albeit weakly. Present knowledge suggests that k_w is proportional to the diffusion coefficient to the power 2/3 (e.g., Opdyke et al., 1987). The k_w of a target compound ($k_{w,i}$) is then related to the k_w of calcium sulfate by

$$k_{w,i} = k_{w,\text{CaSO}_4} \left(\frac{D_{w,i}}{D_{w,\text{CaSO}_4}} \right)^{2/3}$$

8.1. Diffusion coefficients of CaSO_4

The calculation template gives estimates for the value of D_{w,CaSO_4} . The estimation method is slightly different for freshwater than for seawater.

For freshwater, the diffusion of calcium and sulfate ions is coupled, because of the electroneutrality condition (no separation of net charge in water). As a result, the faster diffusing sulfate ions are slowed

down by the slower diffusing calcium ions and vice versa. Calcium sulfate therefore has a well-defined salt diffusion coefficient (eq. 11 from Li and Gregory, 1974). $D_{w,CaSO_4}$ in freshwater can be modelled by

$$\log D_{w,CaSO_4} = 4.593 - \frac{1082}{T}$$

where $D_{w,CaSO_4}$ is given in $10^{-10} \text{ m}^2/\text{s}$ and T is the Kelvin temperature.

For seawater, a salt diffusion coefficient of CaSO_4 is hard to define. Diffusion of sulfate and calcium are not coupled in seawater, because electroneutrality can be satisfied by diffusion of many other ions (see Fig. 1b and 1d from Li and Gregory, 1974). The flux from the alabaster surface is of course the same for calcium and sulfate, but it is harder to assign a diffusion coefficient to this flux. Fortunately it does not matter much if $D_{w,CaSO_4}$ is defined as the arithmetic mean, harmonic mean, or the geometric mean of the ion diffusion coefficient (< 2% difference). The harmonic mean is selected here, but users may adopt other values if needed. The following model is suggested for evaluating the effect of temperature and salinity on $D_{w,CaSO_4}$ in seawater

$$D_{w,CaSO_4} = \frac{815.5}{\eta}$$

where $D_{w,CaSO_4}$ is given in um^2/s and η is the dynamic viscosity of the water (Eqs. 22 and 23 from Sharqawy et al., 2010). Above relationship was based 5 diffusion coefficients from Li and Gregory (3 temperatures for freshwater, 2 temperatures for seawater with salinity = 35 g/kg). Standard error of this model was 5%.

8.2. Diffusion coefficients of target analytes in passive sampling

Diffusion coefficients of organic compounds at 25 °C are conveniently obtained from Fig. 18.10 in Schwarzenbach et al. (2003), who correlated D_w with molecular weight of nonelectrolytes. McGowan molar volume can be used instead (Eq. 17.24a from Schwarzenbach et al., 2016). Diffusion coefficients at other temperatures can be evaluated from the Hayduk-Laudie equation (Hayduk and Laudie, 1974), who showed that the D_w of nonelectrolytes is inversely proportional to the dynamic viscosity of the solvent to the power 1.14. This method is applied in the calculation template for freshwater.

For inorganic analytes the salt diffusion coefficient can be selected when the ionic strength of the exposure water is lower than the analyte concentration. At high ionic strength the tracer diffusion coefficient may be preferred.

9. References

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