# Measurements of dissolved nonmethane hydrocarbons in sea water

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**Summary.** An automated stripping technique for the measurement of dissolved hydrocarbons in sea water is presented together with some results obtained during a ship cruise from Europe to Brazil. The sea water concentrations of NMHC were determined in a three step process: degassing, preconcentration, and gas chromatographic analysis. In a stripping chamber the dissolved gases were purged from sea water with helium. The stripped hydrocarbons were cryogenically concentrated, and after thermal desorption they were injected into the gas chromatograph. The light fraction ($C_2-C_4$) was separated on a packed and the heavy fraction ($C_5-C_{10}$) on a capillary column. All valves were microprocessor controlled in order to achieve an automated process. For the $C_2-C_4$ hydrocarbons the stripping efficiencies exceeded 90% except for acetylene (80%), the lower limit of detection was 1 to 4.5 pmol hydrocarbon per liter of sea water and the accuracy of the method was better than 25%, depending on the individual hydrocarbons. Typical oceanic concentrations were in the 10 and 100 pmol/l range. Alkenes were generally more abundant than the corresponding alkanes and within the homologous series the concentrations decreased with increasing number of carbon atoms.

## Introduction

Global oceanic emissions of nonmethane hydrocarbons (NMHC) into the atmosphere have been estimated to be in the range of $10^{12}$ and $10^{13}$ g $yr^{-1}$ [1, 2, 3]. The contribution of oceanic sources to overall atmospheric budgets of NMHC is considerable [1], especially for the remote marine atmosphere [4]. Emission rates were derived indirectly from atmospheric budget calculations [3], or from transferring the pattern of NMHC concentrations in sea water into an emission pattern [2] scaled by the previously estimated propane emission [5]. Direct calculations of emission rates from air/sea exchange models and sea water concentrations in conjunction with atmospheric NMHC measurements [6, 7] seem most reliable for evaluating atmospheric hydrocarbon budgets. However, since only few data of NMHC concentrations in sea water exist, estimates of oceanic hydrocarbon emissions are scarce and expanding them to a global scale is very uncertain.

Previous measurements of dissolved NMHC in sea water [2, 7–13] were all based on a method developed by Swinnerton and Linnenbom [14]. In this technique, the NMHC are stripped from the water sample by purging with helium, and then concentrated on cold traps; subsequently, they are injected into the gas chromatograph.

In this paper a fully automated process for the determination of NMHC in sea water is described. It was successfully used aboard a ship and some examples of the NMHC concentrations in sea water are given. Detailed results of the measurements are presented elsewhere [7].

## Experimental

The concentrations of NMHC in sea water were measured during a cruise of the German research vessel Polarstern from Europe to Brazil in 1988 as part of an extensive study of the atmosphere over the remote Atlantic [15]. For this purpose a fully automated system was developed with measurement cycles of 3 h duration. Each cycle consisted of three steps: sampling and degassing, cryogenic concentration, and gas chromatographic determination. All steps were microprocessor controlled.

Figure 1 shows a schematic drawing of the sampling and degassing device. The glass stripping chamber (1500 ml) with a glass frit at the lower end was similar to that by Swinnerton

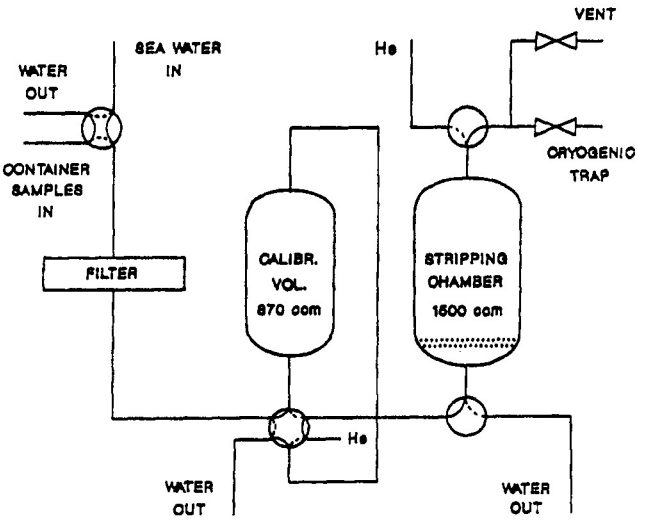


**Fig. 1.** Scheme of the sampling and degassing device

**Table 1.** System performance for individual hydrocarbons

| | Reference air | | Sea water | | | |
|---|---|---|---|---|---|---|
| | Calibr. accuracy [%] | Reproducibility [%] | Blank value [pmol] | Stripping efficiency [%] | Statist. error [%] | Det. limit[a] [pmol] |
| Ethane | 10 | 21 | – | 96 ± 2 | 21 | 1.5 |
| Propane | 20 | 3 | – | 93 ± 3 | 4 | 1.4 |
| n-Butane | 30 | 2 | – | 91 ± 5 | 5 | 1.8 |
| i-Butane | 30 | 4 | – | 91 ± 5 | 6 | 1.4 |
| Ethene | 10 | 3 | 1 ± 1 | 96 ± 2 | 4 | 1.6 |
| Propene | 20 | 10 | – | 93 ± 3 | 10 | 1.5 |
| 1-Butene | 30 | 25 | 9 ± 4.5 | 91 ± 5 | 25 | 4.5 |
| Acetylene | 10 | 3 | – | 80 ± 9 | 9 | 1.0 |

[a] The detection limits include blank value uncertainties and represent calm sea conditions; strong wave action can increase the values up to factors of 2, the limit for 1-butene can increase to 5.2

and Linnenbom [14]. All materials in contact with the samples were glass and stainless steel. Only exceptions were the valves and the glass metal connections which had PTFE seals, as well as the stainless steel filter holder (Sartorius, 130 mm diameter). Glass microfibre filters (Whatman GF/C, pore size 1.2 μm) were used to avoid phytoplankton entering the system. The filter was carefully purged and then used for up to 5 sampling cycles. The sea water was supplied continuously by a stainless steel rotary pump. The sea water inlet was at 11 m depth, 0.5 m below the hull of the ship. The carrier and purge gases (He, $H_2$ and $N_2$) were of 5.0 quality or better and additionally cleaned by passing them through a molecular sieve and charcoal trap at 200 K.

In each sampling and degassing cycle the sea water was first pumped through the filter for 10 min at a flowrate of 100 ml $min^{-1}$. Then the 6 way valve was switched and the glass calibration volume of 870 ml was filled and rinsed for 20 min. Subsequently, by back switching the 6 way valve the water sample was transferred into the stripping chamber by a helium gas flow of 100 ml $min^{-1}$. The dissolved gases were then stripped from the sample with the same gas stream for 30 min. The purged gases were passed through an unpacked stainless steel trap at 273 K for reduction of the water vapour content and subsequently frozen out at 77 K in a trap packed with porous glass beads. The operation of the automatic cryogenic concentration system is described elsewhere [16]. When the stripping of the sample was finished, the water was flushed out of the chamber by switching the 3 way valves attached to the stripping chamber (Fig. 1). In periods with no water in the stripping chamber, it was purged with helium at 100 ml $min^{-1}$.

The gas chromatographic measuring technique has been described in detail in previous papers [16, 17]. Briefly, the hydrocarbons were preseparated into a light ($C_2-C_4$) and a heavier fraction ($C_5-C_{10}$) on a packed precolumn (2 m, 2 mm ID, Porapak QS, 100/120 mesh). The light fraction was separated on an identically packed 5 m column. The heavier fraction was, after a second cryogenic concentration, separated on a fused silica column (DB5, 60 m, 0.32 mm ID). Hydrocarbons and halocarbons were measured in a parallel configuration by flame ionization detector (FID) and electron capture detector (ECD) using a split ratio of 4:1 (FID:ECD). The data were acquired by commercial available interface, chromatography software and personal computer, as well as by a chart recorder.

## Results

### *The instrument performance*

A reference air with NMHC mixing ratios in the ppb range was used to quantify the gas chromatographic determination. The estimated accuracy of the calibration of individual NMHC in the reference air is given in Table 1. The reproducibility of the $C_2-C_4$ hydrocarbon measurements in the reference air was better than 10% for most compounds except for ethane (21%) and 1-butene (25%) (Table 1). In blank runs of the gas chromatographic system only 1-butene showed a detectable blank value corresponding to 6 ± 1.5 pmol, which was subtracted from all 1-butene reference air measurements. The uncertainty of this blank value contributes with about 10% to the reproducibility of 25% of 1-butene. The poor reproducibility of ethane (21%) was most probably due to the fact that the efficiency of the cryogenic concentration occasionally deviated up to 50% from 100%.

The whole system's background was determined with blank runs simulating degassing experiments without a water sample. Blank values were found for ethene and 1-butene corresponding to 1 ± 1 pmol and 9 ± 4.5 pmol, respectively. The stripping efficiency of the method was determined in some duplicate degassing experiments of the same water sample. Comparing the amounts of individual NMHC found in the first degassing step relative to the second, the efficiencies were (96 ± 2)% for ethene and ethane, (93 ± 3)% for $C_3$, (91 ± 5)% for $C_4$ hydrocarbons and (80 ± 9)% for acetylene. If necessary, the data were corrected for blank values and the different stripping efficiencies. The lower limit of detection for hydrocarbons depended on the ship's motion due to wave action. This caused enhanced noise of the FID baseline. Thus, the lower limit of detection was varying in the range from 1 to 3 pmol NMHC. In the cases of 1-butene and partly for ethene (only for calm sea) the lower limits of detection were additionally determined by the uncertainties in their blank values.

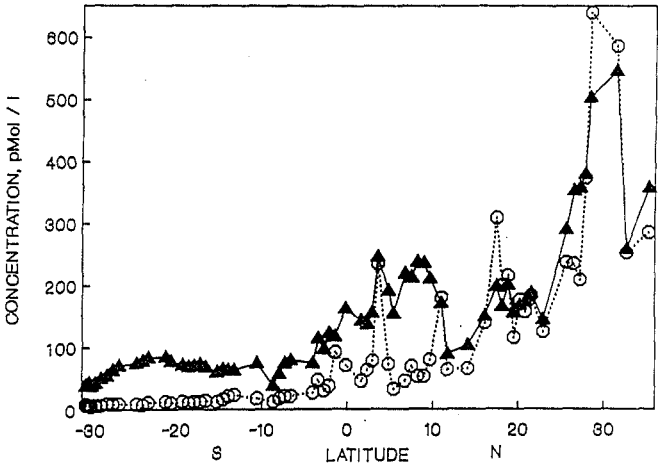


**Fig. 2.** Latitudinal distribution of ethene (triangles) and ethane (circles) in sea water

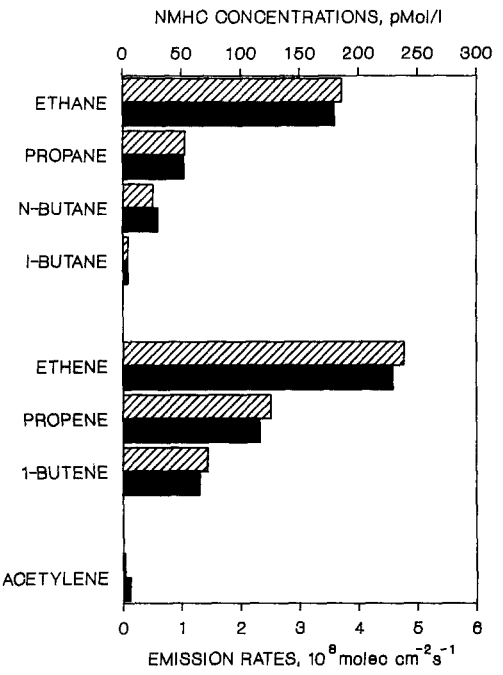


**Fig. 3.** Averages of $C_2-C_4$ hydrocarbon concentrations between 0° N and 30° N and the corresponding calculated emission rates. ■ Concentrations; ▨ emission

The influence of light exposure on the determined NMHC levels was tested by covering the calibration volume and stripping chamber so that no light could penetrate. In an alternating sequence of dark and light experiments no light effects were detected. Possible effects due to the filter could be rejected by duplicate filtration of the same water sample, each with new filters, compared to single filtration. This as well as multiple use of the same filter did not show any effect. Helium blanks run subsequent to sample measurements with high concentrations did not show any memory effects (<2%).

From the reproducibility of the reference air measurements and the uncertainty in the stripping efficiency a statistical error of the measurements can be calculated (Table 1). Except for ethane (21%) and 1-butene (25%) a total reproducibility better than 10% was estimated. However, due to the uncertainties in the absolute calibration of the reference air, the absolute concentrations have overall uncertainties of 10 to 40%. For concentrations close to the lower limit of detection (<10 pmol/l) the uncertainties were higher, up to 30–45%.

*Results of field measurements*

In Fig. 2 the latitudinal distributions of ethene and ethane concentrations in sea water are shown (30° W, 35° N–30° S). They were obtained during Polarstern cruise ANT VII/1 in September/October 1988. Between 35° N and about 10° N the concentrations of ethene and ethane were comparable with maxima of about 600 pmol/l at 30° N and decreasing to about 100 pmol/l at 10–15° N. In the 10° N to 3° S range, ethene concentrations were slightly elevated, around 200 pmol/l, possibly due to enhanced biological activity in the equatorial upwelling zone. South of 3° S ethene concentrations were fairly constant with an average of 63 pmol/l, the ethane concentrations were by a factor of 5 lower. Most of the structures in the latitudinal distributions could be explained by losses due to emissions to the atmosphere and changing oceanic production and destruction processes in the different ocean regions [7]. Ethene and ethane showed the highest concentrations compared to their higher homologues (Fig. 3). All NMHC, except acetylene, were supersaturated in sea water relative to the atmosphere by at least factors of 20. From NMHC concentrations in sea water and sea air exchange models [18] the oceanic emissions into the atmosphere can be calculated. Alkene emissions dominated alkane emissions and for homologues series the emissions decreased with increasing molecular weight. Since acetylene concentrations were generally close to equilibrium, the flux across the sea surface was insignificant.

## Conclusions

The described procedure allows measurements of volatile organic compounds in water samples down to concentrations of a few pmol/l. The technique gives reliable results and is suitable for in-situ measurements, e.g. shipboard operation. The instrument runs automatically and allows measurements of a broad range of volatile organic components. However, we have not yet evaluated the suitability of this technique for field measurements of medium molecular weight substances.

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