Henry's law constant calculation

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Henry's law constants

The Henry's law constant determines the partitioning of a substance between liquid and gas phases such as between the ocean and atmosphere. There are many variants of the Henry's law constant, each of which compares different units. A helpful resource is webpage Sander (2009) which contains a complilation of Henry's law constants, Sander (1999), and allowing allowing interconversion of different units (Sander 2009).

As an example the kH^{CC} of DMS has been calculated to be 5.585 (Steinke *et al.* 2010 submitted), this means that, given equal volumes, the DMS will partition in a ratio of 5.585:1 (aqueous : gas). Therefore 15.2% of the total DMS in the aqueous will volatilise to the gas phase at equilibrium.

This guides described the Henry's law constant determination using an adapted methodology of the multiple equilibration technique of McAuliffe et al (1971) citied in Hunter-Smith et al. (1983).

The technique

- Leave a 100ml syringe and 0.5M NaOH in 30^{o}C incubator in the dark for 1 hour beforehand
- Fill the syringe with 50ml of 0.5M NaOH and 50ml of N_2(l) and inoculate with a set quantity of DMSP.
- The syringe is sealed with parafilm and shaken for 2 minutes.
- It is left at 30^{o}C for 20 minutes then is it re-shaken for a further 2 minutes to assure equilibration
- The N_2(g) within the syringe is then injected into the purge flow line of the P&T at 60ml min^{-1} followed by a further 30ml of N_2(g) from a separate syringe. The DMS in the injected gas will become trapped within the loop and can then be flushed to the GC for measurement.
- The syringe is then refilled with another 50ml of N_2(g) and the process is repeated until 5-6 DMS measurements have been made from one syringe.

- Repeat this process for replication.

Calibration

It is essential to quantify the DMS flushed to the trap, but we do not have a DMS gas standard. To circumvent this problem a 7 minute 1ml purge and trap calibration is performed. This will give you a relative measure of the relative quantity of DMS purged from a series of 1ml volumes of known DMS concentration. The 7 minute 1ml purge has an efficiency of 65.7% (meaning this percentage of DMS in the water is purged from the standard after 7 minutes.

Using the calibration and the known efficiency you can convert the sqrt area result from the GC into a quantity of sulphur.

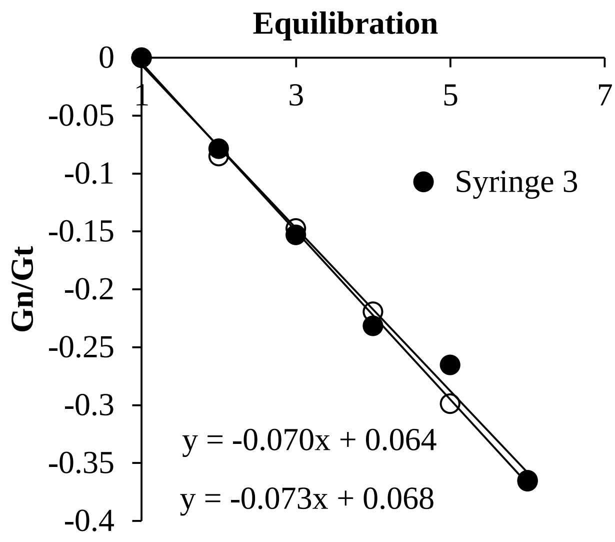

Figure 1. Example McAuliffe plot

Calculating Gn/Gt

For each replicate syringe take the log of the quantity of sulphur in your first sample divided by each equilibration. Equilibration one will be the log of itself divided by itself = 0, while equilibration two will be the log of the first sample divided by the second and so on. Plot the results as in Figure 1.

Calculate the slope of each replicate and take the average. Then calculate H =10^(slope*-1)-1. This gives you the kH^{CC} which is a version of the Henry's law constant, the aqueous concentration/gas concentration (moles/moles). Alternatively this can be reversed to give the KH_{inv}^{CC} ($1/kH^{CC}$).

References

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