



# Amperometric sensor for nanomolar nitrous oxide analysis

Lars Riis Damgaard <sup>a</sup>, Colette Kelly <sup>b</sup>, Karen Casciotti <sup>b</sup>, Bess B. Ward <sup>c</sup>,  
Niels Peter Revsbech <sup>a,\*</sup>

<sup>a</sup> Aarhus University Centre for Water Technology, Department of Bioscience, Ny Munkegade 114, 8000, Aarhus C, Denmark

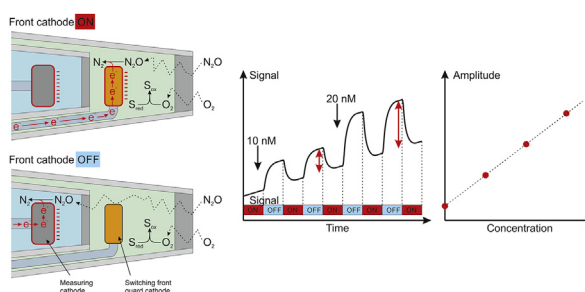
<sup>b</sup> Department of Earth System Science, Stanford University, CA, 94305, Stanford, USA

<sup>c</sup> Department of Geosciences, Princeton University, NJ, 08544, Princeton, USA

## HIGHLIGHTS

- A sensor for measuring atmospheric (nanomolar) levels of nitrous oxide is presented.
- Automatic zero-point determination enables continuous drift compensation.
- The size of the sensor and amplifier allow measurements in the field.
- Nitrous oxide data from the Eastern Tropical North Pacific Ocean are presented.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nitrous oxide is an important greenhouse gas and there is a need for sensitive techniques to study its distribution in the environment at concentrations near equilibrium with the atmosphere (9.6 nM in water at 20 °C). Here we present an electrochemical sensor that can quantify  $N_2O$  in the nanomolar range. The sensor principle relies on a front guard cathode placed in front of the measuring cathode. This cathode is used to periodically block the flux of  $N_2O$  towards the measuring cathode, thereby creating an amplitude in the signal. This signal amplitude is unaffected by drift in the baseline current and can be read at very high resolution, resulting in a sensitivity of 2 nM  $N_2O$  for newly constructed sensors. Interference from oxygen is prevented by placing the front guard cathode in oxygen-consuming electrolyte. The sensor was field tested by measuring an  $N_2O$  profile to a depth of 120 m in the oxygen minimum zone of the Eastern Tropical North Pacific Ocean (ETNP) off the coast of Mexico.

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## 1. Introduction

Nitrous oxide is one of the most important greenhouse gases, having a per-molecule greenhouse warming potential of about 300 times that of  $CO_2$ . The atmospheric  $N_2O$  concentration is increasing

at a fast pace, mainly due to intensified agriculture with application of large amounts of both animal manure and artificial fertilizer. Nitrous oxide is formed in soils both during nitrification, especially at low  $O_2$  concentrations, and during denitrification [1]. Man-made installations such as wastewater treatment plants [2] and various industry and transport installations [3] also contribute to the rise in  $N_2O$ . Power plants with urea dosing to reduce overall  $NO_x$  emission [4] may be hotspots for  $N_2O$  emission. In addition to managed agricultural soils (e.g. Ref. [5]), natural environments such as

\* Corresponding author.

E-mail address: [revsbech@bios.au.dk](mailto:revsbech@bios.au.dk) (N.P. Revsbech).

tropical forests, periodically flooded soils [6], and oceanic oxygen minimum zones [7] are important sources of  $\text{N}_2\text{O}$ .

At present, the  $\text{N}_2\text{O}$  concentration in the atmosphere is at 332 ppbv (October 2019, <https://www.n2olevels.org>), equivalent to 0.0337 Pa or 9.6 nM dissolved in water at 20 °C [8]. It is thus important to be able to quantify  $\text{N}_2\text{O}$  at nanomolar concentrations. Most analyses of low  $\text{N}_2\text{O}$  concentrations in gas samples are performed by gas chromatography using an electron capture detector (ECD), and for large volumes photoacoustic analysis is also possible (e.g., Ref. [9]). With these techniques, a detection level below 50 ppbv (corresponding to an equilibrium concentration of approx. 1 nM in water) can be achieved, but they can only be used to analyze gas samples and the analytical equipment is large and expensive.

Electrochemical sensor analysis of  $\text{N}_2\text{O}$  in the environment has been possible for about 30 years [10]. The first electrochemical sensors were short-lived and fragile, but later developments [11] led to much more stable sensors. These sensors have subsequently been commercialized by Unisense A/S, and according to their homepage ([www.unisense.com](http://www.unisense.com)) the present sensors may detect down to <25 nM. This level is still high compared to the typical oceanic concentrations, and the detection of nanomolar levels of  $\text{N}_2\text{O}$  by these sensors requires frequent determination of the zero signal, as there may be a small drift in the sensor baseline current, which also varies with temperature.

A decade ago, the STOX (Switchable Trace OXYgen) sensor was introduced into oceanographic research [12]. It fundamentally changed the understanding of biological transformations in oxygen minimum zones (OMZs), leading to the suggestion that OMZs should be referred to as Anoxic Marine Zones (AMZs) [13]. The STOX sensors function by having an extra cathode in front of the measuring cathode. When this front guard cathode is polarized, no or little  $\text{O}_2$  reaches the measuring cathode, and the concentration is calculated from the amplitude of signal with and without front guard cathode polarization. This methodology allowed for *in situ*  $\text{O}_2$  determination at water depths exceeding 100 m with a resolution of 1–10 nM (depending on the specific sensor), which was 1000-fold better than the routinely used technologies.

We here explore the possibility for constructing a switchable  $\text{N}_2\text{O}$  sensor analogous to the STOX sensor, as such a sensor would have widespread applications in monitoring  $\text{N}_2\text{O}$  concentrations in water, soil and air. The strength of such a sensor is that it would enable determination of near-ambient nanomolar concentrations by use of simple and compact instrumentation and without the need for frequent calibration.

## 2. Materials and methods

### 2.1. Sensor construction

The working principle of the switchable  $\text{N}_2\text{O}$  sensor presented here (Fig. 1) is similar to that of the STOX sensor [14]: An electrolyte-filled outer glass casing, the front guard, furnished with a silicon rubber tip membrane surrounds an inner  $\text{N}_2\text{O}$  micro-sensor. An electrode, the front guard cathode, is placed in the space between the silicon rubber membranes of the inner sensor and the front guard casing. During operation,  $\text{N}_2\text{O}$  from the environment will diffuse through the membrane of the front guard and, if the front guard cathode is not polarized, diffuse through the electrolyte in the front guard and the tip membrane of the inner sensor to be reduced at the constantly polarized measuring cathode, resulting in a current in the measuring circuit. On the other hand, when the front guard cathode is polarized, a substantial part of the incoming  $\text{N}_2\text{O}$  will be reduced electrochemically on its surface and will thus not reach the measuring cathode. Under the assumption that the

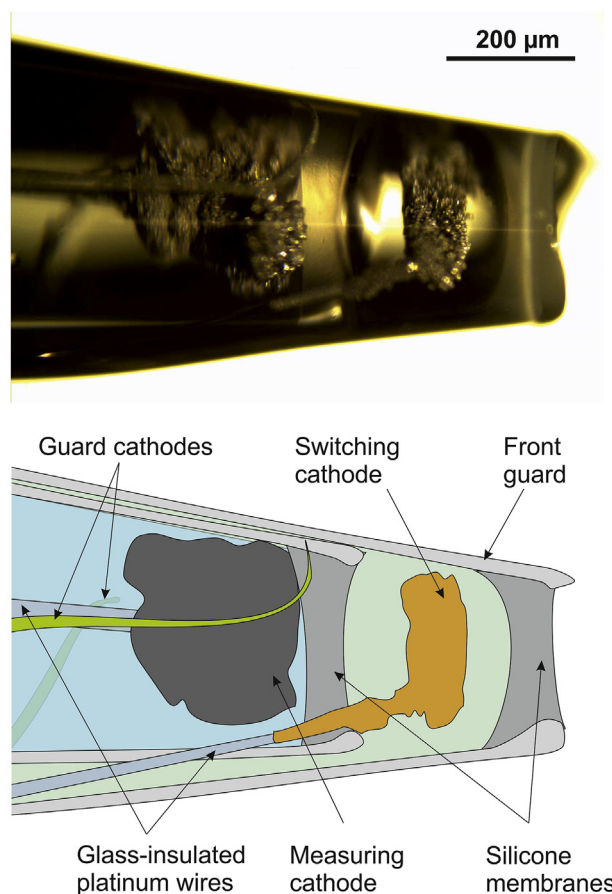


Fig. 1. Photograph and corresponding schematic drawing of a switchable  $\text{N}_2\text{O}$  sensor.

front guard cathode scavenges a constant fraction of the  $\text{N}_2\text{O}$  diffusing into the sensor when polarized, the difference in current signal with polarized versus un-polarized front guard cathode is linearly related to the  $\text{N}_2\text{O}$  concentration outside the tip. And, importantly, this difference is independent of any baseline drift. The function of the silicone membranes is 1) to electrically insulate and thus avoid electrical interference between the electric circuits in the inner  $\text{N}_2\text{O}$  sensor and the front guard as well as to avoid electrical contact to the outer environment and 2) to filter the molecules in the environment that can reach the electrodes. However, as all small uncharged molecules can pass the membranes, it is important to prevent high and variable ambient  $\text{O}_2$  concentrations in the environment from masking the signal from  $\text{N}_2\text{O}$ . To ensure this, a chemical oxygen reductant is added to the front guard electrolyte as described below. Finally, to minimize the build-up of  $\text{N}_2\text{O}$  in the electrolytes of both the  $\text{N}_2\text{O}$  sensor and the front guard, constantly polarized guard electrodes are placed behind the measuring and front guard electrodes.

The construction procedures of the switchable  $\text{N}_2\text{O}$  sensor (Fig. 1) are identical to those described for the STOX sensor [14], except for the following details: 1) both the front cathode and the measuring cathode were plated with indium instead of gold. Gold cathodes do not catalyze the reduction of  $\text{N}_2\text{O}$ , and have previously been utilized to selectively remove  $\text{O}_2$  interference in  $\text{N}_2\text{O}$  sensors [10], and 2) the front guard cathode was plated onto the exposed metal tip of a Teflon-coated 0.025 mm platinum-iridium wire (Goodfellow Corp., USA) instead of a glass-coated platinum wire. The use of platinum-iridium provides much higher mechanical strength, and the flexibility of the Teflon coating contributed to a much improved resistance to mechanical shocks as compared to

the originally described STOX sensors. The plating was performed in 20% (wt/wt)  $\text{InCl}_3$  in 1 M HCl, which was contained in a tapered capillary so that the plating could be observed in the microscope. The plating voltage applied was  $-1.3$  to  $-1.6\text{ V}$  versus a 0.1 mm diameter platinum wire. The plating should result in measuring cathodes that almost filled the lumen of the inner sensor casing, and the front guard cathode should occupy a significant fraction of the lumen in the front guard. For the front guard cathode, the size was a compromise between a relatively short compartment between the two membranes, and thus a relatively fast response, and a relatively high efficiency of  $\text{N}_2\text{O}$  removal when polarized.

As compared to the STOX sensors, which are usually constructed with a tip diameter of about 100  $\mu\text{m}$ , it was necessary to increase the tip diameter to 300–600  $\mu\text{m}$  for the  $\text{N}_2\text{O}$  sensor to get a sufficiently high current in the circuit at low nanomolar concentrations. Part of the reason for this difference is the lower number of electrons per reduced  $\text{N}_2\text{O}$  molecule. The 50–200  $\mu\text{m}$  thick silicone membranes were added by inserting the glass tips into liquid silicone sealant (Elastosil E43, Wacker, Germany) while the process was observed in the microscope at 100 $\times$  magnification.

The electrolyte around the measuring cathode was always 1 M tributylammonium iodide (for ion pair chromatography, Sigma-Aldrich) in propylene carbonate (anhydrous, Sigma-Aldrich). Two different electrolytes were tested around the guard cathode: 1) 1 M diphenylphosphine (98%, Sigma-Aldrich) plus 0.2 M tributylammonium iodide in propylene carbonate and 2) 1 M sodium ascorbate (VWR, USA) in water that was adjusted to pH 12 with NaOH, and added NaCl to a concentration of 0.2 M. The electrolyte around the guard cathode served a dual purpose, as it should intercept and scavenge all  $\text{O}_2$  diffusing in through the tip membrane, as well as support  $\text{N}_2\text{O}$  reduction at the front guard cathode when this was polarized. Diphenylphosphine [15] and alkaline ascorbate [11] have both been shown to be very efficient  $\text{O}_2$  scavengers in electrochemical  $\text{N}_2\text{O}$  sensors.

## 2.2. Laboratory electronics

In the laboratory, the sensor signal was measured by a Unisense Multimeter (Unisense A/S, Denmark), which can resolve currents down to below  $10^{-13}$  A. The multimeter polarized the sensor at a polarization voltage of  $-0.8\text{ V}$  versus the internal Ag/AgCl anode (for the aqueous ascorbate electrolyte) or silver anode (for the organic electrolytes). The multimeter was connected to a portable computer equipped with the software Sensortrace Basic (Unisense A/S), collecting data points at typically 1 Hz. To achieve the signal amplitude, the front guard cathode was connected to a switching unit (constructed in our own workshop), which continuously produced cycles of polarization switched on ( $-0.8\text{ V}$ ) and off (0V). The duration of the two switching phases could vary, depending on the individual sensor, but was typically 2–3 min for both the on and the off phase.

## 2.3. Environmental testing

The switchable  $\text{N}_2\text{O}$  sensor was tested during April 2018 at a coastal station in the ETNP OMZ off the coast of Mexico (17 40.99 N, 102 21.02W, bottom depth 1040 m), where the STOX sensor previously has been used to provide essential information about the *in situ*  $\text{O}_2$  conditions [16]. As the polarization voltage used for STOX sensors ( $-0.8\text{ V}$  relative to an internal silver pseudo-reference electrode) is identical to the one used for diphenylphosphine-based switchable  $\text{N}_2\text{O}$  sensors, it was possible to use the same pressure resistant (down to 6000 m water depth) amplifier unit [12,14] as used for STOX oxygen measurements. It was, however, necessary to use relatively long polarization/depolarization cycles

(about 10 min for a complete cycle) due to the low temperature and the long diffusion path within these comparatively large sensors. The pressure compensation with oil was identical to the procedure used for STOX sensors. The amplifier unit with mounted sensor was attached to a 24-bottle rosette water sampler with the associated CTD (Conductivity, Temperature, Depth) unit equipped with a Sea-Bird SBE-63 oxygen sensor. The CTD was used for supplying power and for logging sensor data. The CTD was lowered to 120 m depth and subsequently raised in 10-m steps. At each analyzed depth, the  $\text{N}_2\text{O}$  sensor signal was collected through several switching cycles (17–36 min) together with the CTD signals, and a water sample was collected. After recovery of the CTD, water from each analyzed depth was used to flush and completely fill 12-ml Exetainers. These water samples were preserved by injection of 0.025 ml saturated  $\text{HgCl}_2$  and stored at  $4^\circ\text{C}$  until gas chromatographic analysis (Agilent technologies; 7820A GC system, ECD detector) on shore.

Immediately after the cast, the  $\text{N}_2\text{O}$  sensor was calibrated in a sealed beaker in the lab at 0, 150, and 450 nM  $\text{N}_2\text{O}$  with the temperature drifting through the temperature range of  $11$ – $27^\circ\text{C}$  at the same switching regime as *in situ*. This was done by placing the beaker in an insulated water bath at initially  $11^\circ\text{C}$  and allowing the temperature to gradually increase to  $27^\circ\text{C}$  over approx. 2 h by gradually replacing the water in the water bath with warmer water. This calibration was used to temperature compensate the *in situ*  $\text{N}_2\text{O}$  sensor data for the *in situ* temperature variations.

## 3. Results

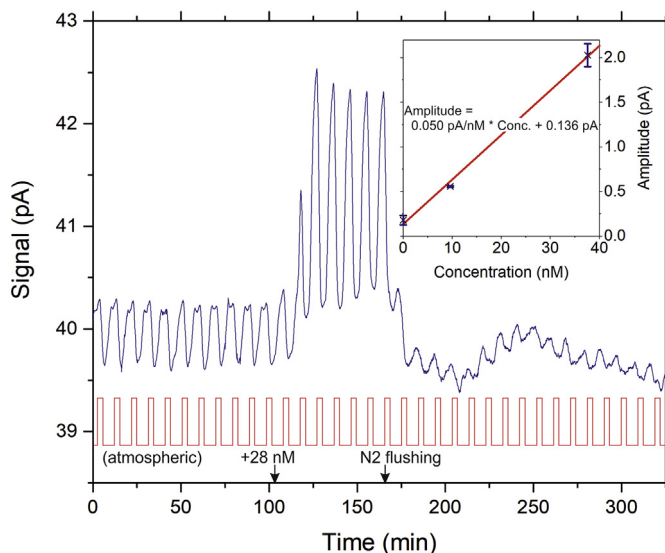
### 3.1. Diphenylphosphine-based versus ascorbate-based guard electrolyte

Sensors were constructed with both aqueous alkaline ascorbate and diphenylphosphine/propylene carbonate in the front guard cathode compartment as combined front guard electrolyte and oxygen scavenger. The use of ascorbate was, however, discontinued after a few initial tests as the cathode efficiency to reduce  $\text{N}_2\text{O}$  decreased rapidly with time (hours), possibly due to polymerization reactions at the cathode surface. In the following, we thus only describe the experiments with diphenylphosphine-based front guard electrolyte.

### 3.2. Laboratory testing of diphenylphosphine-based sensors

Many sensors ( $>20$ ) were tested in the laboratory. The sensor signal for a sensor with 600- $\mu\text{m}$  tip diameter is shown in Fig. 2 for various  $\text{N}_2\text{O}$  concentrations at room temperature. The distance between the membranes of this sensor was 460  $\mu\text{m}$  and the total distance from outside to the measuring cathode was 980  $\mu\text{m}$ . The sensor was initially measuring in air-equilibrated water, corresponding to 9.6 nM  $\text{N}_2\text{O}$  [8], exhibiting an amplitude between polarized/depolarized front guard of 0.56 pA. A volume of concentrated  $\text{N}_2\text{O}$  solution was added to increase the concentration by 28 nM to 37.6 nM, resulting in an amplitude increase to 2.03 pA. After  $\sim 60$  min, flushing with  $\text{N}_2$  gas was initiated, and the amplitude decreased to  $\sim 0.18$  pA. As shown in the inset of Fig. 2, the amplitude was a linear function of the  $\text{N}_2\text{O}$  concentration.

It should be noted that the removal efficiency of the front guard for this sensor was only  $\sim 70\%$ , as seen in Fig. 2 from the elevated “baseline” signal for “front guard on” when the  $\text{N}_2\text{O}$  concentration was increased to 37.6 nM. The magnitude of the removal efficiency is theoretically not important. It should be sufficient, however, to ensure a significant current change above the noise level. It is here important to remember that only the signal amplitude is recorded – the absolute signal levels are in principle irrelevant. However, if the absolute signal level changes quickly relative to the switching



**Fig. 2.** Tracing of sensor signal (blue line) when operated at front guard 180 s on and 400 s off intervals (running signal averaging over 10 s). The periods with the front guard on (high) and off (low) are shown in the red line. Initially, the sensor was immersed in air-bubbled water, containing ~9.6 nM  $\text{N}_2\text{O}$ . At 100 min, the  $\text{N}_2\text{O}$  concentration was increased by 28 nM (to a total of 37.6 nM) by injection of a small volume of concentrated stock solution. At ~170 min, flushing with  $\text{N}_2$  (0 nM  $\text{N}_2\text{O}$ ) was initiated. The inset shows the corresponding calibration curve of the signal amplitude during polarization on/off cycles versus concentration as an average of 4 cycles with standard deviations marked. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

cycle length (e.g. during the  $\text{N}_2$  flushing phase in Fig. 2), the amplitude must be determined via interpolation, for instance as the “polarization off” peak height above a line drawn through “polarization on” minima. It is clear from Fig. 2 that the signal did not reach a complete steady state during the front guard on/off periods; to reach complete steady state would have required impractically long switching phases. By keeping the phases with and without polarization constant it was, however, possible to get good linear calibrations. For the smaller STOX  $\text{O}_2$  sensors it was possible to approach equilibrium, even with complete cycles of less than 1 min [12].

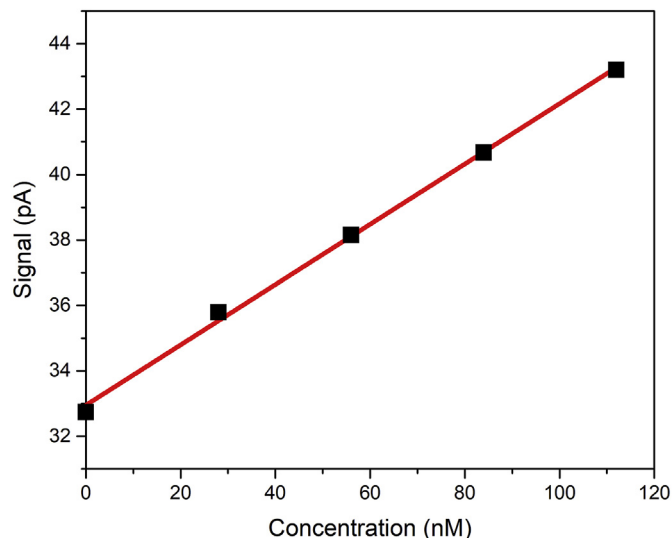
The same sensor as tested in Fig. 2 was also tested for linearity of the signal at low  $\text{N}_2\text{O}$  concentrations with the front guard continuously de-polarized. The resulting calibration curve is shown in Fig. 3.

### 3.3. Noise level (detection limit)

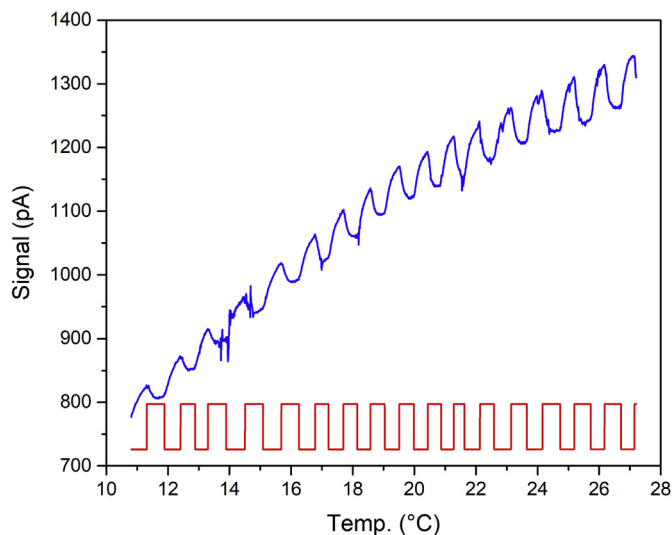
For the calibration in Fig. 2, the sensitivity was 0.050 pA/nM and the variation in the on-off amplitude for  $\text{N}_2$  bubbling was ~0.05 pA. Assuming it is possible to distinguish an increase in amplitude that is double the variation in the  $\text{N}_2$  on-off amplitude, i.e., 0.10 pA, the detection limit is 2 nM.

### 3.4. Temperature effect

The sensors were variable in terms of temperature response. Some sensors exhibited a response of 7–8% (concentration-based) for a temperature increase of 1 °C (Fig. 4) in the 10–25 °C range, which is similar to the temperature response seen for  $\text{O}_2$  by the STOX sensors [14]. Other sensors exhibited a response of 3–4%. In any case, this is substantially higher than the temperature effect on the diffusion coefficient in water in the 10–20 °C range, suggesting that the temperature coefficient for gas diffusion in silicone rubber,



**Fig. 3.** Calibration of the same sensor as used for the data in Fig. 2, but now without polarization of the front anode.



**Fig. 4.** Sensor signal (blue, 5 s running average) for 450 nM  $\text{N}_2\text{O}$  during a steady increase in temperature from 11 to 27 °C, while switching (red) at the same frequency as *in situ*. This sensor was 4 months old and the zero signal had increased by a factor of about 40 as compared to a freshly made sensor. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

which constitutes a relatively large part of the diffusion path in the  $\text{N}_2\text{O}$  sensor, is higher than for that in water.

### 3.5. Stirring effect

The stirring effect was determined for two sensors with tip diameters of 475 and 900  $\mu\text{m}$ , respectively, where the distance from the exterior to the measuring cathode was 850 and 930  $\mu\text{m}$ , respectively. Both diameter and length of diffusion path within the sensor are important parameters for stirring sensitivity, as a large diameter leads to a large stirring effect, and a long diffusion path within the sensor lowers the stirring effect. The theory of stirring effect by amperometric gas microsensors is treated in great detail by Ref. [17]. The stirring effect was determined as the amplitude increase caused by a shift from totally stagnant water to vigorously stirred water (a 25-mm long stirring magnet in a 1000 ml beaker

at ~ 200 rpm) at 2.8  $\mu\text{M}$   $\text{N}_2\text{O}$ . The stirring effect was determined to be 12 and 8%, respectively, for the two sensors, which is in the range that has been observed for other relatively large amperometric microsensors [17].

### 3.6. Lifetime

A continuous deterioration occurred in sensors made with diphenylphosphine in the guard electrolyte. Freshly made sensors usually worked satisfactorily as demonstrated in Fig. 2, but after a few days, the noise level and zero current increased. The sensor used for the oceanographic measurement (see below) was 4 months old, and at this age, it functioned poorly. It was thus only possible to record a characteristic *in situ*  $\text{N}_2\text{O}$  profile due to the relatively high concentrations (see below).

### 3.7. Ocean testing of sensor

The zero signal of the four months old sensor had increased by a factor of 40 to more than 1000 pA at room temperature with a relatively high noise level, as can be seen from the temperature calibration data shown in Fig. 4. The high zero current in combination with *in situ* temperature variations (Fig. 5) negatively affected the accuracy of concentration estimates, resulting in an estimated detection limit of ~20 nM.

One depth profile of  $\text{N}_2\text{O}$  was obtained by use of the  $\text{N}_2\text{O}$  sensor (Fig. 5). Also shown in the figure is the profiles of temperature and  $\text{O}_2$  from the CTD, and  $\text{N}_2\text{O}$  concentration determined by gas chromatography on retrieved water samples. Both methods showed peak nitrous oxide concentrations in the uppermost layers of anoxic water (50–100 m). The two concentration estimates differed substantially, however, with maxima of 170 nM determined by the sensor and 270 nM by GC analysis of retrieved water samples. Independent estimates of  $\text{N}_2\text{O}$  concentration determined from the  $m/z = 44$  peak area via isotope ratio mass spectrometry (McIlvin and Casciotti, 2010) reached 240 nM at the same station, but on a

separate cast conducted a few days earlier (data not shown).

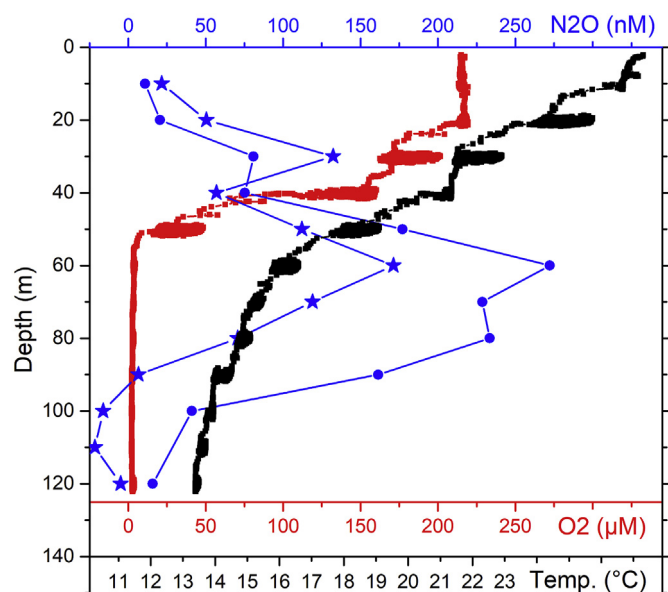
## 4. Discussion

A highly sensitive  $\text{N}_2\text{O}$  sensor was constructed. It is clear, however, that improvements must be implemented in order to produce a tool for routine monitoring of trace concentrations of  $\text{N}_2\text{O}$ . It is possible to construct  $\text{N}_2\text{O}$  sensors that have lifetimes of several months by adding an ascorbate  $\text{O}_2$  trap to the sensor tip [11]. Unfortunately, it turned out that the activity of a front guard cathode inserted into this ascorbate solution was not stable, and we thus could not use this approach to construct a trace  $\text{N}_2\text{O}$  sensor analogous to the STOX sensor for  $\text{O}_2$ . Polymerization of reactive organics on cathodes through free radicals formed by electrochemical reduction is a well-known phenomenon [18]. Use of diphenylphosphine as a reductant did not lead to problems with cathode inactivation, but had other problems. Diphenylphosphine is very aggressive to silicone membranes, causing them to swell and eventually to disintegrate. These effects cause elevated zero signals and noise levels, and clotting of the membrane by oxidation products of the diphenylphosphine (see below) is also a problem. Use of fluorinated solvent-resistant membranes such as Teflon AF would probably result in lifetimes that would allow for routine use. Teflon AF does, however, bind poorly to glass and it may be necessary to apply composite Teflon AF/silicone membranes [19] to ensure sufficiently high electrical resistance and mechanical strength.

After some time of  $\text{O}_2$  exposure, an oxidation product of the diphenylphosphine is deposited within the membrane as a dark band [15], and this deposition apparently reduces the permeability over a few weeks. The gradual decrease in membrane permeability before use due to this precipitation can be avoided by storing the sensor with its tip in anoxic solution such as alkaline ascorbate, and the sensor could subsequently be used for several weeks of monitoring in an oxic environment before the sensitivity becomes too low. It would have been optimal to use an inorganic ionic reductant instead, such as the  $\text{Cr}^{2+}$ , which has been applied in a  $\text{CO}_2$  sensor [20], but suitable inorganic reductants are not sufficiently soluble in compatible organic solvents, and, to be reactive,  $\text{Cr}^{2+}$  requires an acidic solution, in which the negatively polarized cathode would form gaseous  $\text{H}_2$  immediately.

It is remarkable that diphenylphosphine allowed for cathodic  $\text{N}_2\text{O}$  reduction without causing gradual inactivation of the cathode due to polymerization reactions or deposition of oxidation products. A similar stability of  $\text{N}_2\text{O}$  reduction in diphenylphosphine-containing electrolyte was observed by Ref. [15]. The only oxidation product of diphenylphosphine is diphenylphosphine oxide, and neither the mother compound nor the product are candidates for free-radical polymerization reactions. The membranes are not impermeable for a small uncharged molecule as diphenylphosphine, and some diphenylphosphine will thus penetrate into the electrolyte around the measuring cathode. However, this has been shown not to affect the cathode current; regular  $\text{N}_2\text{O}$  sensors are usually made with alkaline ascorbate in a separate front guard compartment as oxygen scavenger [11] to avoid membrane degradation, but it is actually possible to make  $\text{N}_2\text{O}$  sensors with only one compartment where the sensing cathode is bathed in 0.5 M diphenylphosphine [15].

As indicated by the calibration curve in Fig. 3, a simple  $\text{N}_2\text{O}$  sensor based on either ascorbate or diphenylphosphine oxygen scavenger [15] may reach similar low detection limits as observed for the much more complicated switchable sensor described here. Detection of low concentrations with these simpler sensors are, however, dependent on frequent zero calibration at highly controlled constant temperature, as drift or any change in temperature may affect the signal more



**Fig. 5.** Depth profile of  $\text{N}_2\text{O}$  in the upper 120 m in the ETNP west of Mexico (17 40.99 N, 102 21.02 W, bottom depth 1040 m) on 15<sup>th</sup> April 2018 measured both *in situ* by a switchable  $\text{N}_2\text{O}$  sensor (blue stars) and subsequently by gas chromatography on retrieved water samples (blue circles). In addition the CTD data for temperature (black, 1-s average) and  $\text{O}_2$  (red, 1-s average) are plotted. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

than would nanomolar changes in  $\text{N}_2\text{O}$  concentrations. For the switchable  $\text{N}_2\text{O}$  sensor, a small change in temperature only results in a small change in sensitivity and does not affect the detection limit. However, when measuring in environments with large temperature fluctuations, the sensor's temperature response should be determined and the temperature monitored and compensated for in the signal processing, as was done for the *in situ* data presented in Fig. 5.

To our knowledge, there is no investigation of the mechanism of electrochemical  $\text{N}_2\text{O}$  reduction in aprotic electrolytes. For oxygen reduction in aprotic media [21] it is known that the principal product is superoxide, and each  $\text{O}_2$  thus only accepts one electron. The most likely gross reaction for the reduction of  $\text{N}_2\text{O}$  is thus  $2\text{N}_2\text{O} + \text{e}^- \rightarrow 2\text{N}_2 + \text{O}_2$ , and the reduction of  $\text{N}_2\text{O}$  only consumes 1/8 of the electrons required for complete  $\text{O}_2$  reduction in aqueous media. Based on this stoichiometry and the diffusional characteristics in the sensor tip it is possible to calculate the expected current in the measuring circuit at a given concentration, and the measured currents were in the expected range (see supporting information).

According to the working principle of the switchable  $\text{N}_2\text{O}$  sensor, there should be zero switching amplitude at zero  $\text{N}_2\text{O}$  concentration. However, many sensors exhibited a non-zero amplitude (e.g. Fig. 2). The cause of this phenomenon is not resolved, but we speculate that it is the result of capacitive charging of internal structures in the sensor. Fortunately, this zero- $\text{N}_2\text{O}$  amplitude is relatively constant and can thus be compensated for through calibration.

The measured concentration profile in the sea off Mexico exhibited the same shape as the profile obtained by gas chromatography (Fig. 5), but there were substantial deviations in the absolute concentration levels. However, with either method, the measured peak concentration values were higher than values previously reported for this region of the ocean. These high concentrations of  $\text{N}_2\text{O}$  observed just below the shallow oxycline may represent an important source of  $\text{N}_2\text{O}$  to the atmosphere and are the subject of further investigation into their source magnitudes and mechanisms. Switchable  $\text{N}_2\text{O}$  sensors, such as those described here, could improve monitoring of coastal  $\text{N}_2\text{O}$  dynamics and emissions from regional hot spots.

## 5. Conclusion

It was shown that it is possible to design and construct a switchable  $\text{N}_2\text{O}$  sensor that can be used to monitor low ambient  $\text{N}_2\text{O}$  concentrations/partial pressures. A sufficiently stable and sensitive switchable  $\text{N}_2\text{O}$  sensor is highly relevant for quantification of low-intensity, but large-scale sources of atmospheric  $\text{N}_2\text{O}$  such as agricultural fields and ocean surface waters. In the design presented here, it could even be used for depth profiling of soils and water masses. We demonstrated the potential of such a sensor by measuring a concentration profile in the marine waters off Mexico, which is an important natural hotspot for  $\text{N}_2\text{O}$  production. The main advantage of the switchable  $\text{N}_2\text{O}$  sensor as compared to conventional  $\text{N}_2\text{O}$  sensors is the insensitivity to baseline drift on the signal, enabling prolonged monitoring of nanomolar  $\text{N}_2\text{O}$  concentrations without zero calibration. With the present components, the lifetime of the sensors is too short for extensive use. Application of more durable membranes may increase the lifetime considerably and thereby open the way for a compact instrument that can routinely monitor  $\text{N}_2\text{O}$  at relevant ambient levels.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have

appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aca.2019.12.019>.

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