Vial Headspace Purge (VHP) method for DMS/P measurement

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The vial headspace purge (VHP) method is a way to increase the detection limit of standard DMSP headspace measurements. When working with the standard 4.92 mL vials containing 3 mL of sample in 0.5 mL NaOH, the lower detection limit with a200 µl injection is XXXX. The vial headspace purge can increase the detection limit to ca. 10nM of DMS by measuring the DMS in the whole headspace (1.92mL rather than just 200 µl).

The vial headspace is connected in-line with the purge flow on the Purge and Trap, replacing the purge tube. One minute of N_2 carrier gas is then allowed to flow through the headspace of the vial ending with the DMS cryogenically enriched on the trap.

This method is also used to calibrate the Tedlar bag method. From knowledge of the Henry's law constant for DMS in 0.5 M NaOH at 30^{o}C, the quantity of DMS in the headspace is calculated.

Need:

- Training on Purge and Trap.
- Samples/ standards pre-incubated at 30^{o}C in the dark for at least 6 hours before use.
- VHP adaptor (see figure).
- A Box of Microlance 3 sterile needles.
- dud vial (all on shelf behind purge and trap.

Preparation

- Set-up GC and purge and trap and stop the purge flow.
- The adaptor is attached in place of the purge tube on the purge and trap.
- Attach the needles sticking out the top of the dud vial onto the adaptor.
- Open the purge flow and let the system flush through for a minute.

Vial headspace flush

- Cool the trap to -145-150^{o}C and made sure the vial and trap are in-line.
- Stop the N_2(g) flow and remove the dud vial complete with needles.
- Attach two new sterile needles onto the luer fittings of the adaptor.
- The inflow needle (stop valve side) should ALWAYS be lower than the outflow needle. If the outflow needle pierces first then liquid on the inside of the septa can get sucked into the system causing contamination.
- Pierce the needles into the headspace of a first sample vial
- Do NOT push the needles in so far they are submerged
- The vial will now 'hang', held by the needles
- Open the stop valve for 60 seconds then close it.
- Remove the calibration vial along with its needles and place to the side.

- Re-attach the dud vial and flush the system for 10 seconds (this flushes all the DMS remaining within the system to the trap
- Flush the sample to the GC as normal.

Disposal of needles

- All removable needles left in vials must be placed in a yellow sharps box for disposal.

Calibration of the system

- DMS standards are created with known quantities of DMS gas in the headspace of 4.92 mL vials.
- Make these the day before you need them and store overnight in the 30^{o}C incubator in XXX
- Depending on the peak area of DMS in your samples, prepare duplicate vials depending on the range of the calibration needed.

- A linear calibration line of the sqrt areas v pmol DMS is used to calculate the quantity of DMS in each peak (Q) in pmol.

Table 1. Calibration standards for low DMS_{air} measurements, all made in 4.92 mL vials containing 3 mL 0.5 M NaOH. DMS in gas phase calculated using the KH_{CC} of DMS in 0.5 M NaOH at 30^{o}C of 5.585.

	DMSP standard amount (µl)				Initial [DMSP] in liquid (nM)	DMS in gas phase at 30^{o}C (pmol)
Vial number	**7.5uM**	**75uM**	**7.5mM**	**7.5mM**		
1L	4				9.99	3.07
2L	8				19.95	6.13
3L		2			49.97	15.40
4L		4			99.87	30.75
5L		10			249.17	76.52
6L			2		499.67	153.98

Table 2. Calibration standards for high DMS_{air} measurements, all made in 4.92 mL vials containing 3 mL 0.5 M NaOH. DMS in gas phase calculated using the KH_{CC} of DMS in 0.5 M NaOH at 30^{o}C of 5.585.

	DMSP standard amount (µl)				Initial [DMSP] in liquid (mM)	DMS in gas phase at 30^{o}C (pmol)
Vial number	**7.5uM**	**75uM**	**7.5mM**	**7.5mM**		
1H		10			0.25	76.52
2H			2		0.50	153.98
3H			4		1.00	307.49
4H			8		1.99	613.09
5H				2	5.00	1539.81
6H				4	9.99	3074.89