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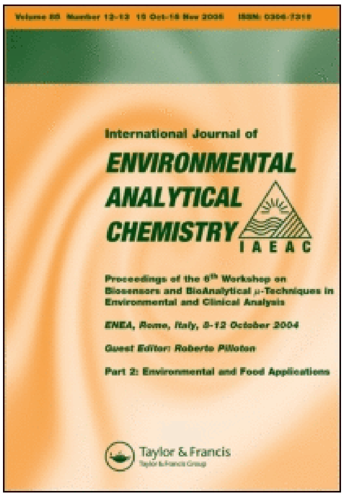

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A Headspace Equilibration Technique for Measurement of Dissolved Gases in Sediment Pore Water

Nicholas J. Fendinger[a]; Donald D. Adams[b]
[a] Chesapeake Biological Laboratory, Solomon, MD, U.S.A. [b] Center for Earth and Environmental Science, State University of New York, Plattsburgh, NY, U.S.A.

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A Headspace Equilibration Technique for Measurement of Dissolved Gases in Sediment Pore Water

NICHOLAS J. FENDINGER
Chesapeake Biological Laboratory, Solomons, MD 20688, U.S.A.

and

DONALD D. ADAMS
Center for Earth and Environmental Science, State University of New York, Plattsburgh, NY 12901, U.S.A.

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Multiphase headspace equilibration with gas chromatographic analysis was used for the simultaneous analysis of CH_4 and N_2 in Lake Erie sediment pore water, with total CO_2 concentrations determined on a separate duplicate sediment sample. The minimum detectable concentrations of Ar, N_2, CO_2, and CH_4 in a Lake Erie sediment were 1.55, 0.96, 2.50, and 1.01 ml/L, respectively, using a thermal conductivity detector. Precision of the dissolved gas analysis ranged from ±0.24 to ±0.41 ml/L.

KEY WORDS: Headspace equilibration, sediment pore water, dissolved gases.

INTRODUCTION

Measurements of sediment pore water gases (N_2, CH_4, Ar, and CO_2) have been used to assess eutrophic status of lakes,[1] microbial activity in sediments,[2] and in sediment oxygen demand studies.[3] Analysis of dissolved pore water gases usually consist of two steps: (1) extraction of pore water from the sediment with a squeezer[4–6] and (2) stripping of dissolved gases from the extracted pore water by an inert gas followed by gas chromatographic (GC) analysis.[7–10] The analysis usually requires bulky, specialized equipment, a large sediment sample to obtain a sufficient amount of pore water for GC analysis, and is time consuming.

An alternative pore water gas analysis technique is by multiphase equilibration with an inert headspace. This approach has been used successfully by Bernard *et al.*[11] to determine light hydrocarbons in Recent Texas continental sediments and by McAuliffe[12] to determine the solubilities of hydrocarbons in water. Described below is a rapid headspace equilibration technique for the simultaneous analysis of $Ar+O_2$, N_2, and CH_4 in sediment pore water. With subsequent analyses Ar, O_2, and total CO_2 concentrations can also be determined.

MATERIALS AND METHODS

Gas chromatograph

The GC used for the analyses was a Carle Model 311M equipped with four microvalves, three columns, and two detectors (Figure 1). The columns used for the separation of analyzed gases included: 370 cm × 0.32 cm with 50/80 Porapak N, 240 cm × 0.32 cm with molecular sieve 5A, and 15 cm × 0.64 cm with 42/60 activated coconut charcoal. The thermal conductivity detector was used for routine analyses. Automation of the four microvalves aided in the analysis.

Reagents

10% degassed saline solution prepared by boiling 10% (W/W) NaCl solution and simultaneously purging with helium (He). The solution was stored in a stainless steel container pressurized with He.

Sediment collection and processing

Replicate sediment cores were collected at a station in the deepest portion of Lake Erie's eastern basin for two separate types of processing: (1) measurement of pore water concentrations of Ar, N_2,

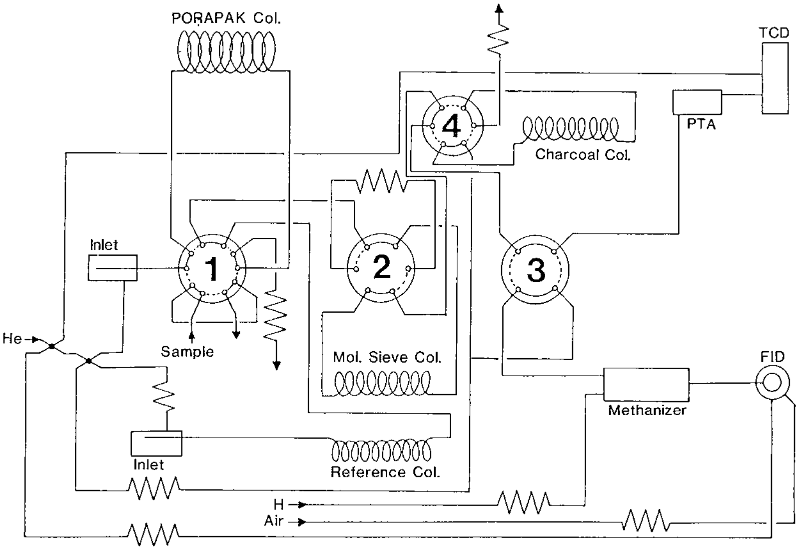

FIGURE 1 Schematic of the modified Carle 311M gas chromatograph. Clockwise (CW) positions are represented by dashed lines and counterclockwise (CCW) positions are represented by the solid lines.

and CH_4, and (2) pore water concentrations of total CO_2 gas. Coring was conducted by free-fall with a model 2171 Benthos (Benthos Inc., Falmouth, MA) gravity coring with 120 cm × 6.5 cm i.d. clear plastic core tubes, modified by drilling 2.8 cm holes (sampling ports) arranged at 90° to each other and at 3 to 5 cm intervals. Clear duct tape was used to retain sediment in the core tubes.

Upon collection of the sediment cores, the overlying water was carefully removed by depressing a machined piston into the core tube to the sediment-water interface. The piston was fitted with a nipple and a length of rubber tubing to allow the overlying water to drain out of the core tube. The core length and temperature were recorded immediately following the removal of overlying water. Cores were refrigerated and subsampled within 3 hours after collection.

The sediment core tubes were placed horizontally into a glove box under an atmosphere of He. An oxygen meter was used to monitor air contamination in the glove box during processing (usually 0.5 ppm O_2 or less). The clear plastic retaining tape was quickly cut and the sediments were subsampled through the sampling ports with 50 ml disposable plastic syringes with their Luer-lok ends removed. All the open-ended syringes were placed in the ports before removing wet sediments from the core. A measured amount (20–30 ml) of sediment was displaced from the open-ended syringes into unaltered 50 ml glass syringes. The plunger handles were machined smaller to allow unrestricted passage through the syringe barrel. A small sediment aliquot (1–2 gm) was dispensed into a preweighed vial and capped for analysis of water content. A plastic Luer-lok cap, fitted with a 8.0 mm septa, was then attached to the syringe. The front portion of the syringe was sealed with wax and about 4 cm of hot wax was poured onto the back side of the plunger and allowed to cool within the syringe barrel. Syringes containing the sediment subsamples were refrigerated until analysis. A 80–100 cm core usually took 20–40 minutes to process sediments for 14–20 syringes.

Surface sediments were also collected in Lake Erie's central basin with an Ekman dredge. These sediments, homogenized in the glove box, were used for sample preservation experiments and the analysis of gas measurement variability. Processing of the homogenized sediment for syringe storage experiments was accomplished as described above.

Multiphase headspace equilibration

Sediments for N_2 and CH_4 analyses were equilibrated at room temperature immediately before injection of 10 ml of the 10% degassed salt solution. A 20 ml helium headspace was then injected into the sediment slurry. The sediment slurry with headspace was vigorously agitated for 2 minutes before gas chromatographic analysis of the equilibrated headspace. Additions of the saline solution and helium headspace, and injection of the headspace into the GC sample loop, were accomplished with a four-way valve to minimize atmospheric contamination.

Measurements of total CO_2 were accomplished with sediments from a duplicate core using the same syringe sampling technique. Sediments were equilibrated at room temperature immediately before addition of 30 ml 10% degassed saline solution to each syringe. The sediment slurry was agitated for 1 hour, then refrigerated to allow sediments to settle. The supernatent water was filtered with an in-line glass fiber filter during transference to a second 50 ml plastic syringe. The exact volume of filtered water was determined by weight difference. After addition of a 20 ml He headspace, the solution was acidified to a pH 2 with concentrated HCl and agitated for 2 minutes before injection of the equilibrated headspace.

Headspace analysis

Simultaneous analysis of $O_2 + Ar$, N_2, and CH_4 was accomplished by maintaining the Porapak N column at 90°C in an external hot water bath and operating the other chromatographic columns isothermally at 30°C. Peak areas were recorded on a strip chart for permanent record and were electronically integrated. A typical chromatogram is illustrated in Figure 2 with explanations found in Table I.

TABLE I

Valve sequence for the analysis of $Ar + O_2$, N_2, and CH_4. Initial valve settings: V1-CCW, V2-CCW, V3-CCW, and V4-CCW

Valve switch	Time (sec)	Comments
A: V1-CW	0	Introduction of a 2 ml sample.
B: V2-CW	140	Molecular sieve column is by-passed. $Ar + O_2$, N_2 and CH_4 are detained on the molecular sieve column. CO_2 is eluted from the Porapak N column.
C: V2-CCW	300	$Ar + O_2$, N_2, and CH_4 are released from the molecular sieve column.
D: V3-CW	900	Optional valve switch for the detection of CH_4 concentrations of less than 2.50 ml/L.

The presence of dissolved oxygen in the samples was periodically assessed by engaging the charcoal column and measuring the Ar peak. Because the charcoal column adsorbs O_2 irreversibly,[13] any differences between this peak and the previous $Ar + O_2$ peak would indicate the presence of dissolved oxygen. An explanation of this valve sequence is found in Table II and a typical chromatogram is illustrated in Figure 3.

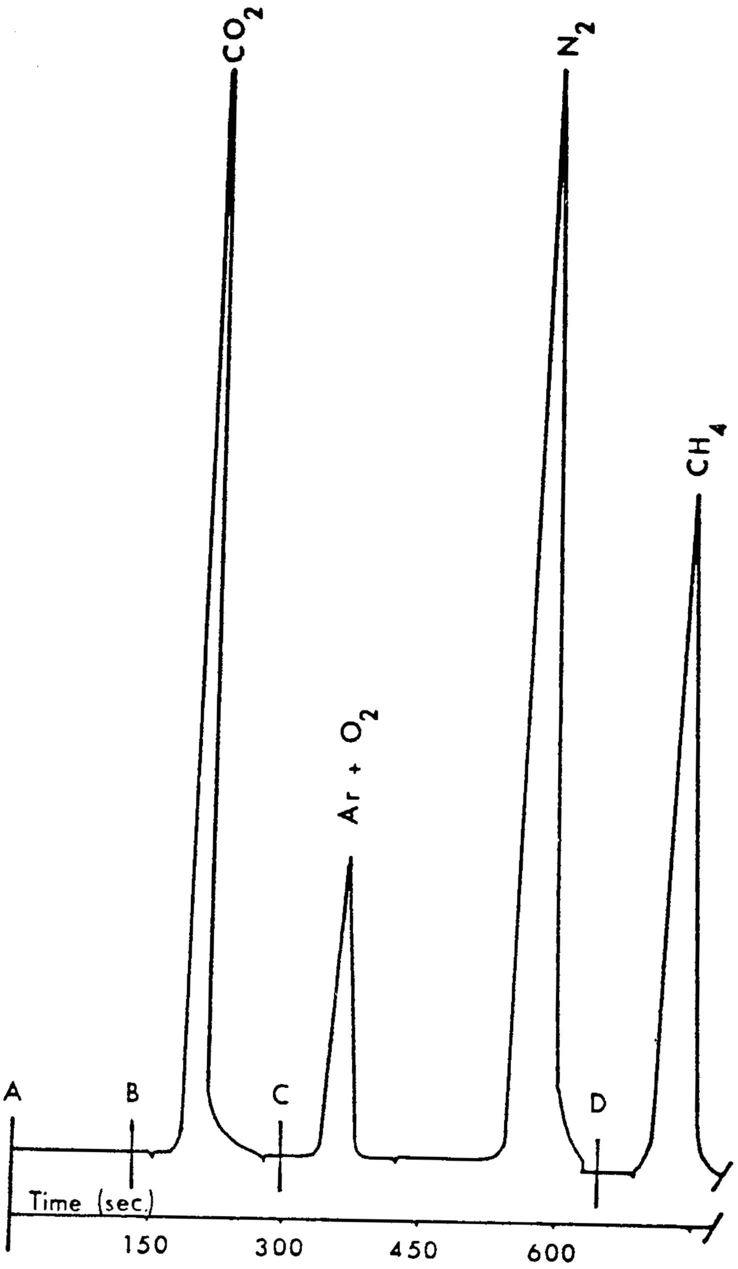

FIGURE 2 A typical chromatogram for the analysis of Ar+O_2, N_2, and CH_4. A complete explanation is found in Table I.

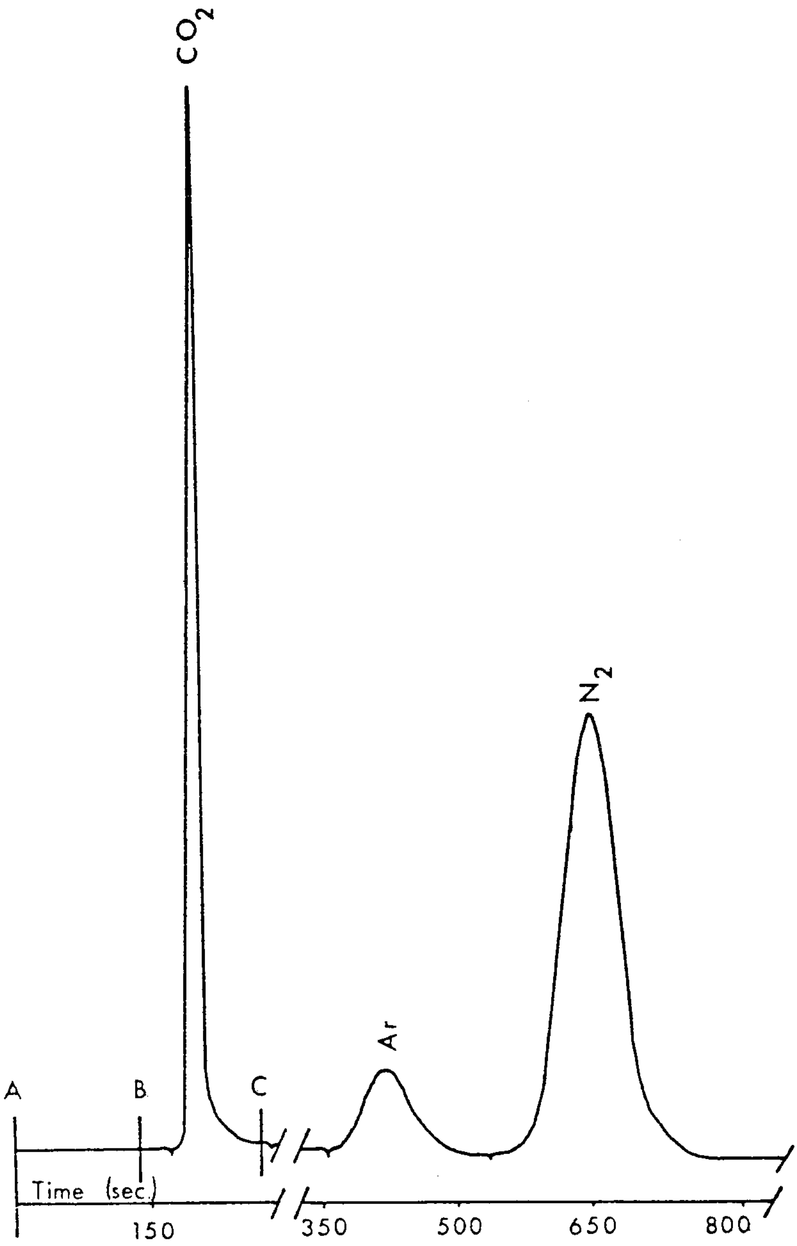

FIGURE 3 A typical chromatogram with the charcoal column employed to assess the levels of dissolved oxygen. A complete explanation of the valve sequence is found in Table II.

TABLE II

Valve sequence for the analysis of Ar and N_2. Initial valve settings: V1-CCW, V2-CCW, V3-CCW, and V4-CCW

Valve switch	Time (sec)	Comments
A: V1-CW	0	Introduction of a 2 ml sample.
B: V2-CW	140	Molecular sieve column is by-passed. $Ar+O_2$, N_2, and CH_4 are detained on the molecular sieve column. CO_2 is eluted from the Porapak N column.
C: V4-CW V2-CCW	300	The charcoal column is engaged. $Ar+O_2$, N_2, and CH_4 are released from the molecular sieve column. O_2 is irreversibly absorbed on the charcoal column. Ar and N_2 are eluted; CH_4 is vented.

Total carbon dioxide was determined with the Porapak N column by placing V2 in the CW position. A 2.0 ml sample was introduced with the sample loop by activating V1 to the CW position. The Porapak N column was maintained at 25°C. Methane, N_2, and Ar eluted as a single peak followed by CO_2.

The chromatograph was routinely standardized by pressurizing a certified gas mixture within the 2.0 ml sample loop. The previously described valve sequence was then used. Alternatively, a pure gas was injected through the inlet with a 100 μl gas-tight syringe by placing V1 in the CW position and engaging the appropriate column. Detection limits using the thermal conductivity detector and flame ionization detector are listed in Table III.

Concentrations of CH_4, Ar, and N_2 in the sediment interstitial water were calculated using the observed concentration in the equilibrated headspace (H_c), a dilution factor (D_f), and the volume of interstitial water (I_w) by the equation:

$$\text{Sediment Concentration} = (H_c)(D_f)/I_w.$$

The dilution factor was calculated from the volume of the original headspace divided by the volume of the sample loop. The total concentration of N_2 and Ar was determined by multiplying the observed concentration by the appropriate distribution coefficient as

TABLE III

Detection limits for the thermal conductivity detector and the flame ionization detector

Gas detected	Minimum detectable quantity ($ml \times 10^{-3}$) FID	TCD	Minimum sediment/water detectable concentration (ml/L)[a] FID	TCD
Ar	—	1.03	—	1.55
O_2	—	0.98	—	—
N_2	—	0.64	—	0.96
CO_2	—	1.67	—	2.50
CH_4	0.017	0.68	0.026	1.01

[a] Calculation assuming a 30 ml headspace and a 20 ml sediment sample ($\%H_2O = 50$).

described by McAuliffe.[14] Distribution coefficients were based on successive gas chromatographic analyses after repeated helium headspace equilibrations of the same sediment/water slurry. These were calculated by back-extrapolating to the total concentration from a plot of gas peak area versus the number of equilibrations. A distribution coefficient was not used for methane because multiple equilibration experiments showed that the amount of CH_4 remaining dissolved in the sediment/water slurry after an initial headspace equilibration constituted less than 2%.

Total CO_2 concentrations were calculated in a similar manner. A second dilution factor was used to account for the 30 ml of degassed water added to the sediment. As with methane, a distribution coefficient was not used because over 98% of the CO_2 partitioned into the headspace after the first headspace equilibration.

RESULTS AND DISCUSSION

Sample storage

Although analysis of the samples was completed within two weeks after collection, the samples maintained their integrity for up to one month in preservation experiments with homogenized sediment using the syringe storage technique. The variability in CH_4 concentrations was less than 10% during the entire span of the experiment when stored at 4°C. Precision for the measurement of CH_4 was ±0.24 ml/L. Nitrogen gas concentrations also remained constant (±3%) in the sediment subsamples for the duration of the storage experiment at 4°C. Statistics were calculated for the 95% confidence interval (2 sigma).

Method verification

The reproducibility and accuracy of the syringe storage technique and gas analysis were determined with successive analyses of air saturated distilled water for N_2 and O_2. Observed concentrations were compared with interpolated solubilities of these gases in distilled water.[15–17] Results of this experiment are shown in Table IV. Precision of the analysis for N_2 and O_2 were found to be ±0.41 ml/L and ±0.24 ml/L (at the 95% confidence interval), respectively.

Argon concentrations in the distilled water approximated the minimum detectable concentration of the technique. This was also the situation encountered in the analysis of Lake Erie sediments. In its present state, the charcoal column used in conjunction with the molecular sieve and Porapak columns can only be used to assess

TABLE IV

Reproducibility of the dissolved gas analysis of air saturated distilled water by headspace analysis

	Concentrations of dissolved gases (ml/L)	
Sample	O_2	N_2
1	6.51	11.14
2	7.21	13.15
3	6.90	12.65
4	7.11	12.01
5	7.07	12.65
Mean	6.96	12.52
Solubility[15,16,17]	6.61	12.37

TABLE V

Reproducibility of the total CO_2 analysis of a sodium carbonate solution by headspace equilibration

Sample	Total CO_2 *concentration* (ml/L)
1	115.67
2	119.09
3	120.31
4	118.60
5	117.38
Mean	118.31
Actual Concentration	108.33
Standard Deviation	± 1.58

oxygen contamination in the headspace when sediments are analyzed.

The integrity of the analysis for CO_2 was determined with successive analyses of a sodium carbonate standard solution prepared with degassed, deionized water. Results of this analysis are given in Table V.

Sediment analysis

Results of the gas measurements made on two cores collected in Lake Erie's eastern basin are shown in Figure 4. Values reported are the mean from two to three duplicate analyses of the equilibrated headspace.

Methane distribution in Lake Erie's eastern basin decreased slightly with depth in the sediment. Nitrogen concentrations as high as 173% above the concentration expected from equilibration with nitrogen saturated overlying water were measured in the surface 10 cm sediments.[18] Atmospheric contamination of the samples was not a source of the enriched N_2 concentrations because this would have been reflected in anomalously high Ar concentrations and the presence of O_2. The distributions of CH_4 and N_2 appear to be controlled by biological activity rather than physical bubble stripping processes suggested by Reeburgh[10] for Chesapeake Bay sediments.

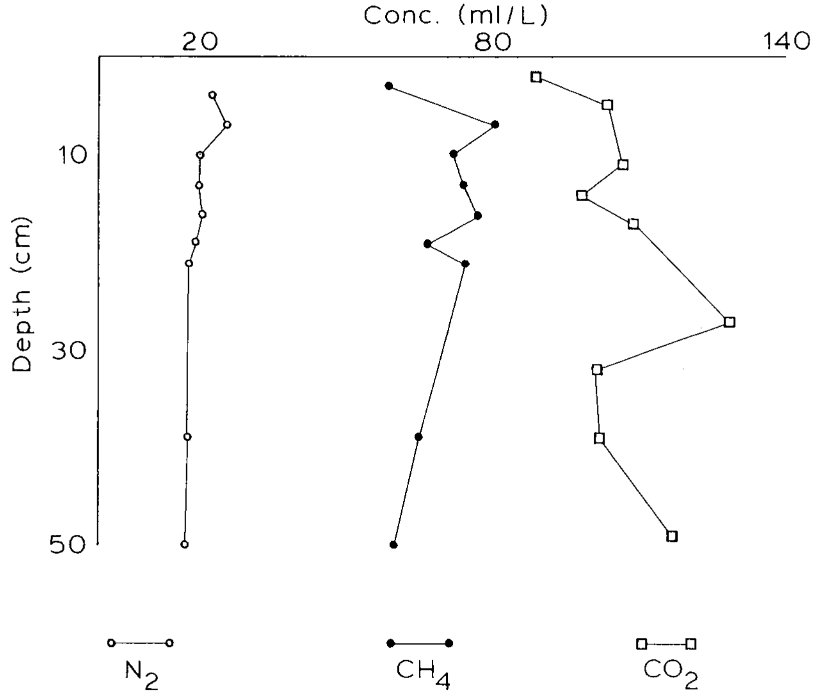

FIGURE 4 Distribution of dissolved gases in the sediment pore water of Lake Erie eastern basin sediments.

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