Protocol for CO2 sampling in waters by the use of the headspace equilibration technique, based on the simple gas equation; second update

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Method Article

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Abstract

The headspace equilibration technique is a tried and well tested method for gas sampling. Nevertheless, differing sampling protocols exist and only a few of them have been published or compared with each other. This renders the development of methods and data computation difficult and it requires a high degree of expert knowledge. This protocol presents a detailed description including technical improvements. In detail, the background correction is new and a precision test ensures data quality. The calculation is based on the simple gas equation and therefore takes pressure and temperature differences into account. The sampling procedure takes approximately 30 to 45 minutes per value including preparation, sampling, analysis and subsequent calculation. Equipment and consumables are cheap and largely recyclable. This protocol can easily be adapted to different experiments and various soluble gases. It has the aim to standardize the headspace equilibration technique and subsequent data processing not only for water researchers. _____ Changes have been made to multiple sections of the protocol. A pdf of the original version can be found in the attachments. - Bronwen Dekker, Senior Editor, Nature Protocols, 27/09/2016 _____ Further changes have been made to multiple sections of the protocol. A pdf of the previous version can be found in the attachments. - Ashleigh Carver, Senior Editorial Assistant, Nature Protocols, 30/08/2017

Introduction

The headspace equilibration technique has traditionally been used to estimate different gas concentrations in liquid samples. The main principle of this technique involves a small headspace volume \(gas phase) and a large liquid sample volume \(water phase) reaching a state of equilibrium within a closed vessel. Hitherto, the definition of what is small and what is big has varied from study to study. Syringes or bottles are often used as vessels [1-5]. The volatile components diffuse into the headspace until a state of equilibrium is reached. The sample for subsequent gas chromatography or infrared gas analysis is taken from the equilibrated gas phase and from the air that was originally injected as headspace [1,5]. Recently developed instruments like CONTROS HydroC^{TM} probes already combine the principle of diffusive equilibration with modern techniques like non-dispersive infrared spectrometry directly [6]. However, it is often not possible to analyse the samples directly in the field. In this case they are stored until analysis, for example in closed evacuated serum vials [7,8]. The protocol presented here describes the use of vials since they are gas-tight and easy to store \(in contrast to syringes). But since it is not possible to evacuate these vials completely the protocol includes a background correction to the sampling procedure and a precision test is described to ensure that data are of sufficiently high quality [8]. Alternative approaches have been described in Aberg and Wallin [5], Lambert and Fréchette [4], or Demarty, et al. [9], for instance. Henry's law and the water temperature at the time of sampling are used to calculate the Henry constant _k_h_ [10,11]. Since there are many different definitions of the Henry constant, the units and also definitions of all other abbreviations used \(including units) are provided in Table 1. **Table 1**


k_h \(here k0) is then often

used to calculate the ambient partial pressure and concentration of CO_2 based on the gas concentration of the equilibrated gas and the volumes of gas and water that were equilibrated, in accordance with Fick's first law [1-3,12,13]. Fick's first law of diffusion states that a diffusive flux is proportional to the concentration \(or partial pressure) gradient between different phases. This calculation ignores the effect of ambient pressure on the solubility of gas as described in the simple gas equation. Details are described in Dickson [13] and Aberg and Wallin [5], for example. The calculation presented here is based on the simple gas equation, also known as combined gas law, since it combines the laws of Boyle and Mariotte and Gay-

Lussac's law. It is based on the assumption of ideal conditions, with p*V/T=nR \(p=pressure, V=volume, T=temperature, R=gas constant, n=quantity of gas)[21]. In contrast to other approaches it takes the effects of both temperature and pressure on the solubility of the gas into account. This is especially important if sampling takes place at different depths or altitudes or under varying weather conditions. **_Application of the method._** The presented application have benefits for different research fields, including sport medicine. The used calculation is for instant relevant for divers that often use the laws of Boyle and Mariotte as basis for the calculation of the gas volume needed for each dive. These laws ignore the effect of temperature on pressure and volume. A correction of this approach could help to reduce known diver accidents like the decompression sickness. However, the original purpose of this article was to address the application of this technique for the aquatic research community. In recent decades the number of greenhouse gas studies - done in freshwaters and oceans - has increased rapidly. For researchers seeking to quantify the anthropogenic proportion of CO_2 emissions and assess their contribution to ocean acidification, obtaining accurate measurements and robust analytical techniques for measuring dissolved CO_2 has become a high priority[13]. CO_2 measurements in particular are increasingly based on automatically collected time series coming from newly developed instruments [1,4,9,14,15]. These can be placed directly in the water or next to it. Details concerning the potential and limitations of the instrumentation are described in UNESCO/IHA [12], Lambert and Fréchette [4] and Dickson [13], for example. Although some of the commonly used instruments are fast and precise, with high data acquisition rates and storage capacities, most of them are expensive and consume a large amount of power [12]. Furthermore, calibration problems hamper the comparability between time series from different probes. For this reason there is a need for a standardized, easy to handle and cheap tool that can bridge the gaps between studies based on different instruments. One alternative to automatically gathered CO_2 data is based on measurements of pH, temperature and concentrations of total alkalinity or dissolved inorganic carbon [12,13,16-18]. This approach has its limitations, especially if it is used in conditions of low carbonate alkalinity and high DOC concentrations, as well as in acid conditions if the pH value exceeds 8 and carbon precipitation takes place [1,17,19]. Furthermore, precise calculation of CO_2 values is highly dependent on accurate pH and temperature measurements, and these are subject to considerable degrees of uncertainty \(up to 50%), especially outside the laboratory [1,19]. In view of this, the classical headspace equilibration technique would appear to be a reliable means of comparing different techniques [4,12,17]. For instance, Lambert and Fréchette [4] demonstrated the stability of air samples \(CO_2 standard of 10000 ppmv) stored in syringes for at least 48 hours, with less than 5% loss. Moreover, samples near ambient air concentration \(350-530 ppmv) remained stable for more than 21 days. In contrast, water samples returned inconclusive results. This was probably related to microbial activity or chemical reactions taking place in the different samples. Thus more robust data can be expected if gas samples rather than water samples are stored. If water samples have to be used it is worth exploring options for sample preservation \(for instance using chloride). The choice of the means of transport \(by air or by car) appears to have no significant effect on data quality [4], so samples can be transported over long distances. In some cases the headspace equilibration technique has already been used to compare

instruments or to test the accuracy of probes. For instance, Abril et al. [14] showed that CH_4 and CO_2 values obtained using the classical headspace equilibration technique with subsequent gas chromatographic analysis correspond with values from an infrared photo-acoustic gas analyser coupled with an in situ equilibrator to approximately 15%. Recently, Aberg and Wallin [5] compared the more frequently used direct headspace method with the acidified headspace method \(in which dissolved inorganic carbon \(DIC) is measured from an acidified sample and the partial pressure is calculated from DIC, pH and temperature). They found no significant differences. This paper presents a detailed protocol of the direct headspace equilibration technique, including significant improvements such as background correction and the application of a statistical quality control routine. The quality control is especially recommended for CO_2 because it is a non-ideal gas and also the CO_2 concentration can vary greatly depending on experimental or environmental conditions. However, CO_2 is only one of several gases that can be analysed following this protocol. Other candidates are CH_4, and N_2O, for instance. Especially where low concentrations of CH_4 are to be analysed, the currently available probes are only of limited use. In this case, the headspace equilibration technique is clearly more advantageous on account of the availability of accurate analytical instruments [9,12]. Moreover, the approach presented here can easily be adapted for research for which the diffusive exchange between different phases has to be calculated, for example in the investigation of rising gas bubbles. In this case the hydraulic pressures at different depths have to be measured instead of the ambient pressure as described here. **_Limitations_**. The headspace equilibration technique is not suitable for cases in which large amounts of high-frequency data are to be gathered over a long period of time \(for instance where long-term, cyclical daily measurements are required). In such situations automated systems are more effective. Furthermore, although this protocol simplifies the sampling procedure and the data processing, the use of analytical instruments demands expert knowledge, so technicians need to receive training in the use of specific instruments.

Equipment

• 60 ml disposable syringe • Needle for the syringe \(maximum 0.90 x 70 mm) • Stopwatch • 3x10 ml serum vial • 3×20 mm butyl stopper \(the stopper must be tested to be suitable for the used serum vial) • 3×20 mm aluminium cap \(suitable for the butyl stopper) • Crimp pliers \(here 20 mm) • Barometer • Water thermometer • Vacuum pump with devices \(needle, tube) for the evacuation of vials • Headspace FID or EC-GC with standard gas and equipment • CO_2-free gas \(nitrogen) If standard equipment is already available, the operating costs can be estimated at 5 EUR per sample, especially since the expensive consumables are reusable \(vial, syringe and needle).

Procedure

PREPARATION Close all serum vials with the stoppers and the aluminum caps. Take care that both are well fixed and centered. Use the crimp pliers to close the vial. Evacuate the closed vials as follows: Insert the needle into the tube and fix both at the outlet of the vacuum pump. Insert the needle into the middle of the butyl stopper of the vial and let the pump run until the vial is completely evacuated \(it

takes one to two minutes, depending on the pump's capacity). The evacuation has succeeded well if the butyl stopper indents a little. Label the evacuated vials with symbols enable you to distinguish between the blind sample \(v_B), ambient air \(v_{AA}) and equilibrated air \(v_{EA}). TIMING: The preparation takes around 10 minutes for 3 samples \(including assembly and dismantling of the pump construction). **SAMPLING AND ANALYSIS** Measure or describe the following parameters: water temperature, air pressure and relevant events \(weather, discharge or wave intensity). The descriptive information can be a help when it comes to interpreting the data. Sample the control. To this end, inject 10 ml of a CO_2-free gas \(nitrogen) or standard gas in v_B using the 60 ml syringe. The gas enters the vial automatically if the evacuation was performed correctly. Since it is impossible to evacuate a vial completely a control measurement has to be taken for the background correction. Take a 10 ml sample of ambient air directly over the water surface and inject it into v_{AA}. As an alternative, artificial air free of CO_2 \(nitrogen or from a scrubber) can be used instead of ambient air. In the latter case the results from v_{AA} should be the same as those from v_B. Now the main sampling takes place: Fill the syringe with 40 ml water. Create a headspace in the syringe by sampling 20 ml of ambient air. As an alternative, CO_2-free air can be used to create the headspace. Equilibrate both phases by shaking the syringe for 1 minute under the water surface. Since the saturation of the water and hence the amount of gas that drifts into the gas phase are dependent on the temperature it is important that the equilibration is done at water temperature and therefore below the surface. This could make a significant difference where springs are sampled during the summer, for instance. The temperature of the spring might be below 10°C whilst the air temperature is around 30°C. Also, if the sample is shaken in the air, the temperature of the sampler's hand could affect the temperature of the solvent and thus the equilibration of both phases. Flush the needle of the syringe by discarding 10 ml of the equilibrated gas after equilibration is finished. Inject the remaining equilibrated gas into v_{EA}. Store all vials at approximately 6°C until further analysis can take place. Analyses should be done within 48 hours, especially where higher concentrations are expected [4]. Subsequent gas analyses can be performed using an infrared gas analyzer or headspace gas chromatography. The choice of device \(for instance the detector) depends on the one hand on the laboratory equipment and on the other hand on the anticipated concentration. **TIMING:** The sampling procedure takes approximately 10 minutes for 3 samples, including registration of environmental parameters. Since different protocols exist on how CO_2 should be analyzed, the analysis itself can take 5 to 15 minutes per sample. The time needed for calibration and the instrument's warm-up time are not taken into consideration. This takes approximately one hour. **CALCULATION** The following values are required for the calculation of the partial pressure and the concentration of CO_2 in water: measured CO_2 concentration from different vials \(unit=ppmv or mgL^{-1}; C_B=concentration v_B; C_{AA}=concentration v_{AA}; C_{EA}=concentration v_{EA}), air pressure \(p_A in atm) water temperature \(T_w in K). A step by step explanation of the calculation procedure is given below. 1. Correct the concentrations \(ppmv) of ambient air \(C_{AA}) and equilibrated air \(C_{EA}) for background concentration by subtracting C_B. If several samples are taken it is necessary to determine the mean of a suitable number of blind samples. Before doing this, discard obvious outliers and calculate the mean, and use this as the correction factor for all samples. The standard deviation can be used for

subsequent sensitivity analysis, if required. 2. **Multiply the resulting C_{EA} by 2**. This is a constant that needs to be included since only half of the equilibrated air was transferred into the evacuated vial \(in this case: 10 ml of 20 ml). According to the ideal gas law, the concentration of C_{EA} was thus halved, and this needs to be compensated by doubling the value. If greater or lesser amounts of gas are transferred into the vial, the calculation must be adapted accordingly. 3. Calculate the gas volume of the experiment \(V_{Exp} in L mol^{-1}) as derived from the ideal gas law: See figure in Figures section. \(1) To describe the ideal gal, the molar volume \(V_i=V/n=22.414 L mol^{-1}) of the ideal gas at standard pressure \(p_i=1 atm) and temperature \(T_i=273.15 K) can be used[21]. 4. Calculate the amount of CO_2 in mol in the headspace before equilibration \(C_{before}) using equation 2: See figure in Figures section. \(2) Whereby 10^{-6} and 10^{-3} are unit-conversion factors. 10 ml indicates the amount of sampled air. Values have to become adapted accordingly. 5. Calculate _C_{after}_ \(in mol), the amount of CO_2 in the headspace after equilibration using the following formula: See figure in Figures section. \(3) 6. For the following step calculate first _k_0_, the Henry constant \(_k_H_, mol L^{-1} atm^{-1}, k_H=k_0) for freshwater. Use the formula given in Weiss [10]: See figure in Figures section. \(4) with A_1=-58.0931; A_2=90.5069; and A_3=22.2940 \(unit in mol L^{-1} atm^{-1}). To my knowledge, the formula given in Weiss[10] is actually state of the art. If waters with higher salinity are sampled, _k_H_, can be calculated according to the full equation given there. If other gases are required \(for instance CH_4) the calculation of _k_H_ must be adapted accordingly [11,20]. 7. Now determine _C_{Equ}_, which is the concentration of CO_2 in water after equilibration according to Equation 5. See figure in Figures section. \(5) 8. Calculate _C_{water}_, the amount of CO_2 in mol in the water after equilibration \(cp. Equation 6): See figure in Figures section. \(6) with _V_w_ as the volume of sampled water \(_V_w_= 40 ml). 9. Finally, calculate the concentration of CO_2 in water \(in mol L^{-1}) and pCO_2 \(ppmv or µatm) as described in Equations 7 and 8 See figure in Figures section. \(7) See figure in Figures section. \(8) 10. Apply the quality control procedure based on precision analysis of duplicates as described in Lambert and Fréchette [4]. To this end, take all samples in pairs. The statistical sampling design must of course be adapted to take account of the specific issue being investigated or environmental conditions. In some cases it is therefore advisable to take three or more samples. Calculate the degree of precision using the following equation: See figure in Figures section. \(9) with _pc_ as the precision coefficient, d_i as the difference between two duplicates, and n as the number of duplicate pairs. Convert the precision to a percentage using equation 10. See figure in Figures section. \(10) where m is the mean of the duplicates. The degree of precision of the results is high if _pc_ \(%) is low \(in the extreme, equal values have a _pc_ of 0%). **_ANTICIPATED RESULTS_** The example given below can be used to illustrate the calculation step-by-step. The experimental conditions of the fictitious experiment are as follows: p_A=0.95 atm and T_w=285 K. The samples were taken at 5 locations with the same environmental pressure \(same depth or same altitude). The water temperature was also the same for all locations. Three control samples were taken for the background correction. The mean concentration of the controls is C_B=21 \(SD 12). The experimental conditions and the results are given in Table 2. Change the input data \(especially pressure and temperature) and observe how it affects the outcome. **Table 2**_ See figure in Figures section.

Timing

Following the protocol given above the overall process takes 30-45 minutes for preparation, sampling, analysis and calculation of one value.

Troubleshooting

It could happen that the vacuum pump runs in the wrong direction or the vials are not sealed. Check whether the vials are evacuated correctly during the evacuation process. To this end, evacuate a test vial initially or in between. Afterwards, insert a syringe filled with 10 ml ambient air into the vial and check whether the air flows into the syringe of its own accord. The needle must be securely fixed to the syringe. If this is not the case it may become detached and get lost during the equilibration process. Make sure you have some additional needles and also an additional syringe with you. The vials could get lost during the sampling procedure. Take some replacements with you. If the background vials return a high variation in the measured gas concentration or the quality control procedure returns a high percentage one can assume that the vials were not sealed or there was a problem during analysis. All of the vial samples should be discarded. This protocol was created based on the actual knowledge of the author. The author of this protocol is not liable for any error in this approach \(including the calculation).

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Figures

$$V_{Exp} = \frac{V_i * P_i * T_w}{T_i * P_A}$$

Figure 1

Equation 1 Equation 1

$$C_{before} = \frac{C_{AA} * 10^{-6} * 10\,ml * 10^{-3}}{V_{Exp}}$$

Figure 2

Equation 2 Equation 2

$$C_{after} = \frac{C_{EA} * 10^{-6} * 10\,ml * 10^{-3}}{V_{Exp}}$$

Figure 3

Equation 3 Equation 3

$$lnk_0 = A_1 + A_2\left(\frac{100}{T_w}\right) + A_3 \ln\left(\frac{T_w}{100}\right)$$

Figure 4

Equation 4 Equation 4

$$C_{Equ} = k_0 * C_{EA} * 10^{-6}$$

Figure 5

Equation 5 Equation 5

$$C_{water} = C_{Equ} * V_w * 10^{-3}$$

Figure 6

Equation 6 Equation 6

$$CO_2 = \frac{C_{water} + C_{after} - C_{before}}{40\,ml\ * 10^{-3}}$$

Figure 7

Equation 7 Equation 7

$$pCO_2 = \frac{CO_2}{k_0} * 10^6$$

Figure 8

Equation 8 Equation 8

$$pc = \sqrt{\frac{\sum_i^n (d_i)^2}{2n}}$$

Figure 9

Equation 9 Equation 9

$$pc(\%) = \frac{pc}{m} * 100\%$$

Figure 10

Equation 10 Equation 10

Variable	Description
A_1	-58.0931 mol L^{-1} atm^{-1}
A_2	90.5069 mol L^{-1} atm^{-1}
A_3	22.2940 mol L^{-1} atm^{-1}
C_B, C_{AA}, C_{EA}	C_B=concentration v_B; C_{AA}=concentration v_{AA}; C_{EA}=concentration v_{EA}
C_{before}	concentration of CO_2 in mol in the headspace before equilibration
C_{after}	concentration of CO_2 in the headspace after equilibration
C_{Equ}	concentration of CO_2 in water after equilibration
C_{water}	amount of CO_2 in mol in water after equilibration
CO_2	Dissolved carbon dioxide
FID-/EC-GC	gas chromatograph equipped with flame ionization detection or electron capture detection
k_0	Henry's constant for freshwater systems
K_h	Henry's constant in mol L^{-1} atm^{-1}
n	Quantity of gas in mol
p_A	Air pressure in atm
pCO_2	Partial pressure of CO_2 (ppmv)
p_i	ideal gas pressure (atm)
R	Gas constant
SD	Standard deviation
T_w	Water temperature in K
T_i	ideal temperature (K)
V_{Exp}	gas volume of the experiment (in L mol^{-1})
V_i	gas volume of the ideal gas (in L mol^{-1})
v_B, v_{AA}, v_{EA}	vials for blind sample (v_B), ambient air (v_{AA}) and equilibrated air (v_{EA})

Figure 11

Table 1 Table 1: Abbreviations and units.

sample ID	measured		calculated	
	C_{AA} ppmv	C_{EA} ppmv	CO_2 mol L^{-1}	pCO_2 ppmv
1	400	765	$8.6*10^{-5}$	1711.3
2	412	800	$9.0*10^{-5}$	1793
3	402	960	$1.1*10^{-4}$	2179.45
4	411	120	$8.0*10^{-6}$	159.34
5	410	1500	$1.75*10^{-4}$	3475.31

Figure 12

Table 2 Table 2: Settings and results of the described example.

Supplementary Files

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