

Analysis of Dissolved Gases by Headspace Sampling Gas Chromatography With Column and Detector Switching. Preliminary Results

Communications



Pierre-Marie Sarradin and Jean-Claude Caprais

IFREMER Centre de Brest, DRO/EP, BP 70, 29280 Plouzane, France

This preliminary study presents a new method for the determination of dissolved gases in sea-water. After headspace extraction, gaseous compounds are separated by GC on a dual column adsorption system. The individual species are thereafter eluted to three different detectors (thermal conductivity, flame ionization and FPD) using a second switching valve. The analysis is quantitative for methane and carbon dioxide with limits of determination of 0.1 and 50 $\mu\text{mol l}^{-1}$, respectively, and corresponding standard deviations of 4 and 7%, and has been applied to deep sea hydrothermal samples. Further optimization is necessary to allow the quantitative determination of hydrogen sulfide, nitrogen, oxygen and carbon monoxide.

Deep sea hydrothermal vents are characterized by the presence of hot fluid sources with unusual chemical compositions, *i.e.*, high temperature, low pH, high sulfide and methane concentrations. Particular ecosystems are associated with these vents. In the absence of light, these are based on chemosynthesis and particularly on the hydrogen sulfide and methane present in the fluid.

The study of the chemical environment of hydrothermal organisms is based on biologically important compounds present in the mixing zone of the hydrothermal hot fluid and the

cold sea-water. Present in the fluid are the dissolved gases CH_4 , H_2S and CO_2 (Table 1).

In this study, sampling was carried out using a sampler deployed from the French deep-sea submersible research vessel Nautile. Samples were difficult to obtain and had to be handled with care as other analyses were carried out on the 150 ml of water.

The objective of this study was to develop a method for the determination of dissolved gases in a minimum volume of water, with a single shot and a good working range. The first part of this work focused on CH_4 , CO_2 and H_2S . Table 2 presents the analytical methods generally used for the analysis of each compound.

The only method existing for the simultaneous determination of CH_4 , CO_2 and H_2S is the method of Childress *et al.*⁹ for the determination of high concentrations of these gases in blood. This procedure can be divided into three steps: extraction of the gases from water, separation and detection.

The purge and trap method seems to be the most efficient method for the extraction of CH_4 , CO_2 and H_2S , because of the enrichment step. However, several unsuccessful attempts were made by us to simultaneously cryotrap CH_4 , CO_2 and H_2S . The experiments were carried out using packed glass columns with different packing materials, the cryogen being liquid nitrogen. Childress *et al.*⁹ used an acid stripping method (dynamic headspace without trapping) in a purpose-built reactor; this method is only available for concentrated samples (blood) and small injection volumes.

An alternative method is headspace sampling which has a good working range for CH_4 and CO_2 . This method was tested for the complete set of gases.

The complete chromatographic separation of CH_4 , CO_2 and H_2S is not possible on a single column. A dual column system with a switching valve must be used.⁹ The first column used in the study of Childress was a Poraplot Q: this separated O_2 , N_2 , CO and CH_4 as a single peak from CO_2 , H_2S and water. The first peak (O_2 , N_2 , CO , CH_4) was trapped on the second column

Table 1 Concentrations of the dissolved gases in sea-water and hydrothermal fluids

Gas	Hydrothermal fluid	Sea-water
CH_4	0.001–3.4 $\mu\text{mol l}^{-1}$	0.4 $\mu\text{mol l}^{-1}$
H_2S	0.5–18 $\mu\text{mol l}^{-1}$	trace
CO_2	2.3–285 $\mu\text{mol l}^{-1}$	2.4 $\mu\text{mol l}^{-1}$

Table 2 Analytical methods used in the literature

Reference	Compounds	Matrix	Method	Detection	Calibration	Working range
1	CH_4	Sea-water	Headspace			3–700 $\mu\text{mol l}^{-1}$
2	CH_4	Sea-water	Headspace	FID*	Gas standard	5–20 $\mu\text{mol l}^{-1}$
3	CH_4	Water	Headspace	TCD†, FID*		0.01–100 $\mu\text{mol l}^{-1}$
4	H_2 , CH_4 , CO_2	Sea-water	Modified MHE‡	TCD†		CH_4 1–100 $\mu\text{mol l}^{-1}$
5	Dissolved sulfides	Sea-water	Purge and trap	PID§		DL 13 $\mu\text{mol l}^{-1}$ ¶
6	CH_4	Sea-water	Purge and trap	FID*	Gas standard	0.02–18 $\mu\text{mol l}^{-1}$
7	CH_4 , CO_2	Sea-water	Purge and trap	TCD†, FID*		
8	CH_4	Sea-water	Ultrasonic	FID*	Gas standard	0.05–45 $\mu\text{mol l}^{-1}$
9	CH_4 , CO_2 , CO , H_2S , N_2 , O_2	Blood	Dynamic headspace	TCD†	Gas standard	CO_2 4–20 $\mu\text{mol l}^{-1}$ H_2S 0–5 $\mu\text{mol l}^{-1}$

* FID, flame ionization detector. † TCD, thermal conductivity detector. ‡ MHE, multi-headspace extraction. § PID, photoionization detector. ¶ DL, detection limit.

(molecular sieve), the valve was switched and CO_2 , H_2S and water were eluted directly to the detectors. When the elution was finished on the Poraplot column, the final separation of O_2 , N_2 , CO , CH_4 was carried out on the molecular sieve after a second valve switching.

Childress *et al.*⁹ used a thermal conductivity detector (TCD) for the detection of the gases. To improve sensitivity more specific detectors were used in this study: a TCD for CO_2 , N_2 , CO , O_2 , a flame ionization detector (FID) for CH_4 and an FPD for H_2S . Species were eluted to the different detectors using a second switching valve.

Experimental

A schematic diagram of the complete analytical device used is presented in Fig. 1.

A preliminary study was carried out using 20 ml headspace flasks, with a 10 ml sample of water and 0.1 ml of 6 mol l⁻¹ hydrochloric acid under He. The flask was heated for 30 min at 70 °C under stirring. The injected headspace volume was 2.5 ml. To reduce the analysis time, a temperature programme was used [40 °C (held for 7 min); raised at 15 °C min⁻¹ to 130 °C (held for 13 min)].

The headspace sampler used was a DANI HSS 86-50 with a Silicostil heated transfer line. The separation was performed using a series 8000 Fisons gas chromatograph equipped with a TCD, an FID EL 980 and an FPD and LIN 700 (linearizer). The switching valves were made of Hastelloy (Valco). The columns and pressure drop were Chrompack Poraplot Q Ultimet 0.53 mm, 25 m and Molecular sieve 5A Plot Ultimet, fused silica 0.32 mm, 5 m. The carrier gas was He N55 (0.49 bar). The integration software was Borwin 4 channels. Calibration was achieved either with a standard gas mixture from Scotty with Hamilton gas-tight syringes 1700 RN series or with standard solutions of sodium sulfide nonahydrate (Rectapur, Prolabo) and sodium hydrogencarbonate (pro analysi, Merck).

Results and Discussion

Fig. 2 presents a chromatogram obtained with this method for concentrations of 35 $\mu\text{mol l}^{-1}$ of H_2S , 200 $\mu\text{mol l}^{-1}$ of CO_2 and

120 $\mu\text{mol l}^{-1}$ of CH_4 . The valves were switched at 315 s (E1), 440 s (E2) and 14 min (E1, E2). The chromatographic resolution enabled quantitative analysis. However, the baseline for the TCD was disrupted by the temperature programme. The use of an isothermal temperature program or a mass flow controller would cancel this problem.

Fig. 3 presents the calibration curves for the three compounds, obtained by the liquid addition of Na_2S and NaHCO_3 and gaseous addition of CH_4 to 10 ml of sea-water. The low sensitivity for H_2S may be due to the adsorption of sulfide on part of the gas chromatograph, although most of the inox parts had been replaced except for the syringe needle of the headspace.

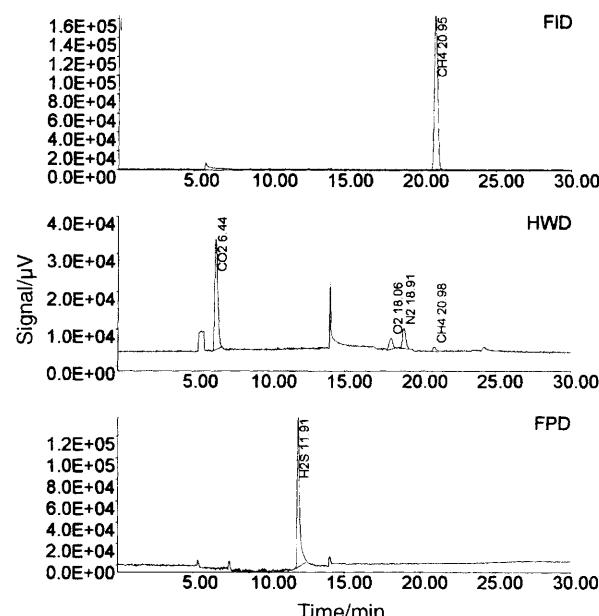


Fig. 2 Chromatogram obtained for a mixture of Na_2S (35 $\mu\text{mol l}^{-1}$), CO_2 (200 $\mu\text{mol l}^{-1}$) and CH_4 (120 $\mu\text{mol l}^{-1}$).

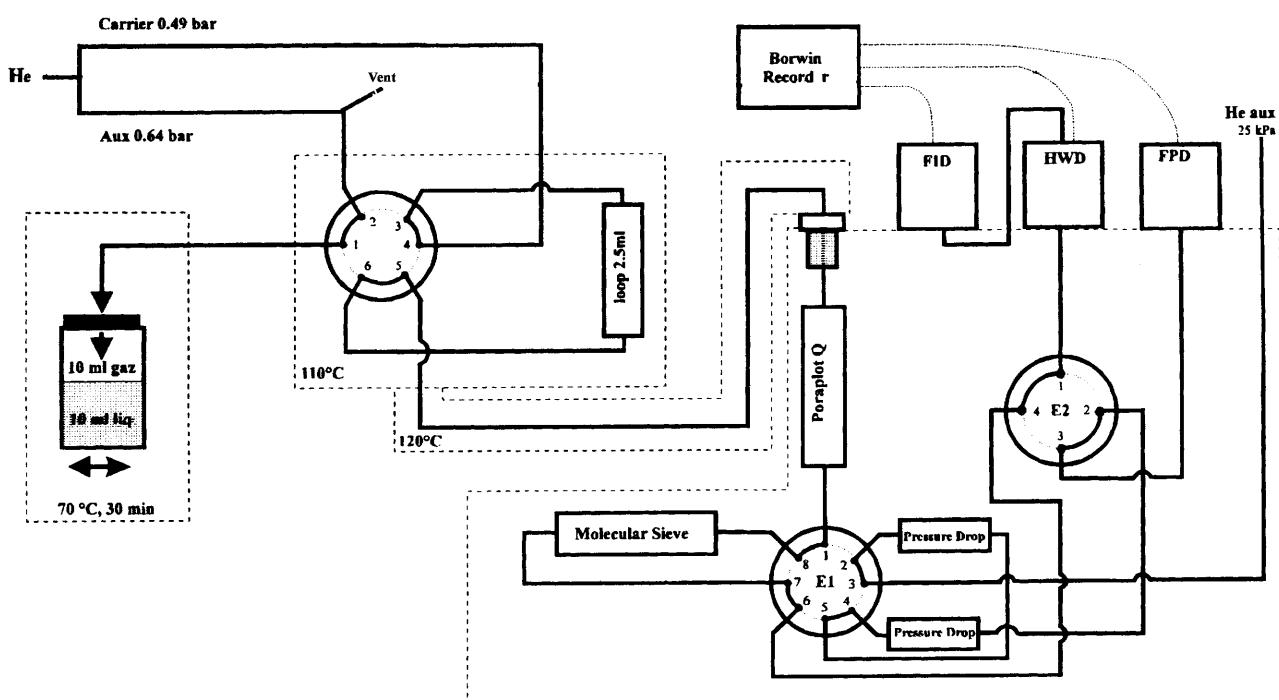


Fig. 1 Schematic diagram of the analytical device.

The determination limits ($3 \times$ noise integration/calibration slope) were 0.1 and $50 \mu\text{mol l}^{-1}$ for CH_4 and CO_2 , respectively. Standard deviations ($n = 5$) were 4% for $80 \mu\text{mol l}^{-1}$ of CH_4 and 7% for $800 \mu\text{mol l}^{-1}$ of CO_2 .

Application

The analytical device described here has been used aboard the French oceanographic vessel 'Nadir' during the HOT 96 diving

cruise undertaken by IFREMER CNRS Marine Research Unit no. 7 on the 9° and 13° N hydrothermal sites of the East Pacific Rise. Fifty water samples were collected of the various organisms present (*Riftia*, Alvinellids and mussels) by the French submersible Nautile using a specific vacuum-based and gas-tight sampler. Hydrogen sulfide was not quantified because of its low sensitivity. For methane and carbon dioxide concentrations of $1\text{--}5 \mu\text{mol l}^{-1}$ (sea-water $0 \mu\text{mol l}^{-1}$) and $900\text{--}8000 \mu\text{mol l}^{-1}$ (sea-water $2280 \mu\text{mol l}^{-1}$) were determined, respectively.

Conclusions

The headspace extraction conditions (temperature, time, pressure) must be further optimized to improve the efficiency and to reduce the amount of water injected. The hydrogen sulfide line must be checked to eliminate the possible remaining inox parts and to study the working conditions for the FPD (air and H_2 amount in the flame) to enhance the sensitivity. The concomitant use of a TCD and a temperature program led to a fluctuating baseline use of a flow controller may overcome this problem.

This preliminary study has focused on the analysis of CH_4 , H_2S and CO_2 . Future work will involve the quantitative determination of O_2 , N_2 and CO using the same method.

This work was supported by a MAST III AMORES contract 950040.

References

- 1 Blanc, G., Boulègue, J., and Gieskes, J. M., *Oceanol. Acta*, 1991, **14**, 33.
- 2 Bange, H. W., Bartell, U. H., Rapsomanikis, S., and Andrae, M. O., *Global Biogeochem. Cycles*, 1994, **8**, 465.
- 3 Hamilton, S. K., Sippel, S. J., and Melack, J. M., *Biogeochemistry*, 1995, **30**, 115.
- 4 Evans, W. C., White, L. D., and Rapp, J. B., *J. Geophys. Res.*, 1988, **93**, 15,305.
- 5 Cutter, G. A., and Oatts, T. J., *Anal. Chem.*, 1987, **59**, 717.
- 6 Charlou, J. L., and Donval, J. P., *J. Geophys. Res.*, 1993, **98**, 9625.
- 7 Ishibashi, J. I., Wakita, H., Nojiri, Y., Grimaud, D., Jean-Baptiste, P., Gamo, T., Auzende, J. M., and Urabe, T., *Earth Planet. Sci. Lett.*, 1994, **128**, 183.
- 8 Schmitt, M., Faber, E., Botz, R., and Stoffers, P., *Anal. Chem.*, 1991, **63**, 529.
- 9 Childress, J. J., Lee, R. W., Saunders, N. K., Felbeck, H., Oros, D. R., Toulmond, A., Desbruyères, D., Kennicutt, M. C., and Brooks, J., *Nature*, 1993, **362**, 147.

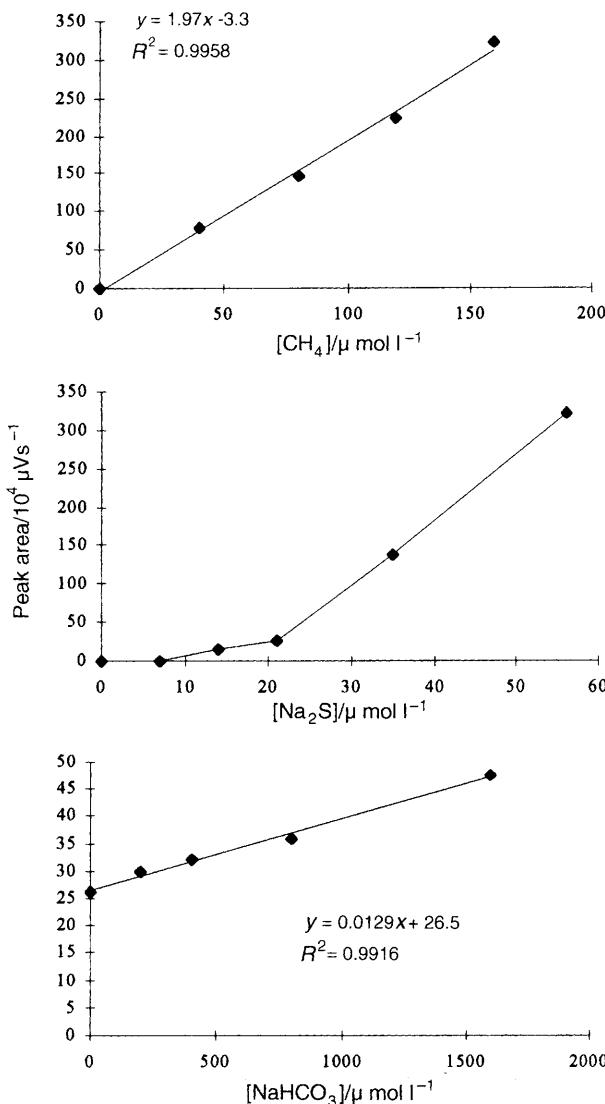


Fig. 3 Calibration curves for CH_4 , H_2S and CO_2 .

Paper 6/05335A

Received July 30, 1996

Accepted August 19, 1996