Highly precise atmospheric oxygen measurements as a tool to detect leaks of carbon dioxide from Carbon Capture and Storage sites
van Leeuwen, Charlotte

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2015

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
van Leeuwen, C. (2015). Highly precise atmospheric oxygen measurements as a tool to detect leaks of carbon dioxide from Carbon Capture and Storage sites [Groningen]: University of Groningen

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Chapter 3

Instruments for atmospheric O\textsubscript{2} measurements

3.1. Introduction

Atmospheric oxygen (O\textsubscript{2}) measurements are challenging and currently still only performed by about a dozen programs in the world (Keeling and Manning, 2014). The first atmospheric O\textsubscript{2} measurements with sufficient precision started in 1989, when flask samples from three different sites were analyzed using an interferometric technique (Keeling, 1988a; 1988b; Keeling and Shertz, 1992). In time several other techniques were developed, including mass spectrometry (Bender et al., 1994), paramagnetic analysis (Manning and Keeling, 1999), gas chromatography (Tohjima, 2000), a vacuum ultraviolet absorption technique (Stephens, 1999) and an electrochemical fuel cell technique (Stephens et al., 2007). All techniques are differential techniques, meaning that they measure the difference between an air sample and a reference gas from a gas cylinder. Air samples are dried and stored in glass flasks to be analyzed later, or sent directly to an analyzer (Keeling and Manning, 2014).

The Centre for Isotope Research (CIO) of the University of Groningen, the Netherlands, is one of the laboratories involved in atmospheric O\textsubscript{2} measurements. Flask sampling for atmospheric O\textsubscript{2} measurements at the CIO started in December 1998 at the atmospheric research station Mace Head, Ireland, followed by the atmospheric monitoring station Lutjewad, the Netherlands, in October 2000. The CIO also measured flask samples from the F3 gas production platform in the North Sea, the Netherlands (van der Laan-Luijkx et al., 2010a), Jungfraujoch, Switzerland (van der Laan-Luijkx et al., 2013), aircraft samples from Fyodorovskoye, Russia (van der Laan et al., 2014), and very recently flask samples are also taken at Halley station, Antarctica. The flask samples are analyzed on a Micromass Optima Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS), in a similar way as described by (Bender et al., 1994), although the DI-IRMS of the CIO measures simultaneously the masses 32 (\textsuperscript{16}O\textsubscript{2}) and 28 (\textsuperscript{14}N\textsubscript{2}).

In August 2008 the CIO started continuous atmospheric O\textsubscript{2} measurements at the gas production platform F3 (van der Laan-Luijkx et al., 2010b). In 2011 an almost identical copy of this instrument was built and placed at the atmospheric monitoring station Lutjewad. Besides these long-term measurement programs at fixed stations, a transportable O\textsubscript{2} – CO\textsubscript{2} instrument to aid in leak detection of Carbon Capture and Storage (CCS) sites was also developed, as is presented in this chapter. All three systems use the fuel cell technique developed by (Stephens et al., 2007) for the atmospheric O\textsubscript{2} measurements with the commercially available Oxzilla II instrument from Sable Systems. All three systems measure simultaneously the CO\textsubscript{2} concentration of the air, which is not only necessary to correct for the dilution effect of CO\textsubscript{2}, according to equation 1.2, but is also essential information to interpret the O\textsubscript{2} measurements.

In this chapter, the different instruments for atmospheric O\textsubscript{2} (and CO\textsubscript{2}) measurements at the CIO are presented. Section 3.2 describes the measurements of the flask samples and working gas cylinders on the DI-IRMS (for O\textsubscript{2}) and HP Agilent HP6890N Gas
Chromatograph (for CO₂). Section 3.3 describes the continuous O₂ – CO₂ monitoring system at Lutjewad and the new, transportable, instrument developed to aid in CO₂ leak detection. The performance of the instruments (accuracy and precision) is also discussed in these sections.

3.2. Flask sample and working gas cylinder analysis

Flask samples and high-pressure working gas cylinders are analyzed for several atmospheric gases at the laboratory of the CIO in Groningen, the Netherlands. Here we present the analysis and performance (accuracy and precision) of the CO₂ and δO₂/N₂ measurements of the flasks and cylinders. The long-term flask sample records of CO₂ and δO₂/N₂ of the measurement stations Lutjewad and Mace Head are presented in chapter 5 of this thesis. Working gas cylinders are used amongst others as reference, calibration and target gases for the continuous O₂ – CO₂ instruments (see section 3.3).

3.2.1. CO₂ measurements: performance of the HPGC

All flask samples have been analyzed on a HP Agilent HP6890N Gas Chromatograph equipped with Flame Ionization Detection (referred to as HPGC) to determine the mole fractions of CO₂, CO and CH₄. The HPGC system is positioned in a climate-controlled room at the laboratory of the CIO and has a set-up similar to the GC-systems described by (Worthy et al., 2003) and (van der Laan et al., 2009). Besides flask samples, also working gas cylinders, used amongst others to calibrate the continuous O₂ – CO₂ system, have been calibrated on the HPGC system. All samples are calibrated against a suite of 5 primary standards linked to the World Meteorological Organization (WMO) X2007 scale with CO₂ ranging between 354 and 426 µmol mol⁻¹ (ppm). These primary standards were provided by the Earth System Research Laboratory (ESRL) of the National Oceanic and Atmospheric Administration (NOAA). The measurement precision and accuracy for flask measurements of CO₂ on the HPGC is typically <0.06 ppm and <0.07 ppm, respectively.

Since the summer of 2013, working gas cylinders are also calibrated for CO₂, CO and CH₄ mole fractions on a Cavity Ring-Down Spectrometer (CRDS) model G2401-m from Picarro (Inc., CA, USA) using the same suite of primary standards. We refer to (Chen et al., 2010) for more details on the CRDS technique. The CRDS CO₂ measurements of the working tank mixtures have a precision of <0.03 ppm and accuracy of <0.07 ppm.

3.2.2. δO₂/N₂ measurements: performance of the DI-IRMS

All flask samples and working gas cylinders used to calibrate the continuous O₂ – CO₂ instruments are analyzed on the Micromass Optima Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) that is placed in a climate-controlled room in the laboratory of the CIO to determine the O₂/N₂ ratio. The measurements are performed in a similar way as described by (Bender et al., 1994), but our DI-IRMS measures simultaneously the masses 32 (¹⁶O₂) and 28 (¹⁴N₂) of both a sample and a machine reference gas which gives δO₂/N₂ as presented in equation 1.1. A suite of working gas cylinders is measured on a regular basis to correct for the long-term drift of the instrument. The measurements are linked to the international “Scripps” scale by a suite of three primary calibration cylinders in the
Instruments for O\textsubscript{2} measurements

range from -805 to -258 per meg purchased from the Scripps Institution of Oceanography (SIO), San Diego, USA.

A detailed description of the calibration of the DI-IRMS and an analysis of the precision and accuracy of the O\textsubscript{2} measurements at the CIO can be found in the appendix of this thesis. Summarized, the precision and accuracy of our O\textsubscript{2} measurements is acceptable although not state-of-the-art at the moment in comparison to some other laboratories. This conclusion, however, is entirely based on high-pressure gas cylinder measurements. The precision of a single measurement of a cylinder is found to be 10 – 14 per meg (based on the working gases of the DI-IRMS, the intercomparison measurements and the measurements of 153 gas cylinders). The precision of single flask measurements was found to be 6 per meg – a factor of two better.

Looking only at the internal scale, the accuracy is found to be about 2 per meg or better. Combining this with the precision of our double flask measurements of \approx 4 per meg, the flask-based time series of Lutjewad and Mace Head can be considered as very reliable. Sampling, transportation and storage of the flasks do, however, also play an important role in the final quality of the dataset. The link to the international scale is difficult to assess, because of problems in our laboratory associated with measuring gas cylinders. Efforts to the improvement of gas cylinder measurements in our laboratory are underway, and the first results look promising.

3.3. Continuous atmospheric O\textsubscript{2} measurements

In this thesis measurements are presented from both the continuous O\textsubscript{2} – CO\textsubscript{2} system placed at Lutjewad (chapter 5) as well as from a new, transportable, O\textsubscript{2} – CO\textsubscript{2} system that was used to demonstrate the use of combined O\textsubscript{2} and CO\textsubscript{2} measurements in CO\textsubscript{2} leak detection at Carbon Capture and Storage sites (chapter 4). In this section both systems are described. The design of the transportable system was based on the fixed systems at F3 and Lutjewad (which are almost identical). Three main things were changed to facilitate the transportability of the instrument: 1) the analyzers, gas handling equipment and belonging electronics were packed in a transportable case, 2) the calibration and reference gas cylinders were packed in a transportable case with special attention to the regulators and 3) the air-drying system was simplified and reduced in size and weight. Next to these three changes to facilitate the transportability, several other parts of the instrument were improved, such as the CO\textsubscript{2} analyzer and the type of valves.

In this section, the CO\textsubscript{2} (section 3.3.1.1) and O\textsubscript{2} (section 3.3.1.2) analyzers that are used in the two systems are described. This is followed by a description of the gas handling of the systems (section 3.3.2). Sections 3.3.3 and 3.3.4 give overviews of the transportability of the new system and the performance of the two instruments, respectively.

3.3.1. Analyzers

3.3.1.1. O\textsubscript{2} analyzer

Both systems use a commercially available differential fuel-cell analyzer to measure the O\textsubscript{2} concentration of the air. Sable Systems’ Oxxilla II O\textsubscript{2} analyzer uses two fuel cells for
measuring the \( \text{O}_2 \) concentration. The fuel cells consist of a lead anode, a gold cathode and a weak acid serving as an electrolyte. In the cells, the following reaction takes place:

\[
\text{O}_2 + 4\text{H}^+ + 2\text{Pb} \rightarrow 2\text{H}_2\text{O} + 2\text{Pb}^{++}
\]

Equation 3.1

The current that is generated by this reaction is linearly proportional to the partial pressure of the \( \text{O}_2 \) concentration in the air sample. The fuel cells are user-replaceable and have a service life of 2 – 3 years. The temperature of the instrument is kept constant at 32°C.

The instrument is a differential analyzer, which means that it is continuously measuring both the sample air and a reference gas (alternating between the two fuel cells) to correct for instrument drift.

3.3.1.2. \( \text{CO}_2 \) analyzers

The original continuous \( \text{O}_2 – \text{CO}_2 \) systems of the CIO (placed at F3 and Lutjewad) use two Vaisala Carbocap GMP343 sensors to measure the \( \text{CO}_2 \) concentration of the air. The sensors are essentially the same as the sensors used in the leak detection strategy presented in the previous chapter, except for the way the air is introduced to the instrument, which is here by a flow-through principle instead of an open path. The two sensors are built inside the Oxzilla instrument and placed in series with the two fuel cells. The combination is kept at a stable temperature of 32°C.

Figure 3.1 shows the two fuel cells of the Oxzilla (left) and the two built-in \( \text{CO}_2 \) sensors (right) in the instrument at Lutjewad.

As was demonstrated already in chapter 2, the performance of the Vaisala Carbocap GMP343 sensors is not very good in the free atmosphere. The present setting, however, is much more favorable, with constant temperature and pressure, dried air, and with a double differential signal, similar to that for the fuel cells. This makes their performance good.
Instruments for O\textsubscript{2} measurements

enough for this application, as the precision of the O\textsubscript{2} measurements by the fuel cells is the limiting factor anyway. At the measurement station Lutjewad, a Cavity Ring-Down Spectrometer (CRDS) from Picarro performs high-precision continuous measurements of CO\textsubscript{2}, making it unnecessary to have a second highly precise record of CO\textsubscript{2} at the station.

For a stand-alone system such as the transportable O\textsubscript{2} – CO\textsubscript{2} system, the use of a more precise CO\textsubscript{2} instrument has merits in itself. In the new, transportable, system therefore a single Uras26 NDIR from ABB is used instead of two Vaisala Carbocap GMP343 sensors. Our specific version of ABB’s continuous gas analyzer Uras26 is able to measure both the \textsuperscript{12}CO\textsubscript{2} as well as the \textsuperscript{13}CO\textsubscript{2} concentration of the air.

Uras is short for the German words UltraRot Absorptions-Schreiber and it was developed in Germany in the 1950s. The basic principle of the instrument hasn’t changed since. Gas molecules can go to a higher energy level when they absorb infrared radiation. When the molecules fall back into their ground state, an increase in temperature is noticed. When the gas is in a closed volume, a change in temperature is accompanied by a change in pressure. By constantly interrupting the incoming infrared radiation with a chopper, the pressure in the gas room is changed all the time. With a membrane or microphone this pressure signal can be translated into an alternating current (Schmidt, 2003).

ABB’s Uras26 is able to measure up to four gas components at the same time. This is done with two different paths with two detectors in series in the end of each path (Rüdiger et al., 2008). The specific Uras26 that is used in the transportable O\textsubscript{2} – CO\textsubscript{2} instrument has only one path with two detectors behind it, as is visible in Figure 3.2.

The most important part of an Uras is the detector, which is filled with the gas component to be measured. Before the light beam hits the detector it goes through the sample or reference cell. The chopper wheel makes sure that the light beam alternates between the two. In case the sample cell does not contain the gas component to be measured, there is no difference between the two beam paths. In case, however, the air in the sample cell does contain the component to be measured, part of the emitted infrared light does not reach the detector as the sample air absorbs it. In this case there will be a pressure difference in the detector between the two moments of the chopper wheel, which is proportional (although not linearly) to the concentration of the gas component in the sample gas. For more details see e.g. (Rüdiger et al., 2008; Schmidt, 2003).

ABB’s Uras26 has an integrated calibration cell, which can move into the optical beam path. The idea behind this is to reduce operation costs since it prevents the need for expensive calibration gas cylinders (Rüdiger et al., 2008). In our setup, however, we do not use this internal calibration method. There is already a need for calibration cylinders due to the O\textsubscript{2} measurements, and so the CO\textsubscript{2} concentration is also calibrated using these cylinder measurements.
Figure 3.2: Schematic of the specific version of ABB’s Uras26 NDIR instrument as placed in the transportable O\textsubscript{2} – CO\textsubscript{2} instrument. The figure is adapted from (Rüdiger et al., 2008). Air is led through the sample cell. The light beam goes through the sample or reference cell to the detectors. A chopper wheel makes sure that the light beam alternates between the two. The instrument contains one path with two detectors placed in series, to measure both \(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\). Due to a leak in the \(^{13}\text{CO}_2\) cell we could, however, not determine the \(\delta^{13}\text{C}\) with a sufficiently high precision. The instrument contains an integrated calibration cell, which can move into the beam path.

Because the Uras26 measures simultaneously \(^{13}\text{CO}_2\) and \(^{12}\text{CO}_2\) we can determine both the CO\textsubscript{2} concentration of the air as well as its \(\delta^{13}\text{C}\) value. Unfortunately, we were not able to reach a precision high enough for \(\delta^{13}\text{C}\) to be useful in discriminating different processes in the atmosphere. A leak in the \(^{13}\text{CO}_2\) cell was probably the reason for this. Therefore, the \(\delta^{13}\text{CO}_2\) measurements play no further role in this thesis.

3.3.2. Gas handling

To reach a high precision for CO\textsubscript{2} and especially O\textsubscript{2} measurements, the incoming sample air needs careful handling. This includes, amongst others, drying of the incoming air stream and pressure stabilization. Figure 3.3 shows the gas-handling scheme of the fixed system placed at Lutjewad.

The air is pumped from the air inlet at 60 meters altitude in the tower through a Nafion column to the system inside the laboratory of the station. The Nafion column uses a counter-flow of dry air coming from the flask sampler in the laboratory and removes about 60% of the water content of the air (van der Laan-Luijkx et al., 2010b). The air is further dried in a cryotrap system. Two different cryotrap systems have been in use since the system was placed at the station in 2011. The system that is visible in the figure is in use since October 2013, after the rebuilding of the laboratory. In this system, the air first goes through a trap of -60°C and next through a trap of -80°C. Both traps consist of two cold fingers: one for the sample air and one for the reference air. There are two -60°C traps (not visible in the figure), one of which is used to dry the air while the other one is heated to remove the water again. The traps are switched every 24 hours. There is only one -80°C cryotrap which can function continuously for several months. This trap is cleaned twice a
Instruments for $\text{O}_2$ measurements

year to be certain it is not clogged with ice. Before the change in autumn 2013, two -80°C traps were alternately used in the same way as the -60°C traps are used now.

Besides sample air the system also continuously measures a reference gas to correct for instrument drift. The reference and sample air are switched between the two measurement lines every 5 minutes (using Switch Y, nr. 17 in Figure 3.3). In this way, both fuel cells and both $\text{CO}_2$ sensors alternately measure sample and reference air. The pressure in the two lines is kept equal by an MKS pressure control system.

![Gas Handling Scheme](image)

Figure 3.3: The gas-handling scheme of the fixed $\text{O}_2$ – $\text{CO}_2$ instrument at Lutjewad. The air is pumped with a flow of 60 mL/min (4) from 60 meters altitude from the tower of the station through a Nafion column (2) to the instrument in the laboratory. Here, the air is dried in a 2-step cryotrap (10). The system continuously measures both the sample air and a reference gas. These two gases are switched between the measurement lines every 5 minutes (17). The pressure in the two lines is kept equal by an MKS pressure control system (13 – 15). Two Vaisala Carbocap GMP343 $\text{CO}_2$ sensors are built inside the Oxzilla $\text{O}_2$ system and the combination is kept at 32°C (19 & 20). Once every 23 hours two calibration gases and a target cylinder are measured instead of the outside air.

The switching of the sample and reference air yields a double differential signal, which is for $\text{O}_2$ defined according to (Thompson et al., 2007):

\[
\Delta(\Delta) = (S_1 - R_2) - (R_1 - S_2)
\]

Equation 3.2
In this formula, \( S \) refers to sample air and \( R \) to reference air while the subscripts 1 and 2 refer to the two different fuel cells. The output of the Oxzilla is set at 0.6 seconds, leading to 500 data points per 5-minute switch cycle. For every measurement period of 5 minutes, an average was calculated using an optimal amount of data points. This optimum was determined by studying the minimum error in the mean of a switch cycle by varying the amount of data points included in the calculation of the average and accompanying error. The last 400 points (so 4 minutes) of every cycle are included in the calculation. The \( \Delta(\Delta) \) value is then first converted into the apparent mole fraction \( \delta XO_2 \) and then converted into the \( O_2/N_2 \) ratio using equation 1.2.

The conversion of the \( \Delta(\Delta) \) value into \( \delta XO_2 \) is done by using two calibration cylinders that are measured once every 23 hours instead of the sample air. A target cylinder, used as a check of the accuracy and precision of the system, is also measured, right after the two calibration cylinders. All three cylinders are measured for 1h15m thus leading to a gap in the dataset of 3h45m every 23 hours. Flushing of the whole line (including regulators and cold fingers) is the reason for the relatively long time the cylinders are measured. For every time that a calibration gas is measured (1h15m), one final \( \Delta(\Delta) \) value is calculated, taking the average of the last 6 out of 15 measurements (30 minutes) of this calibration gas. All \( \Delta(\Delta) \) measurements of a calibration gas within one reference air period (which is about 2 – 4 months, depending on the size of the reference gas cylinder) are then averaged and linked to the assigned \( \delta O_2/N_2 \) value as determined on the DI-IRMS.

For \( CO_2 \) we use a very similar approach, also using a double differential signal. The optimum amount of data points included in calculating the average of a 5-minute time period was found to be 80, which equals to 2 minutes and 40 seconds as the output of the \( CO_2 \) sensors is set at 2 seconds. One calibration is again determined for a whole reference air period. For every 1h15m that a cylinder is measured the last 6 out of 15 measurements (30 minutes) are used to calculate an average. The assigned \( CO_2 \) concentrations of the calibration and target cylinders were determined on the HPGC (for cylinders used before summer 2013) and recently on the Picarro cavity ring-down spectrometer (CRDS).

The gas-handling scheme of the transportable system is very similar to the gas-handling scheme of the fixed instrument just described. A schematic is visible in Figure 3.4. The main differences between the two gas handling schemes are the air-drying, overall pressure control and the \( CO_2 \) analyzer. Also the switching time between the two sample lines is different (3 instead of 5 minutes), just as the output frequencies of the data and the amount of data points included in calculating averages. All differences between the two instruments are summarized in Table 3.1.

For \( O_2 \) the calibration procedure for the transportable system is the same as for the fixed instrument at Lutjewad (also using a double differential signal), except for the switching time, measurement time of the calibration cylinders and amount of data points included in calculating the average of a switching time period (see Table 3.1). Because the Uras26 NDIR \( CO_2 \) analyzer has only one path, it is alternately measuring the sample and reference gas, instead of both lines at the same time. It is measuring 3 minutes of sample air followed by 3 minutes of reference gas. The reference measurements are used to correct the sample measurements for instrument drift. For this we use a Loess interpolation of the reference measurements to find the required correction at the times sample air was measured. For
every sample data point a specific correction factor is then subtracted from the data to result in a signal without instrument drift. This finally results into 1 data point of CO₂ per 6 minutes, which is thus 10 points per hour. Similar to the calibration procedures described before, the raw measurements are then calibrated using the measurements of the two calibration cylinders. In the range of ambient air concentrations spanned by our two calibration cylinders, the NDIR response is essentially linear (see for example Schibig et al. (2015)).

Since the frequency of the CO₂ measurements is half that of the O₂ measurements (one data point per 6 and 3 minutes, respectively), we linearly interpolate the CO₂ signal and use this to correct the O₂ measurements.

The transportable system consists of three different cases (see next section) and a small mast of 6 meter height that can be placed anywhere in the field. The system can run...
without servicing for about one month, after which the reference gas needs to be replaced and the drying system needs servicing. Different from the fixed instrument, the water vapor is not removed automatically by heating the cold fingers. The cold finger needs to be replaced every month.

Table 3.1: Differences between the fixed O₂ – CO₂ system at Lutjewad and the transportable O₂ – CO₂ system

<table>
<thead>
<tr>
<th></th>
<th>Fixed system Lutjewad</th>
<th>Transportable system</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ sensor</td>
<td>2x Vaisala Carbocap GMP343</td>
<td>ABB’s Uras26 NDIR</td>
</tr>
<tr>
<td>Sampling height</td>
<td>60 meters</td>
<td>6 meters</td>
</tr>
<tr>
<td>Drying</td>
<td>Nafion column</td>
<td>No Nafion column</td>
</tr>
<tr>
<td></td>
<td>Alternating two -60°C coolers</td>
<td>One -60°C cooler</td>
</tr>
<tr>
<td></td>
<td>Followed by a -80°C cooler</td>
<td>Followed by Mg(ClO₄)₂ tubes</td>
</tr>
<tr>
<td>Remote running time</td>
<td>≈ 2 – 4 months</td>
<td>≈ 1 month</td>
</tr>
<tr>
<td></td>
<td>Replacing reference cylinder</td>
<td>Replacing reference cylinder</td>
</tr>
<tr>
<td></td>
<td>Changing cold finger</td>
<td>Changing cold finger</td>
</tr>
<tr>
<td>Overall pressure control</td>
<td>-</td>
<td>Pressure controller at the exit</td>
</tr>
<tr>
<td>2-way switching valves</td>
<td>Valco 4-port, 2-way valve</td>
<td>4 x Numatics S-series</td>
</tr>
<tr>
<td>2-way solenoid valves</td>
<td>Parker Skinner</td>
<td>Numatics S-series</td>
</tr>
<tr>
<td>Package</td>
<td>Open racks</td>
<td>Closed cases</td>
</tr>
<tr>
<td>Switching time</td>
<td>5 minutes</td>
<td>3 minutes</td>
</tr>
<tr>
<td>Raw output frequency O₂</td>
<td>0.6 seconds</td>
<td>1 second</td>
</tr>
<tr>
<td>Last xx used for O₂</td>
<td>400 points = 4 minutes</td>
<td>90 points = 1 min + 30 sec</td>
</tr>
<tr>
<td>Raw output frequency CO₂</td>
<td>2 seconds</td>
<td>5 seconds</td>
</tr>
<tr>
<td>Last xx used for CO₂</td>
<td>80 points = 2 min + 40 sec</td>
<td>9 points = 45 sec</td>
</tr>
<tr>
<td>Calibration and target cylinders</td>
<td>2 calibration, 1 target cylinder Measurement time 1h15m Gap every 23h: 3h45m</td>
<td>2 calibration, 2 target cylinders Measurement time 1 hour Gap every 23h: 4h</td>
</tr>
<tr>
<td>Final output frequency O₂</td>
<td>1 point per 5 minutes</td>
<td>1 point per 3 minutes</td>
</tr>
<tr>
<td>Final output frequency CO₂</td>
<td>1 point per 5 minutes</td>
<td>1 point per 6 minutes</td>
</tr>
<tr>
<td>Used for calibration O₂</td>
<td>6 out of 15 points = 30 minutes</td>
<td>6 out of 20 points = 18 minutes</td>
</tr>
<tr>
<td>Used for calibration CO₂</td>
<td>6 out of 15 points = 30 minutes</td>
<td>3 out of 10 points = 18 minutes</td>
</tr>
</tbody>
</table>

3.3.3. Transportability

Three main things of the fixed O₂ – CO₂ instruments were changed to make the new instrument transportable: the package of the analyzers, gas handling equipment and electronics (subsection 3.3.3.1), the package of the cylinders (subsection 3.3.3.2) and the air-drying (subsection 3.3.3.3).
3.3.3.1. Package of the analyzers, gas handling equipment and electronics

Placing the analyzers and all gas handling equipment inside a so-called flightcase, specially designed for our needs, makes sure that the whole instrument is easy to transport. Besides this, the instrumentation is protected from dust and damage, which can be very advantageous, especially when placed at locations that are used by many other instruments and people as well. At the North Sea gas platform F3 we recently suffered from issues with dust due to construction work at the platform. Several parts of the instrumentation (built in open racks) were broken and they needed to be cleaned or even replaced.

Figure 3.5 shows the case that contains the gas analyzers, gas handling equipment and associated electronics.

![Figure 3.5: The package of the analyzers, gas handling equipment and belonging electronics. Top left: the case can be completely closed (also during operation) and fits into a moderately sized car. Top right: the case together with the two other cases that contain the gas cylinders (bottom) and the drying system (right). The top and front panel are removed here, for easy access to the instrumentation. The analyzers are in the bottom of the case: the Oxzilla on the left and the Uras26 NDIR in the middle. The box on the right contains the associated electronics. On the right side of the case there are quick connectors to easily attach the cylinders to the instrument. During transportation they can be closed, as is visible in the picture on the bottom of this figure.](image)

The front and top panel of the box can be removed, but during transport and also during operation it can be completely closed. The necessary gas cylinders and the outside air inlet can be connected through quick connectors, thus making it unnecessary to open the box during operation. Fans are placed in the back of the case to ventilate it during operation. The front contains two openings for fresh air. Three small hatches make sure it is possible to easily access the instruments at the bottom of the case. The box is 118 x 63 x 57 cm and...
fits in a moderately sized car. The case contains two built-in wheels, which makes it much easier to move the whole box, for example when placing it inside the back of a car.

3.3.3.2. Package of the gas cylinders

Another flightcase was designed to transport and protect the different gas cylinders necessary for the continuous O₂ – CO₂ system. The cylinder-flightcase can contain six cylinders: two 20L cylinders used as (spare) reference gas and four 10L cylinders used as calibration and target cylinders.

During operation, the case is closed. The cylinders are connected to the drying case and measurement case through quick connectors in the top of the case. The measurement case can stand on top of the cylinder case. During transportation, the cylinders can stay inside the case. Wheels make sure that the complete system is relatively easy to move.

![Image of gas cylinders]

Figure 3.6: The package of the gas cylinders. The complete case is visible in the top right picture in Figure 3.5. The left picture shows the front of the gas cylinder case, when the cover is removed. The right picture shows the quick connectors in the top panel of the case.

The cylinders can be transported in the case and due to the special caps (see left picture in Figure 3.6) the regulators do not need to be removed before transportation. This saves time when installing the system in a new location, not only because of the installation itself but also because flushing of the regulators before using them again is now not required. The case also thermally insulates the cylinders and makes sure the cylinders remain in a horizontal position all the time. These things are important to minimize thermal-diffusive and gravitational fractionation in the gases (Keeling et al., 2007).

3.3.3.3. Air-drying

The fixed systems of the CIO at Lutjewad and F3 both use -80°C coolers. These coolers have many disadvantages for a transportable system as they are heavy, big and have a high power requirement. The ideal solution would be to only use tubes filled with magnesium perchlorate (Mg(ClO₄)₂), as long as these tubes would last for at least a week. Unfortunately we found that the drying agent did not last for longer than about 6 hours in our configuration (≈ 17 grams Mg(ClO₄)₂ and a flow of 60 mL min⁻¹), as is visible in Figure 3.7. This was surprising, because a simple calculation with the drying capacity of
magnesium perchlorate (0.48 gram H\textsubscript{2}O gram\textsuperscript{-1} (Merck Millipore, 2013)) gave us the idea that this amount would last for 6 – 7 days at this flow rate and an average relative humidity of 65\% and a temperature of 25°C (as was the case during this experiment). This drying method was thus rejected for use in the system. Even at lower temperatures the drying capacity will be insufficient (by far). We therefore decided to use a combination of a -60°C cooler, taking out the large majority of the water, and Mg(ClO\textsubscript{4})\textsubscript{2} drying tubes for final drying.

![Graph showing δ(O\textsubscript{2}/N\textsubscript{2}) (per meg) data over time with red dashed lines indicating when the drying agent was replaced.]

Figure 3.7: Illustration of the ability of the drying agent magnesium perchlorate (≈ 17 grams) to dry the air (flow rate 60 mL min\textsuperscript{-1}) for O\textsubscript{2} measurements. The graph shows the outside air measurements. The gaps (3 hours) represent the calibration measurements: during this time no outside air was measured. In the time of this graph, the drying agent was replaced three times. In the first measurement period of six hours the drying agent is sufficient. The second time outside air is measured (9 hours after replacement) the drying agent is already wet, hereby extremely influencing the O\textsubscript{2} measurements.

The fixed systems at F3 and Lutjewad use glass cold fingers with a somewhat fragile connection. For our transportable instrument, we designed new, sturdy, cold fingers, made from stainless steel with quick connectors. One of the cold fingers is visible in Figure 3.8. The cold fingers are filled with small glass balls, similar to the original glass cold fingers.

![Picture of one of the cold fingers that is specially designed for the transportable O\textsubscript{2} – CO\textsubscript{2} instrument.]

Figure 3.8: Picture of one of the cold fingers that is specially designed for the transportable O\textsubscript{2} – CO\textsubscript{2} instrument.
In the period February – April 2014 we had a Cavity Ring-Down Spectrometer (CRDS) from Picarro available to check the performance of our drying system. The instrument is, unlike almost all other instruments, able to detect very small amounts of water vapor in air. This made it possible to see if the exit of the transportable instrument was indeed dry.

Several calibration and target cylinders appeared to be significantly wet, and the water vapor could not be removed completely by the Mg(ClO$_4$)$_2$ drying tubes. As the calibration and target cylinder air do not pass through the cryotrap, but only through the Mg(ClO$_4$)$_2$ drying tubes (see Figure 3.4), it is very important to use only relatively dry cylinders. Previously, this could not be tested, but as was explained before, since summer 2013 all working gas cylinders are calibrated on the CRDS from Picarro and thus the water vapor content is also determined.

The exit of the flightcase was also not completely dry when sample air was measured. Although the fuel cells produce H$_2$O themselves (see equation 3.1), the Mg(ClO$_4$)$_2$ drying tubes appeared not to be able to fully dry the outgoing air, as became clear in an experiment with an additional Mg(ClO$_4$)$_2$ drying tube that was placed after the exit of the instrument. It also turned out that the moisture content in the outgoing air stream is lower at a higher flow rate, indicating that the air picks up moisture from its surroundings on its way to the exit.

Unfortunately we were not able to test the exit of the fixed instrument at Lutjewad, in which the air is dried with a -80°C cooler.

### 3.4. Performance

Next to sample air and calibration cylinders, the fixed instrument at Lutjewad and the transportable instrument also measure one or two target cylinders, respectively. The target cylinder measurements serve as an independent check of the calibration of the instruments and can be used to assess both the accuracy and precision.

The United Nations World Meteorological Organization (WMO) has set compatibility goals for different atmospheric components. For CO$_2$ this goal is set at ± 0.1 ppm and for δO$_2$/N$_2$ the goal is set at ± 2 per meg, although current international comparisons indicate that the compatibility between laboratories is worse than ± 5 per meg (University of East Anglia, 2015; WMO, 2012, and see also the appendix of this thesis). As a rule of thumb, the internal reproducibility goals are half the compatibility goals, which means ± 0.05 ppm for CO$_2$ and ± 1 per meg for δO$_2$/N$_2$ (WMO, 2012).

In this section, an overview is given of the target cylinder measurements of the fixed instrument at Lutjewad (subsection 3.4.1) and the transportable system (subsection 3.4.2). The precision of an instrument can also be determined based on outside air measurements, which is also done for the two instruments. The results are summarized in subsection 3.4.3.

#### 3.4.1. Fixed system at Lutjewad

Four sets of calibration and target cylinders have been used since the start of the measurements in June 2011 up till January 2015. The first set of three cylinders was used from the start in June 2011 to December 2011. The second set was used from January 2012
to April 2012, the third set from April 2012 to October 2014 (one cylinder was replaced in May 2012) and the last set has been in use since November 2014 and was still in use in January 2015. The reference cylinder needs to be replaced more often as it only lasts for 2 – 4 months (depending on the size of the cylinder).

For CO₂ the first three sets of cylinders were calibrated on the HPGC while the last set was calibrated on the CRDS. For O₂ all cylinders have been calibrated on the DI-IRMS. The third set of cylinders was measured twice on the DI-IRMS: once before they were shipped to Lutjewad and also after they came back. For this whole period we use the average of these two measurements, as it turned out that this resulted in the best outcome for the target cylinder (the value was then closest to the assigned value). The practice of measuring cylinders also after usage was not common before the end of 2014, which is the reason why the first sets of cylinders were measured only once. The current cylinders are still in use but will be measured a second time when they come back to the laboratory.

Figure 3.9: Results of the target cylinder measurements of the fixed O₂ – CO₂ instrument at Lutjewad plotted as the difference with the assigned value of the target cylinder. A change in greyscale marks a new reference cylinder period while a change in the symbol marks a change in the set of calibration and target cylinders. From 17 May 2012 until 1 November 2014 the same set of cylinders was used.

Figure 3.9 shows the results of the target cylinder in time for both the CO₂ concentration and the O₂/N₂ ratio. The values are plotted as the difference with the assigned value. A
change in greyscale marks a change of the reference cylinder, while a change in the symbol indicates a change of the suite of calibration and target cylinders.

For CO₂ the target cylinder is relatively stable in time (certainly given the only limited precision of the used Vaisala Carbocap GMP343 sensors), while for δO₂/N₂ large changes are visible at the times the suite of calibration and target cylinders is changed. This is caused by the relatively high uncertainty in the assigned δO₂/N₂ values of the cylinders, which is likely to be improved when all cylinders are also analyzed on the DI-IRMS after usage and the measurement of cylinders in general is improved.

We calculated the accuracy and precision from the data gathered between 18 March 2014 and 1 November 2014 (the last three reference periods marked with a circle in Figure 3.9). This period seems to have the highest precision and best accuracy achieved so far for both CO₂ and O₂ and thus gives the best-case values for the accuracy and precision of the current system. The values are given in Table 3.2.

3.4.2. Transportable system

![Figure 3.10: Results of the two target cylinders of the transportable O₂ – CO₂ system during the field campaign in Lütjewad (see chapter 4) for both CO₂ and δO₂/N₂, plotted as the difference with the average measured value.](image)
The precision of the CO\(_2\) and O\(_2\) measurements of the transportable system is important as this largely determines the “CO\(_2\) leak detection limit” of the instrument. To establish and monitor these precisions, two target cylinders were measured every 23 hours. The cylinders are treated as unknowns, similar to the outside air. Figure 3.10 shows the target cylinder measurements of the system during the field campaign in Lutjewad in 2014 (see chapter 4) for both CO\(_2\) and \(\delta\text{O}_2/\text{N}_2\). The average measured value of the target cylinders is subtracted from the measurements to plot both cylinders on the same scale.

One of the calibration cylinders was replaced on 11 July 2014, as it was nearly empty. This is likely to be the reason for the fact that both target cylinders showed drift just before this date, and both with the same rate. It is known that cylinders can get slightly depleted in O\(_2\) compared to N\(_2\) as the pressure drops, due to preferred desorption of N\(_2\) relative to O\(_2\) from the wall of a cylinder (Keeling et al., 1998; Kozlova and Manning, 2009; Manning, 2001). This is probably what happened to this calibration cylinder. It is therefore important to replace cylinders well on time before they are empty, so the pressures of all cylinders should be checked on a regular basis. Fortunately, drifts like the one observed do not significantly influence the results of the CO\(_2\) release experiments presented in the next chapter, as the drift is slow and thus \(\delta\text{O}_2/\text{N}_2\) does not significantly change within one day. Replacement of this calibration cylinder shifted the scale slightly, which is caused by uncertainty in the assigned values of the cylinders. However, from 11 July 2014 onwards the scale is stable.

In total the target cylinders have been measured 172 times in the period from 6 June to 19 November 2014. Table 3.3 gives the standard deviations of the two target cylinders for both species, for the last 1.5 month (48 measurements) of the campaign.

### 3.4.3. Results

Table 3.2 and Table 3.3 show the results of the target cylinder measurements of the fixed instrument at Lutjewad and the transportable system respectively.

Next to three different standard deviations, an estimate for the accuracy is given for the fixed instrument at Lutjewad. The accuracy is not very important for the transportable system in case it is used for CO\(_2\) leak detection. The precision is, however, very important for the transportable system, as it determines the leak detection limit.

There is a big difference in the precision of the CO\(_2\) measurements of both systems. For the transportable instrument, the precision of the CO\(_2\) measurements is excellent, while the fixed instrument at Lutjewad does not even meet the WMO standards. The reason is quite obvious, as the transportable system uses a superior CO\(_2\) detector. The fixed instrument uses a simple (and cheap) setup, which is sufficient as an addition to the \(\delta\text{O}_2/\text{N}_2\) measurements.

The precision of the \(\delta\text{O}_2/\text{N}_2\) measurements does not meet the WMO standards for both systems. The precisions we found are in the same range as the precisions found for the system at the gas platform F3 (which is almost identical to the system at Lutjewad). Here the average standard deviation within a measurement of a target cylinder was found to be 16 per meg while the standard deviation over all target cylinder measurements was found to be 8 per meg (van der Laan-Luijkx et al., 2010b). Significantly better precisions have,
however, also been achieved by other laboratories. (Wilson, 2012) reports a very high precision for the continuous δO₂/N₂ measurements at the atmospheric measurement station Weybourne (United Kingdom). Their target measurements show standard deviations of 2.8, 2.5 and 1.1 per meg within the target cylinder measurements, over all the target cylinder measurements and between successive pairs of target cylinder measurements respectively.

Table 3.2: Results of the target cylinder measurements of the fixed instrument at Lutjewad between 18 March 2014 and 1 November 2014. Three different standard deviations are given: the average standard deviation within one target cylinder measurement (consisting of the last 6 out of 15 measurements in 1h15m (30 minutes) for both CO₂ and O₂), the standard deviation over all target measurements and the average standard deviation of two paired successive target measurements. The numbers of target measurements are not equal for CO₂ and O₂, which is the reason that two values for n are given (first CO₂, then O₂).

<table>
<thead>
<tr>
<th></th>
<th>CO₂ (ppm)</th>
<th>δO₂/N₂ (per meg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average measurement – assigned value (accuracy)</td>
<td>0.11</td>
<td>0</td>
</tr>
<tr>
<td>Average stdev within a target run (n = 201 / 195)</td>
<td>0.7</td>
<td>11</td>
</tr>
<tr>
<td>Stdev of all target runs (n = 201 / 195)</td>
<td>0.26</td>
<td>6</td>
</tr>
<tr>
<td>Stdev of pairs, averaged (n = 200 / 194)</td>
<td>0.18</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3.3: Results of the target cylinder measurements of the transportable instrument between 3 October and 19 November 2014. Three different standard deviations are given: the average standard deviation within one target cylinder measurement (consisting of the last 3 out of 10 measurements in one hour (18 minutes) for CO₂ and 6 out of 20 measurements in one hour (18 minutes) for O₂), the standard deviation over all target measurements and the average standard deviation of two paired successive target measurements.

<table>
<thead>
<tr>
<th></th>
<th>CO₂ (ppm)</th>
<th>δO₂/N₂ (per meg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Target 1</td>
<td>Target 2</td>
</tr>
<tr>
<td>Average stdev within a target run (n = 48)</td>
<td>0.011</td>
<td>0.010</td>
</tr>
<tr>
<td>Stdev of all target runs (n = 48)</td>
<td>0.021</td>
<td>0.018</td>
</tr>
<tr>
<td>Stdev of pairs, averaged (n = 47)</td>
<td>0.011</td>
<td>0.009</td>
</tr>
</tbody>
</table>

The precision of the two instruments was also estimated based on outside air measurements. For the fixed instrument at Lutjewad, we looked for the most stable hours in the whole dataset by applying a running average (with accompanying standard deviation) to APO (Atmospheric Potential Oxygen – a tracer defined as a combination of δO₂/N₂ and CO₂ according to equation 5.1 presented in chapter 5), using n = 12, which is 60 minutes. We selected the 30 most stable hours (lowest standard deviation in APO) and removed the 10 hours with the highest standard deviation in CO₂ and δO₂/N₂ to prevent including hours with low variability in APO but nevertheless high variability in CO₂ and δO₂/N₂ (cancelling each other out). The average standard deviation of the remaining 20 hours was found to be 0.4 ppm for CO₂ and 3.1 per meg for δO₂/N₂. The standard deviations of the outside air are in a similar range as (or even better than) the standard deviation of the target cylinders, which implies that the instrument noise is limiting the precision of both the CO₂ and δO₂/N₂ measurements. Especially the result for δO₂/N₂ is surprisingly low, suggesting that the outside air measurements are actually better than the measurements of the cylinders. This would be similar to the flask-cylinder differences when measuring with our DI-IRMS
and is another indication that $\delta O_2/N_2$ measurements on gas cylinders can be and need to be substantially improved.

To estimate the precision of the transportable system based on outside air measurements, we looked at several hours in which the atmospheric concentrations were very stable. We found standard deviations between 0.13 and 0.29 ppm for CO$_2$ ($n = 10$) and in the same hours standard deviations between 8 and 17 per meg for $\delta O_2/N_2$ ($n = 20$). We have found similar values for the CO$_2$ measurements from 7 meters from the main tower of Lutjewad performed by the cavity ring-down spectrometer (CRDS) instrument from Picarro. The precision for the CO$_2$ measurements is thus much poorer for outside air than it is for the target cylinders, indicating that the atmospheric variability of the CO$_2$ concentration is the limiting factor for these measurements. For $\delta O_2/N_2$ the numbers for outside air and target cylinders are in the same range, indicating that the instrument noise is the main limitation.

3.5. References


Kozlova, E.A., Manning, A.C., 2009. Methodology and calibration for continuous measurements of biogeochemical trace gas and O$_2$ concentrations from a 300-m tall tower...

Manning, A.C., 2001. Temporal variability of atmospheric oxygen from both continuous measurements and a flask sampling network: Tools for studying the global carbon cycle. University of California, San Diego, USA.


Merck Millipore, 2013. Dry and safe.


Instruments for \( \text{O}_2 \) measurements


