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Journal

Environmental Science and Technology, 2(2)

ISSN

0013-936X

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Publication Date

1968-02-01

DOI

10.1021/es60014a004

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Peer reviewed

Determination of Gases in Sediments

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■ A method was developed for sampling and analysis of gases contained in interstitial water. Interstitial water was separated from sediments with a filter press-type sediment squeezer and transferred to a specially designed sampler-stripper. Gases contained in the interstitial water were stripped from solution and analyzed by gas chromatography. Argon, N₂, and CH₄ have been measured in sediments. The technique can be used to measure total CO₂ and H₂S with minor modifications.

Because of the large differences in the gas composition of sediments and the overlying water, measurements of gases in sediments should be useful in interpreting the physical and chemical processes taking place at the sediment-water interface. Studies of the depth distributions of gases in sediments have been limited by lack of a suitable gas-sampling and extraction method. Previous studies (Emery and Hoggan, 1958; Koyama, 1953) have involved extraction of gases from slurries of sediment samples and gas-free water by vacuum or stripping, and analysis by manometry, mass spectrometry, or gas chromatography. Gas concentrations in milliliters per liter of interstitial water were estimated either by parallel determinations of sediment water content or by assuming the concentration of N₂ to be identical in the sediment and overlying water and using it as an internal standard. Duplication was not attempted and the data suggest contamination by atmospheric gases.

In the following procedure, interstitial water was separated from the sediment with a filter press-type sediment squeezer (Reeburgh, 1967); varying volumes of interstitial water were sampled in triplicate and analyzed using a liquid stripping gas chromatographic technique similar to that of Swinnerton, Linnenbom, *et al.* (1962a).

Depth distributions of Ar, N₂, and CH₄ concentrations were obtained in Chesapeake Bay sediments using a Fisher Model 29 gas partitioner with He as carrier gas. For these gases, the partitioner was equipped with a Molecular Sieve 5A column (8 feet × 3/16 inch) and was fitted with an external sample inlet (Figure 1) consisting of a four-way bypass valve, columns containing Mallcosorb and Drierite for removal of carbon dioxide and water, and a bulkhead for mounting the sampler-stripper.

Figure 1 also shows the sampler-stripper, which consists of a length of graduated 10-mm. I.D. glass tubing mounted between two 120°-bore pressure stopcocks. A coarse-porosity glass frit welded in one end of the sample chamber serves to disperse the carrier gas into fine bubbles which strip the dissolved gases from solution. The outer loop of the sampler-stripper is constructed of 2-mm. I.D. capillary and used to flush the inlet leads prior to sampling and analysis. To obtain reliable measurements of Ar, which is not separated from O₂ by molecular sieve columns under ordinary conditions, a few milliliters of 0.1N CrSO₄ solution (Lingane and Pecsok,

1948) were placed in each sampler-stripper to reduce O₂ quantitatively. The CrSO₄ solution was stripped with carrier gas prior to sampling. The CrSO₄ enhanced the production of small bubbles, so that tailing due to inefficient stripping (Swinnerton, Linnenbom, *et al.*, 1962b) was no problem. The sampler-strippers have been successfully used for remote sampling and for storage of samples.

Sediment samples were obtained using a Benthos Model 2170 gravity corer with a 2.57-inch I.D. coring tube. The sediment squeezers were filled with sediment inside a well-flushed glove bag filled with either CO₂ or He by extruding samples from the coring tube at suitable depths. The squeezers were assembled and pressurized inside the glove bag. After interstitial water had been allowed to flow for a short time, the squeezers were capped and stored in an ice chest until sampling was begun. The nylon screens usually used as filter supports in the squeezers trapped bubbles of the glove bag contents during the loading operation and led to variable results. A stack of paper filters was substituted for the nylon screens and released these bubbles when the squeezers were pressurized.

Interstitial water was sampled by attaching the sampler-stripper to the squeezer with a glass tubing adapter. The sampler-stripper was inverted so that the frit did not come in contact with the sample solution. After the interstitial water

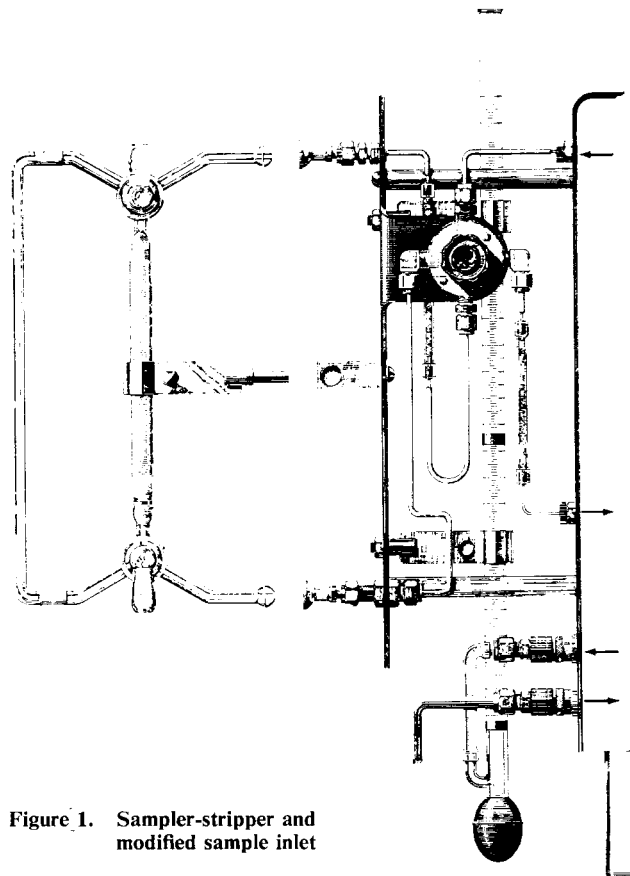


Figure 1. Sampler-stripper and modified sample inlet

Table I. Reproducibility of Determination of Gases in Sediments

Gas	Depth	Gas Concentration, Ml./L.		
		Core I	Core II	Core III
Ar	Surface	0.349	0.324	0.344
		0.365	0.333	0.339
		0.448	0.381	0.331
	Mean, %	0.387 ± 13.7	0.346 ± 8.9	0.338 ± 1.9
	100 cm.	0.121	0.115	0.140
		0.101	0.085	0.156
0.102		0.100	0.123	
Mean, %	0.108 ± 10.4	0.100 ± 15.0	0.140 ± 11.8	
N ₂	Surface	13.51	12.74	13.57
		13.83	12.67	13.73
		15.46	13.06	13.37
	Mean, %	14.27 ± 7.3	12.82 ± 1.6	13.37 ± 1.3
	100 cm.	2.26	1.84	3.28
		2.05	2.21	3.44
1.94		1.64	2.76	
Mean, %	2.08 ± 7.8	1.90 ± 15.2	3.16 ± 11.2	
CH ₄	Surface	0.00	0.00	0.00
	100 cm.	149.5	148.0	163.2
		142.0	151.5	151.2
		125.2	120.7	138.9
	Mean, %	138.9 ± 9.0	140.1 ± 12.0	151.1 ± 8.0

had been allowed to flush the outer loop and the adapter and sample inlet bores were free of bubbles, the lower stopcock was opened slightly and a sample of 4 to 5 ml. was taken. The absence of bubbles and leaks in the flowing sample stream indicated no means for loss or contamination of the sample. The sample volume was measured as the difference between the initial CrSO₄ volume and the final volume. The outer loop of the sampler-stripper was dried, and the sampler-stripper was attached to the gas partitioner oriented so that the sample came in contact with the frit. The leads were flushed with carrier gas and stripping was begun by turning the stopcocks so that carrier gas flowed through the frit and sample. Peak areas were measured with a Disc integrator.

The partitioner was calibrated for Ar and N₂ by analyzing samples of air-equilibrated distilled water. Methane standards were injected with a mercury-calibrated gas-tight syringe. Relative standard deviations for calibrations of Ar, N₂, and CH₄ were, respectively, 3, 1, and 1%.

Attempts to prepare synthetic sediment standards of known gas content were unsuccessful because the necessarily high water content of these sediments prevented sampling by coring. To estimate over-all precision, replicate field measurements were undertaken in an area where horizontal variations in gas content were expected to be small. Table I gives the results of a field experiment in which three sediment cores were taken at the same station and sampled at the surface and 1-meter depth. Although the precision is somewhat poorer than for distilled water standards, *t* and *F* tests show that the means and variances do not differ at the 0.1% level. The poorer precision for natural samples may be due to the procedure or to natural inhomogeneities within the sediment interval

sampled. The high CH₄ values at depth and variations in precision with depth suggest the latter.

In Chesapeake Bay sediments, the CH₄ concentration varied with water depth and was near saturation at depths in the sediment of about 1 meter. The low concentrations of Ar and N₂ observed in deeper parts of the cores appear to be the result of in situ stripping by CH₄ bubbles. Surface sediment samples contained no CH₄ and had Ar and N₂ concentrations near that of the overlying water.

A limited number of total CO₂ and H₂S determinations have been made using a short silica gel column in the partitioner. Magnesium perchlorate was used as desiccant and dilute H₂SO₄ was used in the sampler-stripper. The large concentration differences observed between these gases in the interstitial waters studied make simultaneous analysis difficult and require use of different sample volumes for each gas.

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Received for review October 2, 1967. Accepted January 17, 1968. Contribution 114 from the Chesapeake Bay Institute and the Department of Oceanography, The Johns Hopkins University. Work supported by U. S. Atomic Energy Commission Contract AT(30-1)-3497. Doc. No. NY0-3497-14.