

A Best Practice Guide for dissolved CH_4 and N_2O

CHAPTER 5 Quantification of dissolved methane and nitrous oxide via headspace equilibrium



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SOPs on CH₄ and N₂O

QUANTIFICATION OF DISSOLVED METHANE AND NITROUS OXIDE VIA HEADSPACE EQUILIBRIUM

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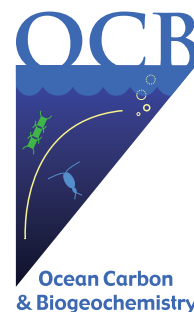


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Background

1.1 Introduction

The headspace equilibrium method is commonly used to prepare a water sample for subsequent dissolved CH_4 and N_2O analysis, traditionally by gas chromatography (GC). It relies on the theoretical partition ratio of N_2O and CH_4 between a gas and an aqueous phase at equilibrium, at a specified sample temperature and salinity. Briefly, a known volume headspace of “equilibration gas” with predetermined partial pressures of N_2O and CH_4 is introduced into a gas-tight vessel containing a known volume of the water sample.

Once equilibrium is attained between the aqueous and gas phases, in which their partial pressures reach the same value, a sample of the headspace is injected into the gas analyzer for the quantification of N_2O and CH_4 . Using the known headspace and water sample volumes, the equilibration gas partial pressures and the gas solubilities at the sample salinity and its equilibration temperature, the original CH_4 and N_2O partial pressures in the water sample can be calculated.

Since this technique was first introduced by McAuliffe (1980), different laboratories have applied varying versions of the basic approach, e.g., by optimizing the sample and/or headspace volumes, modifying the equilibration procedure, and varying the way in which the equilibrated headspace is injected into the GC (Upstill-Goddard et al., 1996; Zhan et al., 2003; Walter et al., 2005). Despite the intrinsically higher analytical sensitivity of the purge and trap method, recent inter-comparison measurements of oceanic N_2O and CH_4 demonstrated that the analytical precision and accuracy of the headspace equilibrium method is comparable to that of the purge and trap method (Wilson et al., 2018).

For optimal best performance when using the headspace equilibrium method with GC, careful attention should be paid to sample preparation and analytical conditions. Obtaining high precision and accuracy intrinsically depends on minimizing the uncertainty in sample and headspace volumes, and holding both the equilibration temperature and the total pressure in the gas phase constant. In addition, transfer of the equilibrated headspace into the GC should avoid to the maximum extent possible any “dead volume” associated with incomplete flushing of the GC sample loop.

Here, we present detailed recommendations for conducting and optimizing the headspace technique using a basic approach that will enable high-precision measurements of dissolved CH₄ and N₂O in seawater samples.

1.2 Theoretical and practical considerations in the optimization of experimental procedures

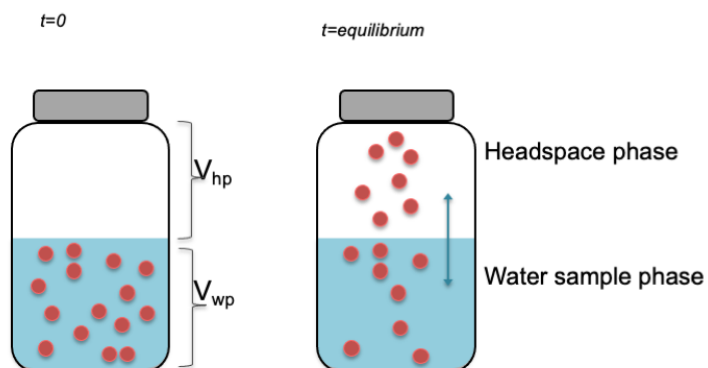
Optimizing the headspace equilibrium technique requires an appreciation of some attendant theoretical considerations. First is the partition coefficient (K_d), defined as the equilibrium concentration of the gas in question between the aqueous (sample) phase (C_{wp}) and the gas (headspace) phase (C_{hp}) (Figure 1). The value of K_d is gas-specific and is a function of both the sample equilibration temperature and its salinity. Second is the phase ratio (B), the ratio of headspace volume (V_{hp}) to sample volume (V_{wp}) in the sealed vial/equilibration system (Figure 1). Combining K_d and B , and the initial concentration of the sample (C_0), the equilibrium gas concentration in the headspace will be given by: $C_{hp}=C_0/(K_d+B)$.

This equation can be used to optimize B and the equilibration temperature to suit the expected range of CH₄ and N₂O partial pressures in a set of water samples. Once this is done, any variation in the method's analytical precision arising from variability in these properties can be minimized. Full automation of the procedure in a sophisticated analytical system can enable this (Upstill-Goddard et al., 1996), but it can also be routinely achieved for less complex techniques by using an automatic burette (de la Paz et al., 2015) or gas-tight syringe (SOP 1). Furthermore, the sensitivity of the headspace-GC system can be improved by an optimal selection of B and by maximizing the headspace volume injected into the GC.

Important variables in headspace analysis

$$\text{Partition coefficient (K}_d\text{)} = C_{wp} / C_{hp}$$

$$\text{Phase Ratio (B)} = V_{hs} / V_{wp}$$



C_{wp} = concentration of analyte in water sample phase
 C_{hp} = concentration of analyte in headspace phase
 V_{hs} = volumen of headspace phase
 V_{wp} = volumen of water sample phase

Figure 1. Gas and water phases in a sealed vial used for headspace analysis.

2

Step-by-step guide for N₂O and CH₄ headspace analysis

2.1. Determination of the phase volumes

Accurate determination of the headspace (V_{hp}) and water (V_{wp}) volumes is critical to achieve good reproducibility. This can be achieved gravimetrically, by sequentially weighing (± 0.01 g) the equilibration system empty, when full of sample water, and when the headspace has been introduced. The total sample volume is calculated from the difference in weight between the full and empty flask, considering the water sample density (computed from temperature and salinity). Although automated systems can enable highly reproducible generation of the water phase volume without routine weighing (Upstill-Goddard et al., 1996), for most applications the weighing of sample is required, but it is not usually possible at sea due to ship movement. An alternative means of determining V_{hp} with high confidence involves using an automatic burette or syringe (de la Paz, 2015), and volume-calibrated bottles.

2.2. Preparing the headspace gas source

Typically, the gas introduced to create the headspace is inert such as N₂ or He, and free from any measurable CH₄ and N₂O, ideally the same as the carrier gas. Alternatively, a gas mixture with precisely known CH₄ and N₂O mixing ratios can be used. Unless the equilibration vessel's internal pressure can be precisely monitored, it is critical to maintain the headspace at atmospheric pressure during both equilibration and subsequent transfer to the GC. A recommended method of keeping the headspace at atmospheric pressure during its creation is to use a gas-tight bag filled with the headspace gas, instead of a high-pressure tank (de la Paz et al., 2015, Figure 3). Prior to use, the gas-tight bag should be filled and evacuated with the headspace gas three times to avoid contamination. After that, the composition of the headspace gas source should be checked for contamination by sub-sampling it with a gas-tight syringe and injecting it directly into the GC.

2.3. Introduction of the headspace

In order to minimize sample manipulation, the headspace should be introduced directly

into the sampling bottle. This can be done by perforating the septum simultaneously with two needles (Figure 2). One long needle is introduced to the bottom of the vial and a short one is placed right below the septum.

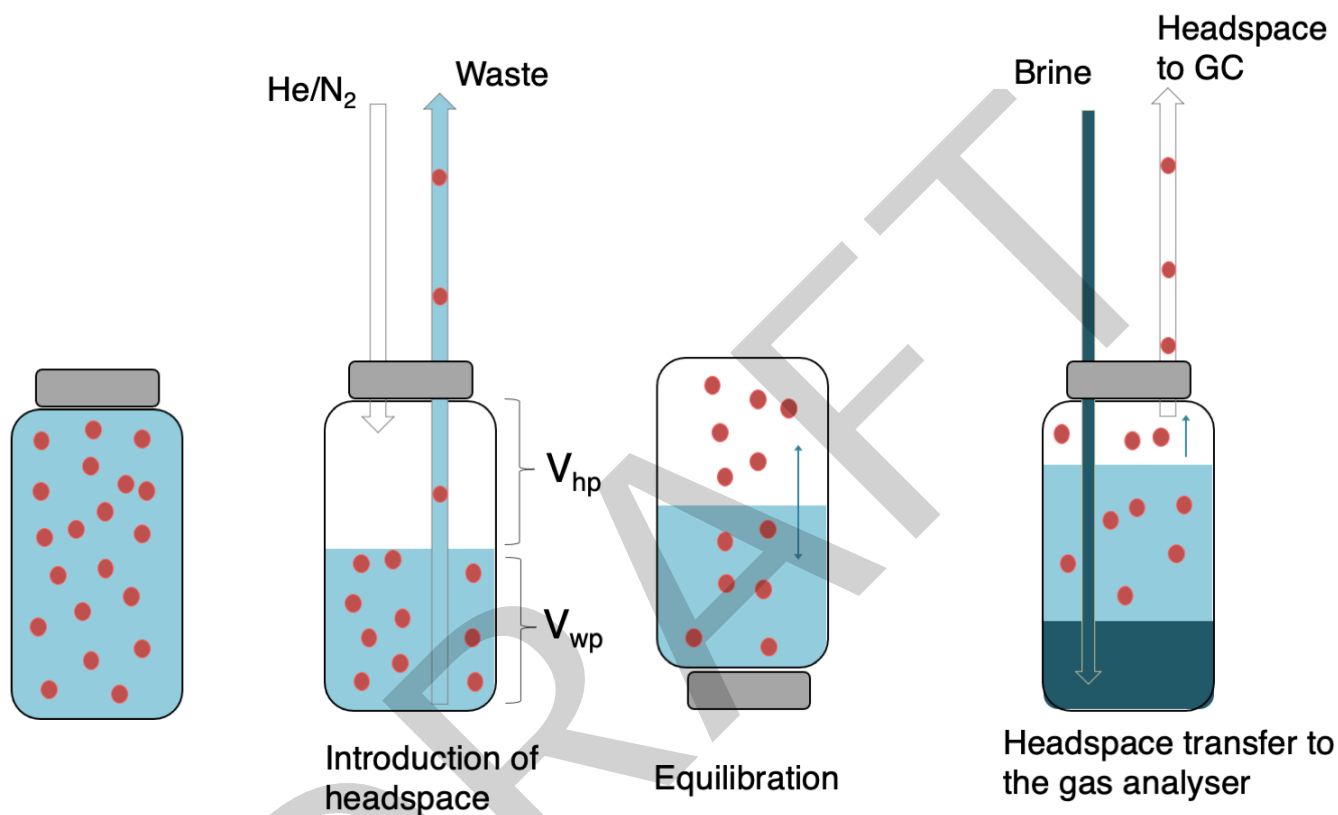


Figure 2. Schematic diagram of the sequence during static headspace method.

There are different ways for introducing the headspace into the vial. In order to carefully and reproducibly introduce the headspace, the long needle can be connected to a syringe pump or an automatic burette to withdraw the water sample while the headspace gas flows into the vial through the top needle, which is directly connected to the gas-tight bag (Neil et al., 1996; de la Paz et al., 2015, Figure 3a).

Alternatively, the headspace can be introduced manually using a gas-tight syringe attached to long needle. In this case, the bottle is first inverted so that the headspace is

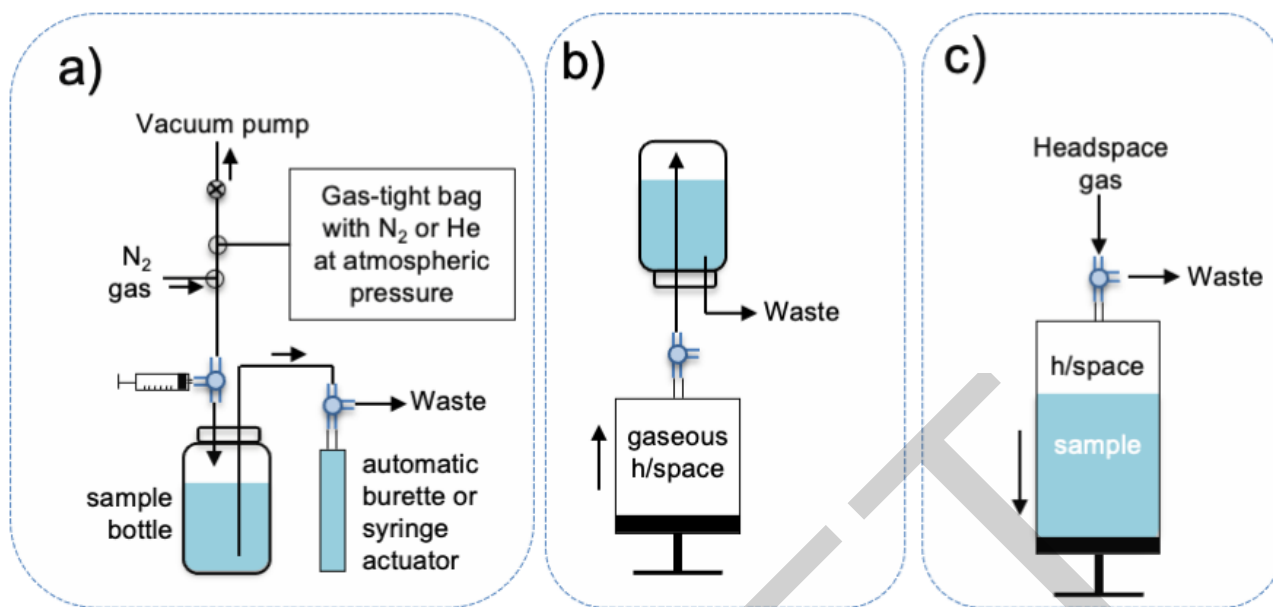


Figure 3. Examples of different set ups to introduce the headspace in the sample. 3a) The gas source is a 5 L gas-tight bag filled with ultra-high purity N₂, after filling it and evacuating it three times to avoid contamination. The gas port is connected with a three-way stopcock fitting to the gas-tight bag via 1/16" PTFE tubing. In order to carefully and reproducibly remove the volume of water sample, the liquid port is connected to an automatic burette (Dosimat, Metrohm). Then, the water sample is withdrawn very slowly (20 mL per minute) to ensure that the introduction of headspace gas is conducted at atmospheric pressure (de la Paz et al., 2015). A gas-tight syringe is incorporated to flush the He/N₂ from the gas-bag between samples using a three-way valve stopcock. 3b) The headspace is pushed manually with a syringe (slightly over-pressured) and a fraction of the water sample flows out of the vial. 3c) Water is collected in a gas-tight syringe and the headspace is introduced directly through a three-way stopcock.

not in contact with the septum. This avoids leakage and any potential for contamination by laboratory air. The headspace is thus introduced into the bottom of the vial through the long needle while a fraction of the water sample flows out of the vial through the short needle, and stops flowing when the headspace pressure comes to atmospheric (Figure 3b). In this case, it is recommended to determine V_{hp} and V_{wp} by sequentially weighing the vial empty, full, and after headspace addition. An alternative approach is to collect the water sample in a gas-tight syringe and introduce the headspace directly into the syringe through a three-way stopcock (Figure 3c). This option is typically used for a direct injection into the analyzer, and precludes fixing the water sample to inhibit biological activity. In this case, long-term storage of the sample can only be facilitated by re-injecting the equilibrated headspace into another pre-evacuated gas-tight vial (e.g., pre-evacuated Exetainer[®] vial).

In all cases, care must be taken to avoid inadvertently introducing any laboratory air into the equilibration vessel, thereby contaminating the headspace. Single-use, stainless steel hypodermic needles are the most affordable option for introducing the headspace (Figures 3a and b; e.g., for a 120 mL vial a long 0.80 x 120 mm needle and short 0.60 x 30 mm needle would work). Alternatively, a custom concentric needle can be used (Neill et al., 1997). Any connecting tubing between the headspace gas source and the bottle should be flushed with headspace gas before introducing the headspace in between samples. Gas-tight borosilicate glass syringes are recommended to allow better cleaning during sample manipulation. Polypropylene syringes can be a more affordable option, but their gas-tightness and potential interferences from impurities (e.g., from the rubber plunger that may impact methane measurements) should be thoroughly evaluated, for example by injecting pure N₂/He into the GC.

In addition, it is important to keep a low flow rate when introducing the headspace gas to avoid perturbing the N₂O/CH₄ integrity of the liquid sample. In general, precision is improved when the generation of the headspace is automated. When the headspace is introduced manually, precision can vary substantially depending on the skill and care of the analyst.

2.4. Sample equilibration

Following headspace creation, the two phases need to come to equilibrium with respect to their gas partial pressures, prior to injection into the GC. During the equilibration, the samples are stored in the dark, inverted so that the headspace is not in contact with the septum. The time for full equilibration varies, depending on the temperature, the nature and degree of sample agitation (Zhan et al., 2013), the sample volume, and the values of K_d and B . Intrinsic differences in the value of K_d for N₂O and CH₄ mean that the optimum equilibration times differ for the two gases. Shaking or vibrating the vial can assist in reducing the equilibration time. This can be done manually after introducing the headspace or can be automated using a shaker. We recommend the use of a water bath, ideally incorporating some means of sample agitation, to maintain a constant temperature during equilibration.

Alternatively, if a water bath is not available, a large volume cool box filled with water at room temperature in a temperature-controlled laboratory can be used. The water temperature in the water bath or cooler can be monitored with a precise thermometer (0.01°C). The equilibration temperature needs to be registered to calculate the equilibration concentration of N₂O and CH₄ in the water sample. It is important to keep the sample temperature relatively constant during transfer of the headspace to the GC.

It is also important to ensure that equilibration has been reached. Once the equilibration temperature and agitation conditions are set, the time to reach complete equilibration should be determined through time-course experiments, testing the GC response as a function of equilibration time (Upstill-Goddard et al., 1996; Zhang et al., 2013). For convenience, the equilibration can be done overnight when running the analysis for several consecutive days, simplifying the daily routine in the laboratory and ensuring that complete equilibrium has been reached.

2.5. Transferring the headspace to the gas analyzer

Once the headspace reaches equilibrium with the aqueous phase, an aliquot of the headspace is transferred into a GC gas sample loop for subsequent injection into the GC carrier gas line. This can be done by introducing two needles into the equilibrated sample bottle, one that sits at the bottom of the vial (liquid port) and the other protruding just below the bottom of the septum in the headspace (gas port).

There are different ways to transfer the headspace to the gas analyzer. A recommended procedure to gain reproducibility consists of using an automatic burette for introducing a brine solution (3 times saltier than the water sample $\approx 105 \text{ mg L}^{-1}$ NaCl solution) into the bottom of the bottle through the liquid port needle. The denser brine will remain at the bottom and will not contact the headspace. As the brine is introduced, the headspace is pushed through the gas port which is connected directly to the gas analyzer (Figure 4a). This ensures direct transfer into the GC loop without any dilution or pressure change. An alternative approach is to introduce the brine manually using a syringe through the liquid port, which will push the headspace either directly into the analyzer or into a gas-tight syringe connected to the gas port. Another alternative is that the syringe containing

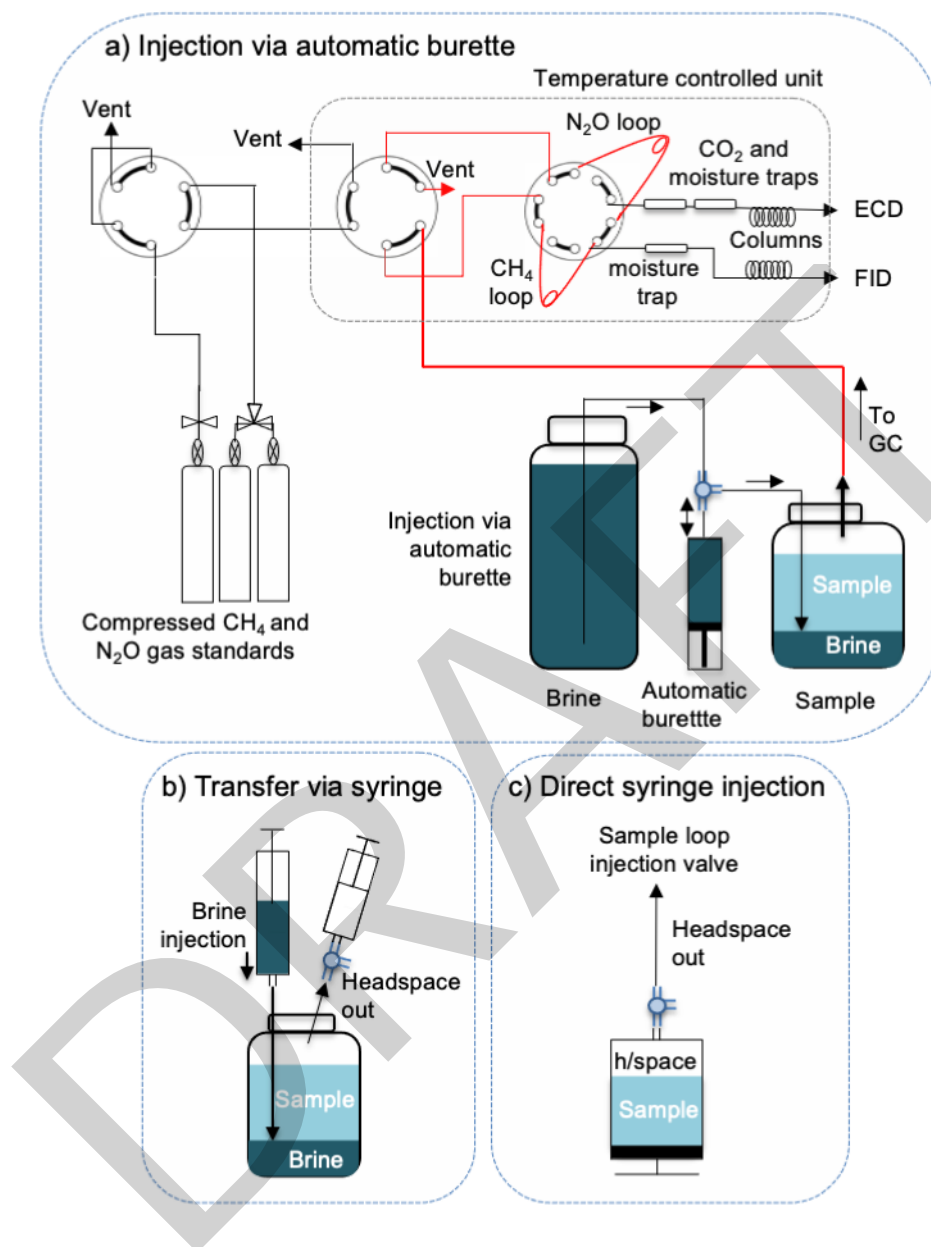


Figure 4. Optional methods for transferring the headspace to the gas analyzer. a) This schematic shows the gas chromatography system used by de la Paz et al. (2015), including the automated transfer of the headspace from the sample flask to the GC loop. As the brine is introduced using an automatic burette, the headspace is pushed through the gas port which is connected directly to the gas analyzer. b) The brine is introduced manually using a syringe through the liquid port, which will push the headspace either directly into the analyzer, or into a gas-tight syringe connected to the gas port. c) When the sample is collected and equilibrated in a gas syringe, once the equilibrium has been reached, the headspace can be directly transferred to the GC loop by opening the three-way stopcock valve.

the brine is open to the atmosphere (piston removed) and the headspace is sucked with “gas syringe”; once the headspace has been sub-sampled into the “gas syringe” the needle is removed after 30 seconds to ensure pressure equilibration with the ambient laboratory atmosphere. In the latter case, the aliquot can be then injected into the gas analyzer (Figure 4b). Finally, when the equilibration is conducted inside a gas-tight syringe, the headspace can be directly transferred into the GC sample loop by opening the three-way valve stopcock and pushing (Figure 4c).

Regardless of the method used to transfer the headspace, method precision and accuracy can be greatly improved by introducing the brine solution through a needle attached to an automatic burette or syringe (Johnson et al., 1990; Neill et al., 1996; de la Paz et al., 2015). Adding a dye to the brine can help monitor any mixing (which should be avoided) when introducing the brine solution. It is important to maintain a low flow rate to avoid any perturbation of the pressure and composition of the equilibrated headspace during transfer. It is also important to ensure that the volume of headspace gas being transferred is sufficient to effectively flush the transfer line and the sample loop. The inner volume of the line of tubing that connects the gas port with the GC loop can be estimated from the inner diameter and length of tubing. It is recommended to flush the loop system with at least 10 to 20 times the inner volume (including sample loop). Using 1/16” diameter tubing will considerably minimize the volume of the circuit tubing, increasing the flushing capacity and minimizing any possible carryover between consecutive samples.

2.6. Gas sample injection and quantification

Once the headspace gas is transferred to the gas sample loop, the gas in the loop is injected into the GC carrier gas line for analysis. The simultaneous analysis of N_2O and CH_4 can be achieved using a 10-port chromatography valve fitted with two independent sample loops: one for CH_4 and one for N_2O (Figure 4). Once the gas sample flow stops, the gas sample is kept in the sample loops for 30 seconds before injection onto the GC, to allow it to equilibrate to atmospheric pressure and the loop temperature. When the 10-port switching valve is used (see also SOP 2), all the gases, including calibration standards and air, are injected using the same gas sample loops used for the samples.

As described in the SOP 4 for carbon dioxide (Dickson et al., 2007), the sample loop should be kept at a constant temperature. It is preferable that this is higher than the equilibration temperature to avoid water vapor condensation, and is similar to the temperature of the oven containing the chromatographic columns.

One key consideration for GC analysis is to set the operating temperatures of the oven and detectors to optimize the GC output signals. As a reference, a diagram of a GC system is shown in Figure 4. Prior to chromatographic separation, the gas stream passes through a column filled with Carbosorb® to remove CO₂ for N₂O measurement, and then a column filled with magnesium perchlorate to remove water vapor for both N₂O and CH₄ (note that for N₂O analysis, inversion of the order of the CO₂- and H₂O-traps makes the Carbosorb ineffective). N₂O and CH₄ are chromatographically separated using Porapak Q columns operated at 60°C (Upstill-Goddard et al., 1996; de la Paz et al., 2015). The procedures described for drying the gas stream in SOP 4 can be also adapted for the headspace method.

3

Computation of concentrations

3.1. Determination of in-situ dissolved CH₄ and N₂O concentrations prior to equilibration

The gas concentration originally in the water sample before equilibration (C_{wp}^0) can be calculated following Johnson et al. (1990), by applying the following mass balance for the equilibration conditions:

$$(1) \quad C_{wp}^0 V_{wp} = C_{wp} V_{wp} + C_{hp} V_{hp}$$

Where V_{wp} and V_{hp} are the volumes of the water and gas phases, respectively. C_{wp} and C_{hp} are the gas concentrations at equilibrium in the water and headspace phases, respectively (Figure 1). Here we calculate C_{wp}^0 assuming that the initial concentration of CH₄ and N₂O in the headspace is zero. If a gas mixture with well-known N₂O and CH₄ concentrations is used for the headspace, the above mass balance equation requires some modification (see Upstill-Goddard et al., 1996).

The gas concentrations in the water and headspace phases at equilibrium can be related by the partition coefficient, K_d :

$$(2) \quad C_{wp} = K_d C_{hp}$$

Substituting and simplifying, equation 1 can be rewritten as:

$$(3) \quad C_{wp}^0 = \frac{C_{hp}}{V_{wp}} (K_d V_{wp} + V_{hp})$$

K_d is related to Henry's law constant, K (mol L⁻¹ atm⁻¹), through the following expression:

$$(4) \quad K = \frac{K_d}{RT}$$

Where R is the gas constant (0.08205746 L atm K⁻¹ mol⁻¹), and T is the equilibration temperature in Kelvin (K). In addition, the concentration of CH₄ or N₂O in the gas phase can be computed from the dry mixing ratio (x) of the given gas in the headspace, as measured by gas chromatography:

$$(5) \quad C_{hp} = \frac{xP}{RT}$$

where P is the headspace pressure (namely atmospheric pressure). By substituting C_{hp} and K in equation 3, the original concentration of the gas in the water sample is calculated as:

$$(6) \quad C_{wp}^0 [\text{mol L}^{-1}] = \frac{xP}{V_{wp}} \left(KV_{wp} + \frac{1}{RT} V_{hp} \right)$$

where K for N₂O and CH₄ are determined by using the solubility equations provided by Weiss and Price (1980) and Wiesenburg and Guinasso (1979) (Table 1), respectively. Note that K calculated using the constants provided in Table 1 have different units for N₂O and CH₄. The polynomial equation used to compute K as a function of temperature (T) in K and salinity (S), including the correction for water vapor, is as follows (Weiss and Price, 1980):

$$(7) \quad \ln K = A_1 + A_2 \left(\frac{100}{T} \right) + A_3 \ln \left(\frac{T}{100} \right) + A_4 \left(\frac{T}{100} \right)^2 + S \left[B_1 + B_2 \left(\frac{T}{100} \right) + B_3 \left(\frac{T}{100} \right)^2 \right]$$

Table 1. Constants for the calculation of the solubility coefficient for N₂O (mol L⁻¹ atm⁻¹) and CH₄ (nmol L⁻¹ atm⁻¹) in moist air at 1 atm total pressure using equation 7. Source: Weiss and Price (1980) and Wiesenburg and Guinasso (1979). To simplify the terminology we use the term K for N₂O and for CH₄ in this document, but, in the original papers K refers to F in the case of N₂O and C* for CH₄.

	A1	A2	A3	A4	B1	B2	B3
CH₄	-415.2807	596.8104	379.2599	-62.0757	-0.059160	0.032174	-0.0048198
N₂O	-165.8806	222.8743	92.0792	-1.48425	-0.056235	0.031619	-0.0048472

Calculations for determining CH ₄ and N ₂ O concentrations using the headspace equilibrium technique			
Calibration parameters			
Standard Identification	Concentration (ppm)	Volume Injected (ml)	Peak Area
N2	0	1	0.0
STD1	3	1	28.3
STD2	4.866	1	47.4
STD4_SCOR ARS426347	1.959	1	18.3
STD5_SCOR WRS464537	4.827	1	47.1
Column A	Standard identification		
Column B	Concentration of the standard in ppm		
Column C	Volume of standard injected into the GC (ml)		
Column D	Peak area of standard		
Column E	Calibration slope		
Column F	Calibration intercept		

Figure 5. Snapshot of Supplementary File example calculations.

Example calculations for determining CH₄ and N₂O concentrations using the headspace equilibrium technique are included in the Supplementary File ([spreadsheet link](#)). The Supplementary File hosts example calculations for all of the SOPs in the Best Practice Guide for CH₄ and N₂O. (Figure 5)

The solubility can be obtained from the literature in terms of the equilibrium constant (K) or the Bunsen coefficient (β), which is defined as the volume of gas at standard temperature (0°C) and pressure (1 atm) conditions (SPT) dissolved per unit volume of solution. K_H is related to b by $K_H = \beta/dv$, where d is the density of the solution and v is the molar volume of the gas at STP.

3.2. Correction for water vapor pressure

In some configurations water vapor is removed before the sample loop (note that in Figure 4 the water trap is located after the sample loop). In these cases, a correction needs to be applied to the P term used in equation 5 and 6 to account for the increase in the partial pressure of N₂O and CH₄ in the gas sample due to the removal of water:

$$(8) \quad P_{equi}^{wet} = (P_{equi} - pH_2O)$$

Where P_{equi} is the total pressure (1atm) and pH_2O (atm) is the water vapor pressure in the headspace in contact with the water sample and that can be determined as a function of salinity, S, and T (K) following Weiss and Price (1980):

$$(9) \quad pH_2O = \exp \left(24.4543 - 67.4509 \left(\frac{100}{T} \right) - 4.8489 \ln \left(\frac{T}{100} \right) - 0.000544 S \right)$$

This correction is typically small. For example, for equilibration temperatures ranging between 20 and 25°C and a water sample with a salinity of 35, the correction is approximately 3% of the dissolved gas concentration.

4

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This SOP is part of a Best Practice Guide for dissolved CH₄ and N₂O measurements. The individual chapters are listed below, plus the accompanying calculations template:

Chapter 1 Sampling and sample storage for dissolved CH₄ and N₂O

Chapter 2 Calibration of CH₄ and N₂O

Chapter 3 Internal control procedures for dissolved CH₄ and N₂O analysis

Chapter 4 Quantification of dissolved CH₄ and N₂O via the purge-and-trap method

Chapter 5 Quantification of dissolved CH₄ and N₂O via headspace equilibrium

Chapter 6 Underway measurements of CH₄ and N₂O in surface seawater

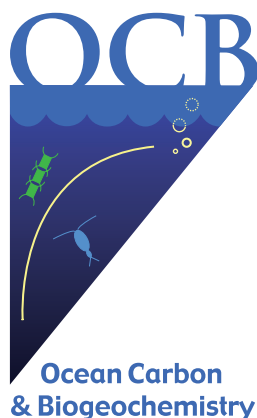
Chapter 7 Data reporting and archiving for dissolved CH₄ and N₂O

Supplementary File: Template calculations for the Best Practice Guide on Dissolved CH₄ and N₂O measurements ([link](#))

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