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M.J. Singleton, G.B. Hudson

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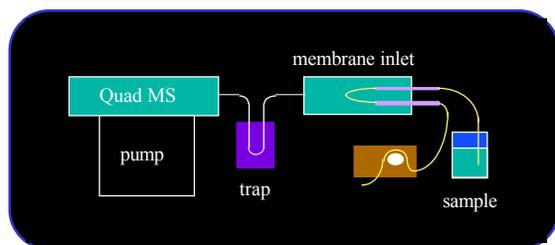
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## Membrane Inlet Mass Spectrometry for measuring dissolved gases

Michael J. Singleton and G. Bryant Hudson

### Overview

A Membrane Inlet Mass Spectrometer (MIMS) is used to measure dissolved gas concentrations in environmental water samples. Gases are exsolved out of water by passing the sample through a silicone gas permeable membrane that is under vacuum. A quadrupole mass spectrometer attached to the vacuum system is capable of measuring a variety of gases over a wide range of concentration. The MIMS is a versatile and field portable instrument.



**Figure 1.** Schematic of the Membrane Inlet Mass Spectrometer.

### Sample Collection

Dissolved gas samples are collected in 40 mL, amber glass vials (EPA VOA with screw-top septa). The vials are filled to the top with no headspace, and bubbles are carefully avoided. Samples are taken in triplicate. Samples are stored on ice and analyzed within 24 hours of collection.

### Sample Analysis

Dissolved gas analyses are carried out on a MIMS, based on the technique described by Kana (*Anal. Chem.*, 1994, 66, 4166-4170). The MIMS consists of a vacuum inlet fitted with gas permeable silicone tubing. The inlet allows gas to pass into the vacuum system, where it is routed through a cold trap (crushed dry ice) and into a SRA RGA200 quadrupole mass spectrometer. Water from samples or standards is pumped through the membrane using a Gilson peristaltic pump at 1 mL/minute. Masses monitored include those expected for the gases CH<sub>4</sub>, N<sub>2</sub>, Ar, O<sub>2</sub>, and CO<sub>2</sub> (15, 28, 40, 32, and 44). Mass 15 is used for CH<sub>4</sub> to avoid interferences from O<sub>2</sub> and CO<sub>2</sub>.

### Standards

The primary standard for MIMS analyses is air-equilibrated water. This standard is prepared by allowing a bottle of de-ionized water to sit at room temperature and pressure for at least 24 hours. The bottle is fitted with a plastic cap, which has been perforated by a 1 mm hole in order to maintain room pressure and keep humidity close to 100% inside the bottle.

The temperature of the standard water is recorded (to +/- 0.01 °C) prior to running a set of unknown samples. Standards are prepared by filling (with no headspace) VOA

vials with air-equilibrated water. Standards and unknowns are then placed in a room temperature water bath for at least 30 minutes.

Due to the very low concentration of CH<sub>4</sub> in air, a separate standard is used to calibrate CH<sub>4</sub> data. This standard is prepared by bubbling CH<sub>4</sub> (as natural gas) through a bottle of de-ionized water.

### Blanks

At the beginning of a run, the peristaltic pump is turned off to record the background or “zero” pressure in the system. A background reading ( $P_{background}$ ) is taken once all gas pressures reach steady values with no liquid flowing in the system. Unknowns are bracketed by a background reading and a standard for every 3-4 samples.

### Data Reduction

Real-time partial pressure data is collected at 3 second intervals for each gas of interest. Five readings from the RGA quadrupole are averaged for each sample.

There is a slight interference caused by CO<sub>2</sub> at mass 28 (N<sub>2</sub>). In order to correct for this effect, a calibration of the instrument was carried out using a range of mixtures between pure research grade tanks of CO<sub>2</sub> and N<sub>2</sub> gas. The compositions of the gas mixtures were set using mass flow controllers. From this calibration it was determined that 1.85% of the CO<sub>2</sub> measured pressure contributes to the pressure measured at mass 28. The N<sub>2</sub> pressure is corrected with the following equation to remove this effect:

$$P_{corr_{N_2}} = P_{meas_{N_2}} - 0.0185P_{meas_{CO_2}}$$

The measured partial pressure for each gas ( $P_o$ ) is then normalized to air-equilibrated water using the equation:

$$p_{rel} = \frac{P_{meas} - P_{background}}{P_{standard} - P_{background}}$$

### Data Reporting

Dissolved CO<sub>2</sub> and CH<sub>4</sub> are reported relative to DI water in equilibrium with 1 atm of pure gas. For CO<sub>2</sub> this fraction is calculated assuming an air concentration of 330 ppm. The CH<sub>4</sub> content is calculated relative to the DI water standard equilibrated with 1atm of natural gas.

The relative pressure values ( $p_{rel}$ ) are converted to cm<sup>3</sup> at STP based on the equilibrium concentrations of N<sub>2</sub>, O<sub>2</sub>, and Ar in water at the temperature recorded for the standard water at the time when the VOA vials were filled. The solubilities of N<sub>2</sub>, O<sub>2</sub>, and Ar in water are calculated as moles of gas per mole of water ( $X$ ) using the equation:  
 $\ln X = A + 100B/T + C \ln(T/100)$

where  $T$  is temperature in degrees Kelvin, and parameters  $A$ ,  $B$  and  $C$  are constants particular to each gas as listed in the *CRC Handbook of Chemistry and Physics*.

The correction factor for the effect of elevation on gas pressure is accounted for using the barometric formula:

$$a_h = e^{-mgh/kT}$$

where  $m$  is the average atomic mass of the atmosphere (29 amu),  $g$  is the gravitational acceleration constant ( $9.81 \text{ m/s}^2$ ),  $h$  is the height above sea level (183 m for LLNL),  $k$  is the gas constant divided by Avogadro's number, and  $T$  is the temperature in degrees Kelvin.

The concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and Ar in units of  $\text{cm}^3$  at STP/g water ( $C$ ) are calculated from the equation.

$$C = 22414 \times a_h P_{\text{rel}}$$

where the constant ( $22414 \text{ cm}^3$  at STP/g/mole) is from the ideal gas law.

### Laboratory Reporting Conventions

The detection limit for each gas is determined based on variability in the instrument background during each individual run. Typical values for the detection limit are as follows:

$\text{CH}_4$	0.02% relative to 1 atm of $\text{CH}_4$ in equilibrium with DI water
$\text{N}_2$	$2 \times 10^{-4} \text{ cm}^3$ at STP/g water
$\text{O}_2$	$4 \times 10^{-4} \text{ cm}^3$ at STP/g water
Ar	$2 \times 10^{-6} \text{ cm}^3$ at STP/g water
$\text{CO}_2$	0.02% relative to 1 atm of $\text{CO}_2$ in equilibrium with DI water

### Quality Control

The variability for each run is calculated based on repeated runs of the air-equilibrated water standard. The relative standard deviation ( $1-\sigma$ ) is typically 1-2% of the measured value for  $\text{N}_2$ , Ar, and  $\text{O}_2$ . The measured values for  $\text{CO}_2$  and  $\text{CH}_4$  typically vary by 5-8%.

At least 10% of the unknown samples are run in duplicate. The run is considered acceptable if the variation in duplicate samples falls within the variability of the standards. The final value for duplicate samples is calculated as an average of the two runs.

### Acknowledgements

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### References Sited

Kana, T. M.; Darkangelo, C.; Hunt, M. D.; Oldham, J. B.; Bennett, G. E.; Cornwell, J. C. Membrane inlet mass spectrometer for rapid high-precision determination of nitrogen, oxygen, and argon in environmental water samples. *Anal. Chem* **1994**, *66*, 4166-4170.