# Protocol for running the Fast DMS Sensor

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The Fast DMS Sensor (FDS) is an instrument that can measure real-time changes in DMS production by algal cultures. The instrument utilises the chemiluminescent reaction between ozone and DMS, measuring the light produced in photon counts second$^{-1}$ using a photomultiplier tube (PMT). The instrument can measure at a maximum rate of 0.1 hertz (10 samples second$^{-1}$).

**1) On/Off procedure for the FDS:**

On:

a) Switch on **in order**: Power Switch; Fans Switch; Flow Controllers Switch; Pump Switch.

b) Turn on oxygen supply ("high purity" >99.995%) up to 40 psi on the regulator.

c) Turn on Reaction Cell Switch and Catalyst Switch. (Note the reaction cell switch has a dodgy electrical connection, and occasionally turns itself off mid-sampling. The best way is to have the switch in a 'half-on' position.

d) Wait for the Reaction Cell heater to reach 45°C and the Catalyst heater to reach 140°C. (about 5 minutes)

e) Turn on Ozonizer. Wait 5 minutes for light pulse to go from reaction cell and ozonizer to get up to temperature.

f) Turn on PMT Switch. Now open the FIS Software Oct 07 file on the laptop's desktop. Press Start, and then Cancel when it asks you to save a log file. The software should start reading the background DMS levels every 0.1 seconds without saving a file.

g) Leave for ~1 hour for the signal to stabilise. The readings should be around 100 ± 40 photon counts min$^{-1}$ before running samples.

Off:

a) Switch off the Ozonizer and Catalyst

b) Wait 10 minutes, then switch off Reaction Cell, PMT.

c) Turn off oxygen supply, then turn off Pump, Flow controllers, Fans, Power.

**2) Setting up the Flow Controllers for Sampling**

a) It is important to know what the flow controllers are reading each time you sample. Note there is a switch next to each flow controller LED array on the front – they can be on set or read (self explanatory). Note what you set it to is not always what it reads as!!!

b) The $O_2$ flow controller should always be set at 800 sccm throughout calibration and sampling. This flow controller is normally reliable.

c) The reaction cell flow controller is set to whatever you want the sample flow rate to be at. I However, the reading on its LED array is **not reliable** (it is meant to read the $O_2$ flow rate + sample intake rate). This is probably related to the pump slowly failing. The method used by Green *et al*. (in prep) is to set it to intake sample at **100 ml min$^{-1}$**. To measure this rate, you need to use the bubble flow meter, attaching the FDS sample inlet tube to the top of the glass tube. By turning the reaction cell flow controller knob, a bubble needs rise up the 10ml tube in 6.0 seconds to be sampling at 100ml min$^{-1}$. It normally reads around 1260 sccm on the LED array.

**3) Manually Calibrating the FDS using the DMS standard cylinder**

a) Turn on the 6ppmv DMS standard cylinder to 10 psi (twist regulator knob 1 to fully open, adjust knob 2 so the small regulator meter reads 10 psi).

b) Hold the Bleed Switch on for 15 seconds to flush the sensor. Switch the Calibration ("Standard") Switch to on.

c) Start a new log file. Using the round knob on the Isoprene Standard flow controller, turn it to the right so it is fully open (this is about 19.6 sccm).

d) Let the sensor stabilise and run at this standard concentration for 2 minutes. Using the knob, turn to the left and set at the following standard concentrations, leaving them to stabilise for 2 minutes each time: 10, 5, 2.5, 1.75, 1, 0.5 sccm.

e) Turn off the Calibration Switch, turn off the standard cylinder; hold Bleed Switch open for 15 seconds. To get the zero reading for the calibration, switch on the Zero Switch and leave for 5 minutes (during this time, the sample flow gets passed through the catalytic converter before entering the reaction cell).

f) Turn Zero Switch off. Stop the log file. The FDS returns to sample mode.

g) To calculate the calibrations, open the log file in Notepad. Copy the whole sheet into Excel (you may have to use the 'Text to Columns' function using the comma delimiter). Next, Sort the data using the time(hrs) column to remove the empty cells.

h) Calculate DMS concentration in reaction cell for each standard concentration using the following:

$$[DMS]_{RC} = [DMS]_{st} (F_{st}/F_{RC})$$

where [DMS] = conc. in ppbv, RC = reaction cell, st = standard cylinder, F = flow controller rate in sccm (note $F_{RC}$ = 900 if you have the sample intake rate set at 100 ml $min^{-1}$ and the $O_2$ flow controller set at 800 ml $min^{-1}$).

i) Make a graph of time(hrs) and photon counts. This should enable you to see the changes in standard concentration over the calibration period. Each standard concentration was run for two minutes. For each concentration, ignore the first 30 seconds of data, and calculate the average photon count for the last 90 seconds. Plot this against $[DMS]_{RC}$ for each standard conc, and plot a linear trendline ($y = mx+c$). Note the trendline slope, m. This is the instrument's sensitivity value, *S*. This is important when calculating the DMS sample concentrations.

**4) Manually Calibrating the FDS using Tedlar Bags**

A second option is to calibrate the instrument using 1L Tedlar bags injected with a known amount of DMS gas to make your own standard curve. Whilst this method is mathematically easier, it requires a new calibration to be performed for every different sample intake rate, and also takes approximately ½ a day to run (compared to 30 minutes for the above method).

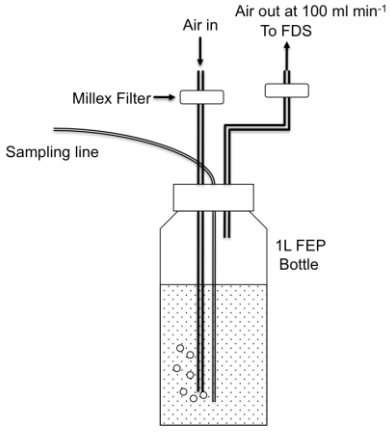
a) Make sure all Tedlar bags are clean by filling them with nitrogen and sucking out completely using a vacuum pump. Repeat this three times. The bags must be completely empty before calibrating.

b) Set System 2 on the FPD Purge & Trap so the $N_2$ gas is flowing through the sample line at 150 ml $min^{-1}$ (see the Purge and Trap protocol on how to do this). Unscrew the line going into the glass wool tube. Screw on the omnifit 'female' adapter for syringes. Attach a Tedlar bag to the line for exactly 6 minutes and 23 seconds. This should fill up the empty bag with exactly 1L of nitrogen gas. It is important to get the flow rate and timing correct for accurate calibration.

c) Using either the 0.1ml or 2.5ml gas syringes and the 100 ppmv DMS standard cylinder with the septum regulator, inject a range of DMS volumes into the Tedlar bag. E.g. 0.1, 0.5, 1, 1.5, 2ml. Calculate the molarity of DMS in the Tedlar bag at STP.

d) Add the FDS 'female' omnifit adapter onto the FDS sample inlet (screws onto Swagelok adaptor). For each Tedlar bag, push into the omnifit adapter and run as an individual sample, logging at 0.1 hz. Also run a zero sample.

e) Repeat parts 'g' and 'i' in method (3), plotting photon counts against molarity, making a standard curve. This can be used directly against samples, **providing that they are running at the same flow rate**.




**5) Running a sample on the FDS**

a) First attach the sample vessel (already containing the culture) to the FDS. All the tubing used should be PTFE, but silicone tubing may be required to get gas-tight seals or to join parts of PTFE tubing together. The sample vessel contains 3 lines: an air inlet line (with attached sterile Millex filter), with a sintered glass bubbler; an air outlet line (also with filter) which leads to the FDS; a smaller 0.2mm PTFE sample outlet tube for taking samples of algae during measurements.

b) To support the FDS pump, positive pressure is used to drive the bubbling. Attach an air pump to the air in line. Using the Restek flow meter, measure the flow of the air outlet line. This should be the same as the sampling rate of the reaction cell flow controller (100 ml $min^{-1}$, see above). If the air pump flow is too high, the ozonizer can leak ozone. If it is too low, a vacuum builds up in the sample vessel and can damage the FDS.

c) Set up LabView to measure at the required rate. Note that sampling at 0.1 Hz for long periods of time (i.e. longer than 2 hours!) will give you huge datasets that Excel/SigmaPlot cannot cope with. Sampling every 10-60 seconds is ideal. Start the log file. Regularly check the FDS for blockages and that the air outlet rate is correct.

d) To access the data in Excel, repeat part (g) in section 3 above. To calculate DMS concentration, $[DMS]_{sample}$, in the sample using the DMS standard calibration method, use the following:

$$[DMS]_{sample} = F_{sample} \times (FIS_{sig} - FIS_{zero}) / S$$

where $F_{sample}$ = sample intake flow rate in sccm, i.e. 100 (ml $min^{-1}$), $FIS_{sig}$ = photon counts $second^{-1}$ of sample, $FIS_{zero}$ = mean photon counts $second^{-1}$ of zero mode measurement, $S$ = instrument sensitivity (see above).

Divide the $[DMS]_{sample}$ by the flow rate to calculate the **DMS production.**

**6) Troubleshooting & important things to note while running the FDS:**

1) **The worst thing that can happen: the $O_2$ cylinder empties whilst the ozonizer is running – this will kill the ozonizer. If running long-term experiments, check the $O_2$ cylinder regularly. One size L/V cylinder normally will run continuously for ~1 week.**

2) If you smell ozone, immediately turn off the ozonizer. This is probably due to the silicone sealant on the white caps of the ozonizer coming loose, and need to be resealed. Also check for damage in the tubing from FDS exhaust port.

3) If the sensitivity value, *S*, is declining rapidly over time, then the reaction cell window probably needs to be cleaned. Note that the window is actually a 317nm short-pass filter, and is a barrier, preventing the ozone in the reaction cell leaking out and coming into contact with the PMT. One side of the filter is coated in a special chemical. This side **must be placed facing the PMT**. If it is placed facing the reaction cell, then the ozone will destroy the filter coating.

4) If seawater gets into the system, the metal sample inlet filter will probably clog up, reducing the sucking strength of the pump. The filter should be cleaned first in milliQ water, sonicated in water and then finally washed in methanol to return it to a good condition.