



university of
 groningen

faculty of mathematics
 and natural sciences

Assessing the CIO Automatic CO₂ Extractor

BACHELOR THESIS

by Daniël Siepman

student number: S1777637

supervisor: drs. S. M. A. C. van Heuven

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Centre for Isotope Research

Nijenborgh 4

9747 AG Groningen

Abstract

The Automatic CO₂ Extractor setup is designed to extract CO₂ from globally collected (sea)water samples. Extractions are performed by acidification and subsequent sparging of each sample with pure nitrogen. The CO₂ yield is measured in a calibrated volume and the CO₂ is stored for further isotope analysis.

In the pursuit of an optimal extraction and storage sequence, elements of the ACE setup were subjected to tests. This thesis reports on several subjects concerning the operation of ACE. The latest design of the CO₂ cold trap turns out to be highly effective with regard to full capture of CO₂. Sparging rate and duration are recommended to be increased to respectively 20 litres/hour for 900 seconds. Advised is to adjust the amount of acidification to 1 ml of 85% orthophosphoric acid for each 250 ml of sample volume. ACE shows consistent yields when extracting from identical samples, both in absolute quantities as in isotope occurrence. The hardware was improved after detection of water vapour in the CO₂ calibration volume, by installing an extra water trap.

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1 Introduction

1.1 CO₂ in the oceans

The oceans and atmosphere show a permanent exchange of gases, striving towards an equilibrium. Due to the strong connection with climate change and global warming, marine research programmes emphasize on the CO₂ balance. Currently, the CO₂ flux is directed towards the oceans; increasing concentrations of atmospheric CO₂ result in a net uptake by the ocean surface.

After diffusing into the ocean's surface, CO₂ is distributed through oceanic currents (adjective transport) and diffusive transport. The latter is driven by differences in CO₂ concentrations. To enable the mapping of the circulation and concentration of CO₂ in the oceans, large numbers of seawater samples are collected worldwide. Not only at many different locations, but also at different depths at these locations.

An important aim is to gain insight into the mechanisms that control the intake of anthropogenic CO₂ by the world's oceans. The ocean is an important sink for CO₂ and the rate of absorption and distribution of CO₂ is a vital link in the complex models of greenhouse gases and their role in climate change. Understanding the mechanisms by which ocean water distributes CO₂ contributes to better climate models and improved predictions of future developments in the world's climate.

In the 400,000 years prior to the industrial revolution, atmospheric CO₂ concentrations varied between 200 and 280 ppm (parts per million) [Tedesco et al., 2005]. Today we have arrived at 392 ppm [ESRL, NOAA, 2012] with a current annual growth of 1 percent. To put matters in perspective: this is equivalent to a doubling time of just 70 years.

About 30 percent of all anthropogenic CO₂ is taken up by the oceans and a doubling of the pre-industrial value is expected by the middle of the 21st century. These increases lead to a higher acidity and a decrease of CO₃⁻ ions. An article in Nature suggests a level of acidification in the coming centuries, which has not occurred for 300 million years [Caldeira et al., 2003]. Ocean acidification is expected to increase the rate of corrosion on corals and other organisms that build calcium carbonate shells and skeletons [Tedesco et al., 2005].

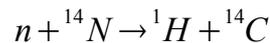
1.1.1 ^{13}C and ^{14}C depleted anthropogenic emissions.

Atmospheric carbon dioxide contains approximately 1.1% ^{13}C and 98.9% ^{12}C . From these values the $\delta^{13}\text{C}$ value can be calculated:

$$\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1$$

In which the $^{13}\text{C}/^{12}\text{C}$ standard ratio (0.0112372) is the Vienna PeeDee Belemnite, a widely used reference material. The current $\delta^{13}\text{C}$ for atmospheric CO_2 is -12 ‰, while the pre-industrial was -8 ‰. Due to the emission of fossil fuels the ratio has become lower, since fossil fuels are depleted of the ^{13}C isotope. The plants from which fossil fuels were formed millions of years ago, prefer absorbing the ^{12}C isotope, leading to an average $\delta^{13}\text{C}$ of -28 ‰ [O'Leary, 1988].

^{14}C isotopes are produced when high energy cosmic rays collide with air molecules when entering the atmosphere, freeing neutrons which subsequently eliminate a proton in nitrogen-14, resulting in ^{14}C atoms [Libby, 1961]:



The produced radio carbon is rapidly contained into carbon dioxide, distributed through the atmosphere and eventually enters the oceans, occupying a certain fraction of the different types of isotopes occurring in the oceans.

^{14}C has a half life of 5730 years (decays to ^{14}N) and since even the most recently formed fossil fuels are at least 10 million years old [Mann et al., 2009], no ^{14}C traces are found.

The anthropogenic emission of fossil CO_2 that started with the industrial revolution, caused a shift in the composition of atmospheric CO_2 . The contribution of ^{13}C and ^{14}C decreased over the years, since fossil fuels contain primarily ^{12}C and a small fraction of ^{13}C .

The same shift becomes visible in the oceans, while the water subsequently starts to absorb the new mix of isotopes. Over time, the new ratio will start to penetrate deeper parts of the oceans and is distributed through currents. These processes can be monitored, giving insight into the motion mechanisms of the oceans and their interaction with atmospheric CO_2 .

Recent history also showed a pulse of increased ^{14}C levels, due to the world-wide fallout of ^{14}C from atmospheric testing of nuclear weapons around 1960. The thermal neutron fluxes from these tests lead to a doubling of the presence of ^{14}C in the atmosphere [Šilar, 2004]. The

subsequent response of the oceans to this ^{14}C pulse turned out to be another tracer to map the ocean's mechanisms.

In reality, the carbon cycle contains much more variables, as figure 1 shows. The illustration also shows the considerable contribution of anthropogenic CO_2 (here in gigatonnes) and the mechanisms by which it is taken up by the atmosphere and biosphere.

Models of the uptake of anthropogenic CO_2 by the oceans are compiled from the many seawater samples that have been collected through the years. These samples have to be analysed individually, for which several CO_2 extraction devices are used worldwide.

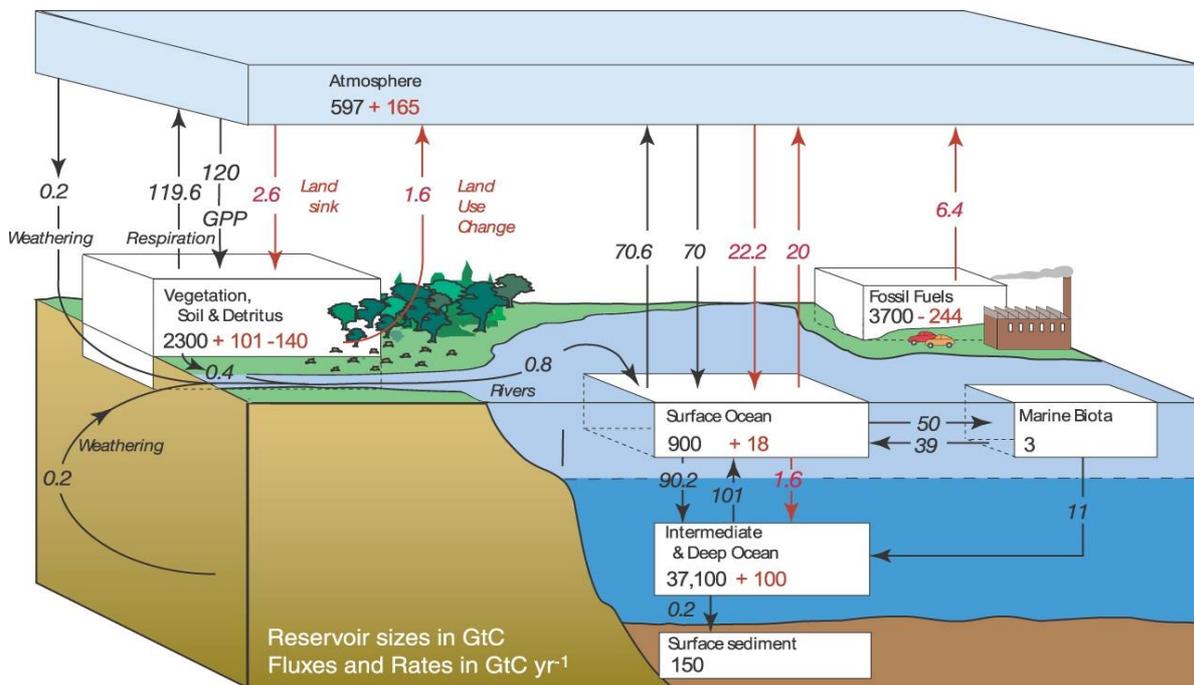


figure 1: The perturbed global carbon cycle in the 1990s. Black numbers are the reservoir sizes and fluxes of the pre-industrial natural carbon cycle. Red numbers represent the size of the anthropogenic perturbation. [Solomon et al, 2007].

2 Extraction methods

Goal of extraction of CO₂ from seawater samples is to determine the amount of CO₂ in millimol present in each sample and storage of the yielded CO₂ for isotope analysis.

Laboratories deploy several methods to extract CO₂ from water samples. In general, each water sample is acidified to free all CO₂ which is confined in dissolved carbonates. The extraction process is performed through several techniques. Before elaborating on the Automatic CO₂ Extractor (ACE), some other extraction methods are described.

2.1 Vacuum extraction of CO₂

Currently, the Centre for Isotope Research (CIO) extracts CO₂ by evacuating the flask containing the acidified water sample. The vacuum induces the diffusion of the CO₂ from the sample and the yield is subsequently frozen in a liquid nitrogen cooled trap. This process takes 40 minutes to collect 99.9 percent of the CO₂ in the water sample, making it somewhat time consuming. Also, due to excessive accumulation of ice in the water trap, resulting from the “boiling” of the water under vacuum, constant monitoring is necessary. Automating the process is therefore hard.

2.2 Gas-permeable polymer membrane contractor

Kalina Gospodinova describes an extraction method in which more than 99% of the dissolved CO₂ is collected in less than 20 minutes [Gospodinova, 2012]. The CO₂ extraction is executed using a LiquiCel 1x5.5 MiniModule membrane contractor. Basically, the water is pumped through hydrophobic polypropylene fibres and the CO₂ passes through the membrane walls, thus being separated from the liquid. The CO₂ is subsequently flushed from the membrane unit with helium gas and cryogenically stored the same way as in the ACE device described in the next section.

The aforementioned paper also reads that the membrane method is designed to replace the existing extractor in which a nitrogen stream is used in the extraction process. The replacement is primarily to accommodate a wider range of types of sample containers, speed up the extraction process and enabling processing samples with a larger variation in dissolved carbon. According to Gospodinova, the membrane technique also leads to a higher precision. She states that sparging strips more than 98% of the inorganic carbon from each sample, stable isotope analysis has a precision of 0.03 – 0.05‰, and radiocarbon analysis 3 – 4‰. The

membrane method extracts more than 99% in less than 20 minutes. Stable isotope precision shows a system precision of 0.02‰ and radiocarbon isotope a precision of 3.5‰.

Our findings show, however, that ACE performs well above these specifications, also accommodates a variety of sample containers and has the ability to process variations in CO₂ yields. As yet, the membrane technique provides no obvious advantages over the sparging technique.

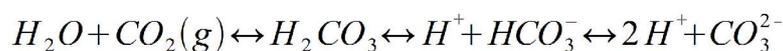
2.3 The CO₂ extractor at WHOI

The extractor at the Woods Hole Oceanographic Institution (WHOI) uses, like ACE, sparging to extract CO₂ from samples. An interesting feature of the WHOI extraction line is the recirculating pump [McNichol, Jones, 1992]. ACE dumps the nitrogen flow after it's stripped from CO₂, monitoring potential residue's of CO₂ with the CO₂-detector. The WHOI's system returns the nitrogen back through the water sample after it has passed through the CO₂ trap. Only when the extraction has been completed, the nitrogen is pumped away, similar to the procedure of ACE. Thus, the whole extraction is performed in a closed system, reducing the risk of losing CO₂ in the process. Drawback is the possibility that some CO₂ may be left in the system and is not being trapped. Depending on the design of the system, this may lead to a certain loss of yield.

2.4 Automated extraction of CO₂ with the Automatic CO₂ Extractor (ACE)

Figure 2 shows a schematic overview of the ACE setup

Focus of this report lies at the Automatic CO₂ Extractor, ACE. It is conceived by drs. Van Heuven, who is still developing and refining ACE at the moment of publication of this report. Both tap water and seawater have the majority of the CO₂ captured in carbonates, leading to an equilibrium:



The CO₂ in these carbonates can be fully freed by applying a small quantity of 85% orthophosphoric acid prior to each extraction. The equilibrium between the carbonates and the dissolved free CO₂ shifts to the left side of the above formula, freeing virtually all CO₂ from the carbonates. Acidification to pH=2 leads to more than 99% extractable carbon. Goal of ACE is to extract CO₂ from an attached (sea)water sample automatically. To exclude human error and speed up the extraction process, the computer takes over when a number of

samples are manually connected to the setup. The extraction should be close to 100% to avoid possible fractioning of the isotopes. Heavy isotopes tend to take longer to leave the water sample; if part of the CO₂ is not extracted, there can be no certainty that the occurrence of isotopes is preserved after extraction. Also, a quantitative measurement is made of the yield of CO₂. Obviously, no absolute amount of CO₂ can be determined, when not all CO₂ is actually extracted.

ACE uses a stream of nitrogen gas which is led through an acidified water sample. The stream of bubbles provides a large increase of exposed surface through which CO₂ molecules can diffuse. The interface between each bubble of gas and the liquid has a continuous exchange of gases in both directions. Since the liquid has a higher concentration of CO₂ than the inside of the nitrogen bubbles, statistically more CO₂ molecules enter the bubble than vice versa. Together with a certain amount of water vapour, the CO₂ is carried away by the nitrogen flow and first transported through a cold trap in which any water vapour is trapped, while all CO₂ passes uninterrupted. The water trap is submerged in a slurry of dry ice mixed with ethanol, cooling to -78.5°C, suggesting that the passing CO₂ could also be trapped. However, since the entering gas mixture is at room temperature, the CO₂ is not cooled down enough while passing through the trap. If a small fraction of CO₂ would deposit during a large flux, it will sublime again later in the process, when virtually all CO₂ has been extracted from the sample.

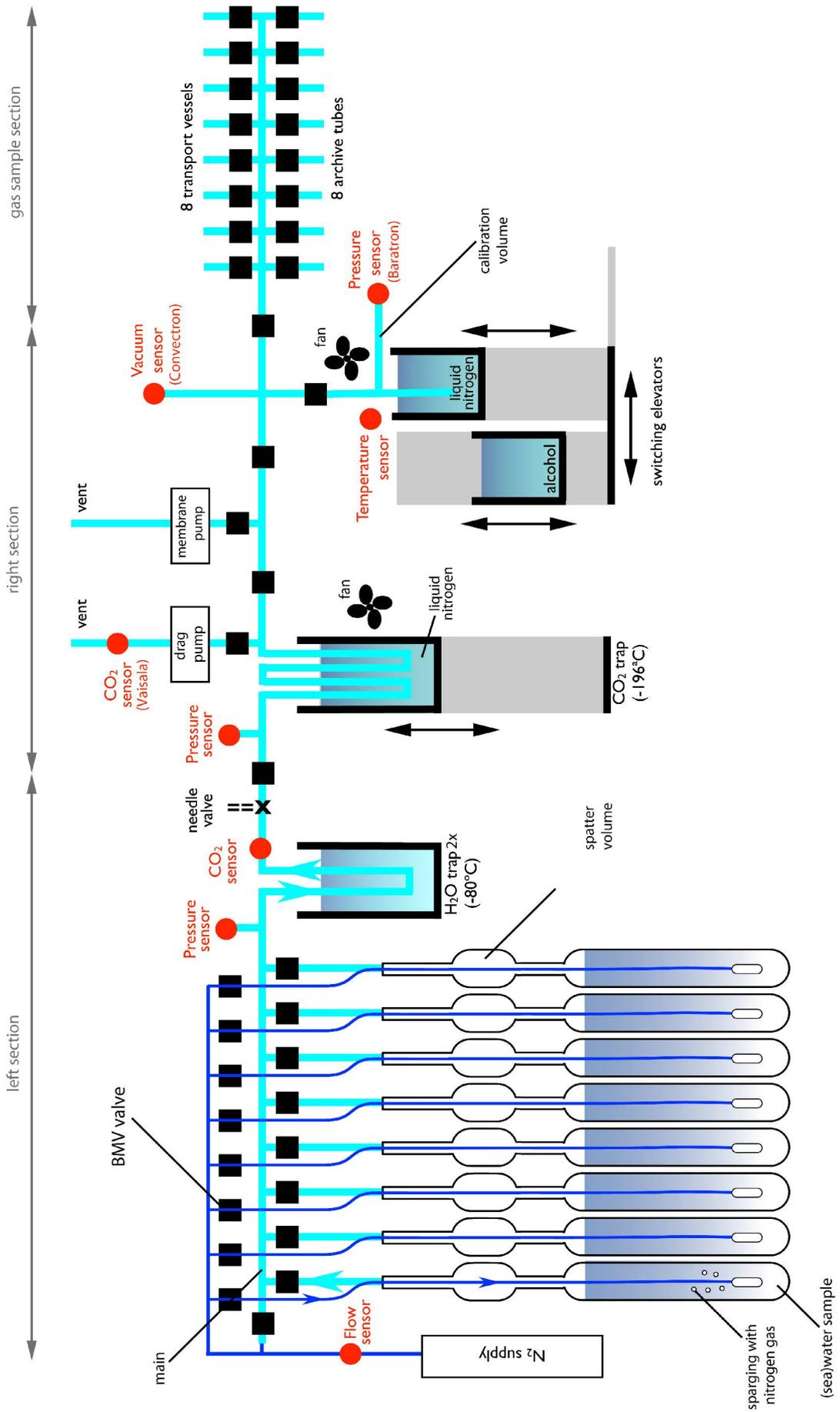


figure 2: The Automatic CO₂ Extractor



figure 4: The large CO₂ cold trap. During extraction the Dewar contains liquid nitrogen. Note the ventilators to speed up the warming up after removing the Dewar.



figure 3: The large CO₂ cold trap, different perspective.

The nitrogen cooled CO₂ cold trap

The dried gas mixture of nitrogen and carbon dioxide continues to a second, larger cold trap, submerged in liquid nitrogen. Figures 3 and 4 show the setup, here without the liquid nitrogen in place. Again, the nitrogen flow passes freely, but all passing CO₂ is caught and stored during the sparging process. The CO₂ trap consists of a meandering glass tube, which enters and exits the liquid nitrogen six times.

Based on earlier observations by van Heuven, losing CO₂ from the nitrogen cooled cold trap is probably only resulting from detaching flakes of CO₂ due to vibrations. Initially, the flake will just travel further through the trap and emerge in the part of the trap which it not submerged in liquid nitrogen. The design of the cold trap aims at sublimation of possible flakes of CO₂ while residing in the somewhat warmer environment and be trapped again when entering one of the submerged fingers of the cold trap.

If any CO₂ should still escape from the cold trap, it is detected by a CO₂-detector which is situated after the vacuum pump (membrane pump) that is pumping the nitrogen into the lab.

The CO₂-detector gives a baseline signal which fluctuates with 2 ppm. However, when averaging the signal over several minutes of measuring, rising CO₂ concentrations as little as 1 ppm can be detected.



figure 5: Transport vessels are bundled by four and can be opened and closed individually by the computer.

Cryogenic transfer of CO₂

After approximately 20 minutes the sparging process is stopped and while the large cold trap is still submerged in the liquid nitrogen, the whole right section (see figure 2) is pumped down to the microbar level by the drag pump to remove traces of other gases.

The large cold trap containing the CO₂ frost, the calibration volume and the connection between them is isolated and the liquid nitrogen Dewar is removed. The large cold trap is then raised to room temperature with the help of a ventilator, releasing the CO₂ in the isolated part of the setup. By submerging the calibration volume next to the Baratron in liquid nitrogen, the CO₂ is frozen once more. The pressure in the now isolated part is constantly monitored and when it enters the

microbar range another pump down is performed. Usually pressures below 1 microbar are now achieved.

When the pump down is completed, the calibration volume is closed and cooling is removed. With the help of three ventilators, the Baratron and the calibration volume are brought to lab temperature. Since the volume, the temperature and pressure are known, the yield of CO₂ in millimol can be calculated.

By the same process of cryogenic transfer, the sample is transferred to a transport vessel (figure 5), to be subjected to $\delta^{13}\text{C}$ and ^{14}C analysis. During future operation, the yield will be divided over two vessels: a transport vessel and an archive tube.

3 Tests and precision assessments

Several tests and measurements were performed to obtain insight in the quality of future measurements and to find possible problems in the extraction sequence or setup. The aim is to extract 99.99% of the CO₂, corresponding to a precision of 2 micromol. Also, the consistency of the $\delta^{13}\text{C}$ occurrence will be assessed. The performance of the setup will be tested concerning nitrogen flow, efficiency of the cold traps and sparging time.

3.1 Rough approximation size of calibration volume

In this stage of development of ACE, there is no need to know absolute values yet. Prior to extractions from actual seawater samples, the calibration volume will be determined by using certified reference material. These Dickson-2000 samples have known concentrations of CO₂, which enables an accurate fix of the calibration volume [Dickson, 2001].

For now, to be able to provide yields in millimol, a rough calculation has been performed of the volume of the calibration volume, by attaching a calibration unit with known volume. The volume turns out to be 35 ml.

In literature, at least one description is found in which a comparable calibration volume is determined using the same method. The volume of this trap was 19.44 ± 0.08 ml [Gospodinova, 2012]. The error is only mentioned and not clarified further. A similar

accuracy can be expected for the calibration volume of ACE when using this slightly different approach. Therefore, the systematic error of 0.08 ml will be used in the error analysis.



figure 6: moisture visible in calibration volume

3.2 Moisture retainment of water trap

During test runs, some condensation could be observed in the calibration volume, raising the suspicion that the water trap was not collecting all water vapour. This could influence the final pressure, thus raising the suggestion of a higher CO₂ yield.

The system was tested with a CO₂ depleted water sample to check if the water trap did indeed capture all water vapour carried by the nitrogen flow.

When the CO₂-detector no longer detected any residual CO₂,

the liquid nitrogen was put in place, collecting any water that would escape from the water trap. Then the depleted water sample was sparged for 34 minutes at 12 litres per hour. Any water that was caught in the nitrogen trap was then transferred to the final volume next to the Baratron sensor and brought to lab temperature. During this process vapour became visible with the naked eye in the final volume (figure 6). A pressure of 25.5 millibar (at 21.6° C) was found after 35 minutes of sparging, meaning the water trap was not working sufficiently.

3.2.1 Testing for moisture leakage after installing second water trap



figure 7: Combining desired properties with two traps

After installing a second water trap the experiment was repeated. In figure 7 the two water traps are displayed. Initially, only the left water trap was installed. These kinds of traps do not clog up easily, but the construction also increases the risk of leakage. The water trap on the right in figure 7 trap guarantees good contact between passing water vapour and the cold glass, but has poor performance when

handling larger amounts of water. Testing with both cold traps in place did indeed solve the problem with escaping vapour: after 35 minutes of sparging a final pressure was established of 0.2 millibar (at 21,6° C). Since sparging time during actual extractions is considerably shorter,

an even smaller pressure can then be expected.

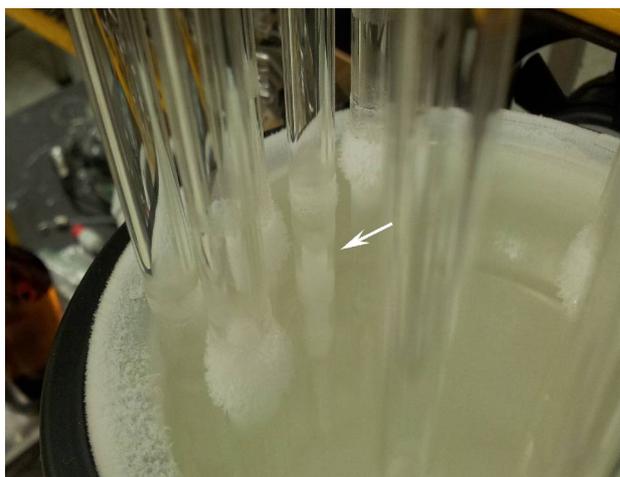


figure 8: CO₂ accumulation while large cold trap is submerged in liquid nitrogen

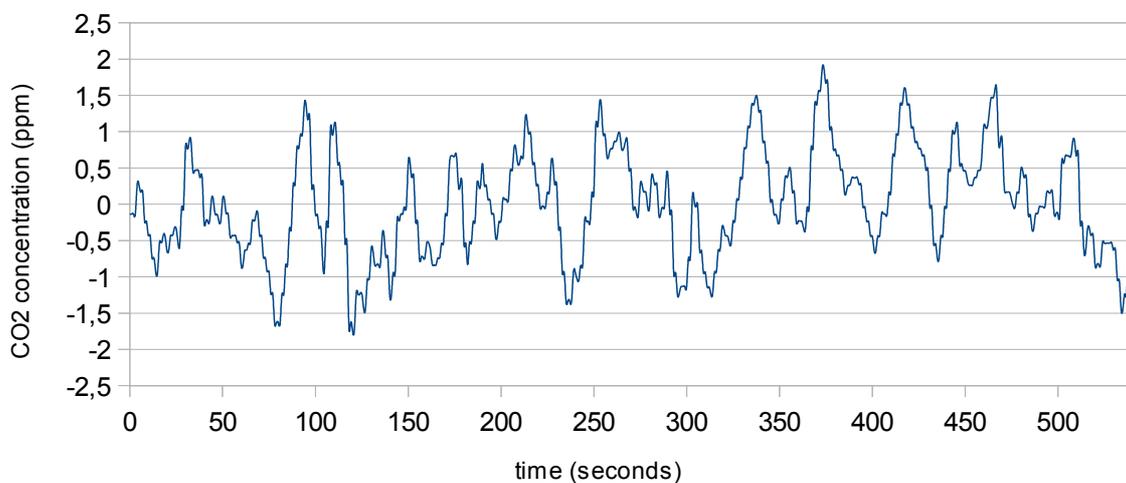
3.3 Testing cold trap for CO₂ leakage

To make sure no CO₂ escapes from the trap, even at high sparging flow, a test is performed using acidified tap water. If any CO₂ would escape, the CO₂-detector will detect it.

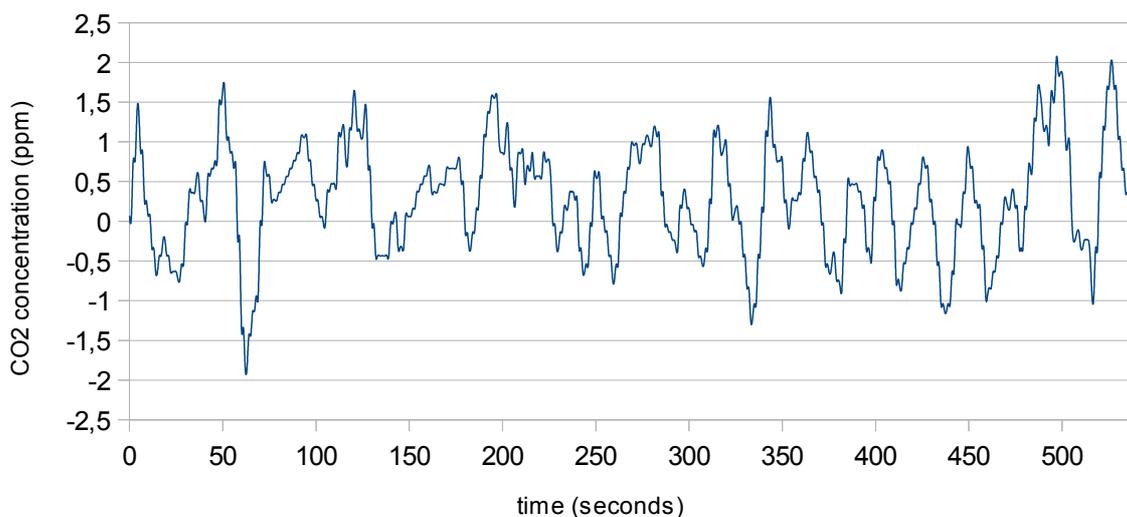
Visually, the yielded CO₂ can be seen accumulating at the inside of the tube, right

at the point where it enters the liquid nitrogen (figure 8).

Graph 1 shows the curve while only pure nitrogen passes through the CO₂-detector, showing the device-caused fluctuation in ppm count. During the test, the nitrogen flow was redirected through the sparger. Due to a higher resistance, the nitrogen flow dropped to 17 litres per hour. Graph 2 shows the behaviour of the CO₂-detector during the sparging process. Sparging was performed during 10 minutes, during which the CO₂-detector gave no significant change. The ten minutes of sparging gave an average value of the CO₂-detector of 0.29 ppm, which is no significant elevation of the initial ppm-count with pure nitrogen



Graph 1: behaviour of the CO₂ detector while flushing with 21 l/h nitrogen, no sparging, baseline value is subtracted



Graph 2: behaviour of the CO₂ detector with 17 l/h nitrogen sparging rate, baseline value is subtracted

Since the CO₂-detector did not get beyond values that correspond to its own zero signal, it's hard to connect a significant number to the loss of CO₂ in micromol. However, if throughout the full extraction period every second 2 ppm would escape, this would be equivalent to 0.46 micromol or 0.02 percent of the CO₂ yield from a typical seawater sample.

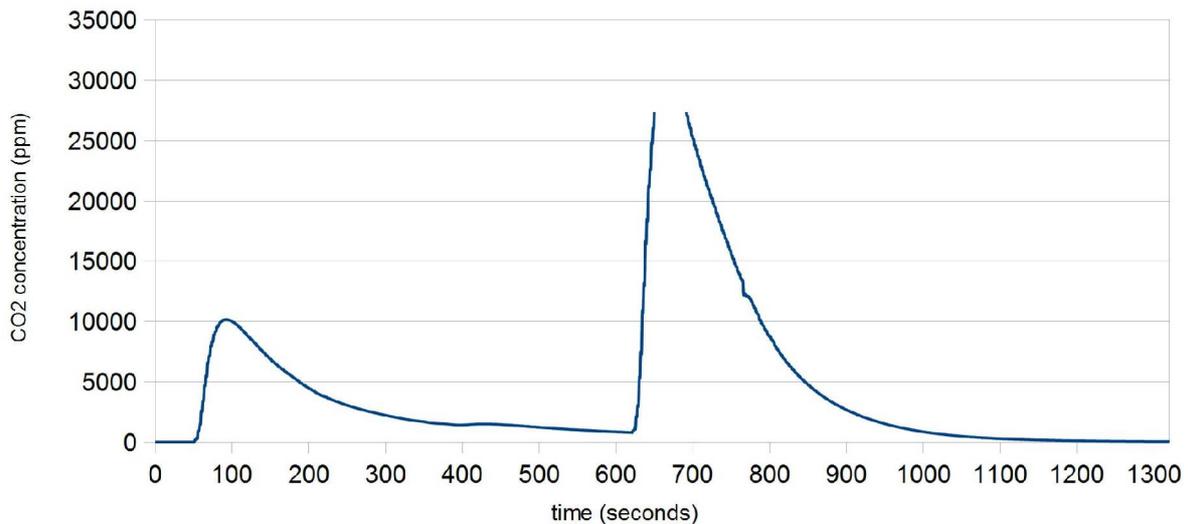
3.4 Adjusting acidification

After performing some preliminary extractions, yields varied from 1 to 3 millimol of CO₂, leading to the suspicion that the acidification of the samples was not performed correctly. Applying acid to free all carbonates in the water sample had basically been done differently every time. The assumption was that even the smallest drop of H₃PO₄ would be sufficient to make sure all CO₂ was released by the carbonates in the water samples. In reality the volume of applied acid varied considerably.

3.4.1 Testing for sufficient appliance of phosphoric acid

A standard sample of seawater typically contains 2.30 mmol of CO₂ per litre of which 0.01 mmol is free CO₂, the rest is contained in carbonates. Acidification is done with 85% phosphoric acid. H₃PO₄ is triprotic, but only releases one proton in a strongly diluted solution. [OICCP, 2007]. Therefore 2.29 millimol of phosphoric acid is expected to be necessary to obtain full CO₂ extraction. This corresponds to 0.16 ml 85% orthophosphoric acid per sample, taking into account that 15% of the applied solution is water.

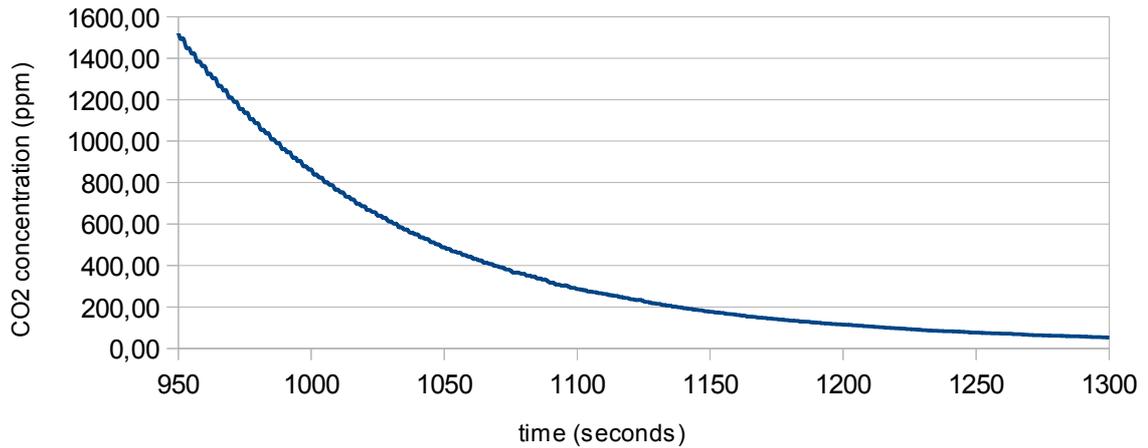
To make sure sufficient acid is applied, a test was done with a new sample of tap water (272 gram). No nitrogen trap was placed, so all CO₂ was able to escape to the membrane pump and would be detected by the CO₂-detector. Sparging was started with 12 litres of nitrogen gas per hour.



Graph 3: CO₂ detection during sparging a tap water sample. Second peak corresponds to the acidification of the sample.

Twenty seconds in graph 3 corresponds to the start of the sparging. After another 30 seconds a small flux of CO₂ is picked up by the CO₂-detector. Only dissolved CO₂ is detected at this point, since no acid is added yet. After 600 seconds 0.5 ± 0.2 ml of acid was applied. After about half a minute, the CO₂-detector shows a huge response from the freed CO₂ from the carbonates in the sample. Note that the peak is cut off, since the CO₂-detector does not give significant data at high ppm.

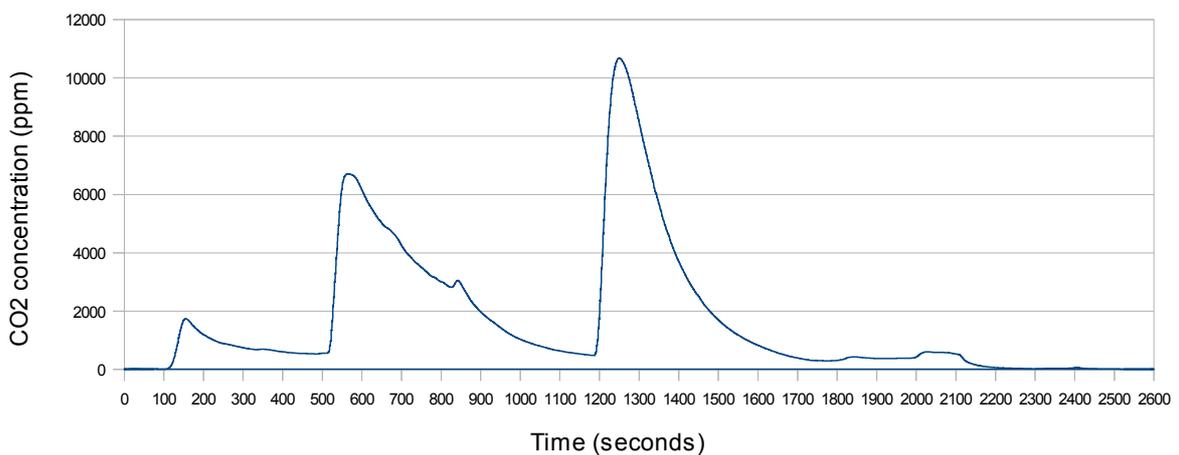
After peaking, the CO₂-detector readout slopes gently back to zero, as expected. 1050 Seconds into the graph another 0.3 ml of acid was applied, but this did not result in any response, which can be observed in graph 4. 1170 seconds into the graph a final 0.2 ml of acid was applied, bringing the total to 1 ml. As expected, no further peaks were detected. This also refutes the claims that the acid itself may contain traces of CO₂, thus contaminating the samples.



Graph 4: no response to second dose of acid at 1050 seconds

3.4.2 A second acidification test

To get a better insight in the required amount of phosphoric acid, a new test was performed. This time seawater (279 gram) was used, so more representative data can be derived. Also, a smaller syringe was applied with a scale partition that allowed for more accurate quantities of acid. Sparging was started without any acid and nitrogen flow was set at 12 l/h. The baseline of the CO₂-detector was 6.6 ppm, which was subtracted.



Graph 5: response to small amounts of acidification applied in steps



figure 9 - flooding of spatter volume due to foaming

Sparging was started and the spatter volume started filling with water due to severe foaming of the sea water sample (figure 9). Graph 5 shows an initial CO₂ flux which peaks 155 seconds into the graph. Again, this peak originates from dissolved CO₂. After 475 seconds a first, small drop of acid was added to the spatter volume. The resulting peak is considerably lower than in the previous test, since the applied volume of acid is smaller. After 790 seconds the spatter volume was emptied, resulting in a small bump in the graph.

After 1,150 seconds another large response after applying a second drop of acid. A third drop, after 1,668 seconds gave only a minimal response. The small bumps around

1,800 seconds into the process are caused emptying the spatter volume, which has filled again with water. Another 7 drops of acid after 2,455 seconds gave no response.

The first three drops were enough to free all carbonates in the water, which correspond to 0.14 ± 0.05 millilitres of phosphoric acid. The large error is in place, since the third administered drop of acid may not have been fully used up.

Since the quantity of carbonates may vary between samples, it is recommended to apply more acid. In all subsequent extractions 1 millilitre of acid will be added, which is 7 times the established minimum.

From calculation 0.16 ml of phosphoric acid per sample of seawater was derived, while 0.14 ml per liter was applied in the actual test. Considering the error in estimating the volume of a drop of acid, the calculated amount is in accordance to the actual administered amount.

When getting the first, highly varying yields, less than three drops of acid in some samples, providing a plausible explanation for the initial variations.

In the aforementioned extractor at the WHOI 4 ml of acid is applied in a water sample of 500 ml, effectively being twice the amount used for the ACE extractor [McNichol, Jones 1992].



figure 10: Submerging the large cold trap consumes considerable amounts of liquid nitrogen

3.5 Liquid nitrogen consumption

After each extraction, the large cold trap that traps the CO_2 needs to be lifted from the Dewar and gets warmed up close to lab temperature by means of the ventilators. Obviously, the cold trap needs to be cooled again prior to each extraction. As can be seen in the figure 10, the cold trap is quite a bulky contraption, which leads to considerable consumption of liquid nitrogen during each cool-down. When using a Dewar with an inner diameter of 100 millimetres, the liquid nitrogen level decreases with a minimum of 25 millimetres during each run. When the maximum of eight sample bottles is connected, a decrease of at least 200 millimetres of the liquid level can be expected. Although the cold

trap has a considerable length, towards the end of the sequence the liquid nitrogen will only submerge a small part of the cold trap. Manually or automatically adding nitrogen during the sequence may be necessary.

3.6 Vacuum test

Before each extraction series, the right part of the system (figure 2) is tested on the quality of the vacuum. During the pump down, a pressure of less than 1 microbar was reached. After reaching the best possible vacuum, the drag pump was switched off and a 30 seconds test was performed to monitor the buildup of pressure due to leakage of evaporation of left behind moisture in the system. If the pressure does not increase more than 5 microbar during the 30 second test, the vacuum is considered to be excellent. The vacuum test is done several times throughout the day in all experiments described in this report.

3.7 Zero point of CO_2 -detector

Before each extraction the CO_2 -detector was tested for its zero value by leading pure nitrogen

through it. The output of the CO₂-detector never reached zero, but stayed around 6 ppm. The computer continuously logs the CO₂-detector data, so any leakage of CO₂ would be detected during the extraction process.



figure 11: large volume for obtaining homogeneous mixture of sea water

3.8 Dependence on sparging speed in seawater extractions

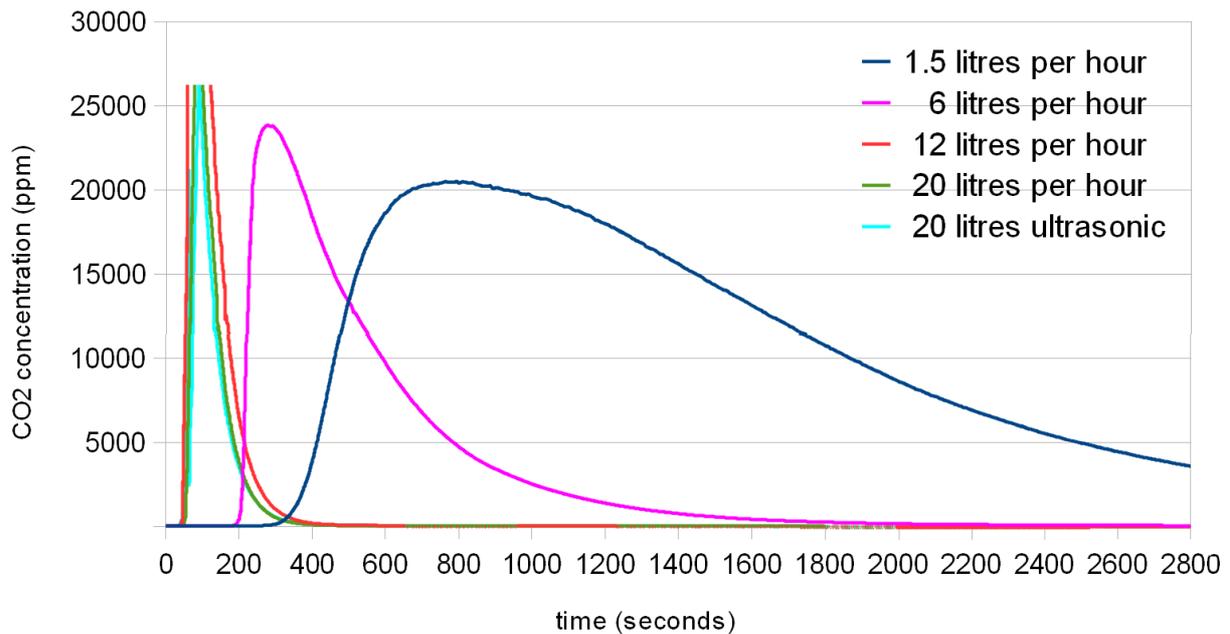
From an previous research project, the CIO still possesses a few crates with bottles containing twenty year old samples of seawater. These will be used to do further testing. By mixing the contents of several bottles in a large glass container (figure 11), a homogeneous mixture of sea water was obtained, which was split over a new series of sample bottles.

Using the identical samples of seawater, a series of extractions was performed in which all CO₂ was led through the CO₂-detector. This enabled monitoring the passage of CO₂, giving insight in the duration of extraction as a function of the sparging speed. Nitrogen flows varying from 1.5 to 20 litres per hour were set, resulting in table 1 and graph 6.

Using the identical samples of seawater, a series of extractions was performed in which all CO₂ was led through the CO₂-detector. This enabled monitoring

	N2	sparging	baseline	Pa	Pb	remarks
water	flow	time	Vaisala			
gram	l/h	sec	ppm	mbar	mbar	
265.75	1,5	1343	6.6			Still over 16000 ppm count after 22 minutes of sparging
266.23	6	2800	6.7			Still 31 ppm after 45 minutes of sparging
276.39	12	1230	6.3			6 ppm after 1230 seconds of sparging
266.07	20	1800	7.7	678	13	0.01% left after 1200 seconds of sparging
266.19	20	1800	6.4	674	13	Using ultrasonic table: same yield after 15 minutes

Table 1: Extracting at different sparging speeds



Graph 6: CO₂ count at different extraction rates

Interpretation of graph 6:

@ 1.5 litres/hour: as expected, the 1.5 litre flow does not provide sufficient extraction capability. Only a tiny trail of bubbles could be observed and it took the CO₂-detector a full four minutes to actually detect some CO₂. This extraction was aborted after 22 minutes, while the CO₂-detector still counted over 16000 ppm.

@ 6 litres/hour: much better yield. However, even after 45 minutes of sparging the concentration was still around 31 ppm.

@ 12 litres/hour: Full extraction after 1230 seconds (20.5 minutes) of sparging.

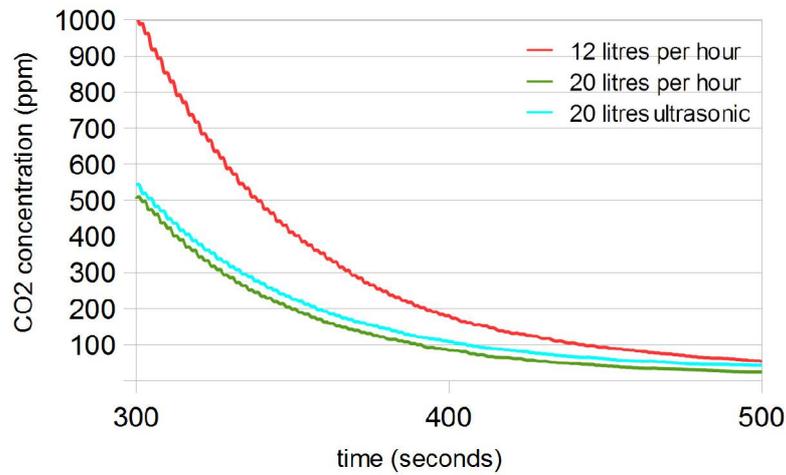
@ 20 litres/hour: Sparging at 20 litres per hour gave highly satisfactory results. After a mere 15 minutes, the process had extracted all CO₂ and the ppm count had dropped to around 10 ppm (this includes the baseline of 7.7 ppm the CO₂-detector had prior to this extraction, when flooded with pure nitrogen). This is by far the best result which has been reached in all extractions. Sparging at 20 litres per hour gives a fast and complete extraction in no more than 15 minutes.

Graph 6 shows all extraction curves at different sparging rates. Note the overlap of the extractions with and without an ultrasonic table; use of this device does not add to the extraction speed.

Sparging at 12 litres per hour gives a similar pattern when comparing to 20 litres per hour.

However, as graph 7 shows, the ppm count when nearing the end of the extraction is higher at

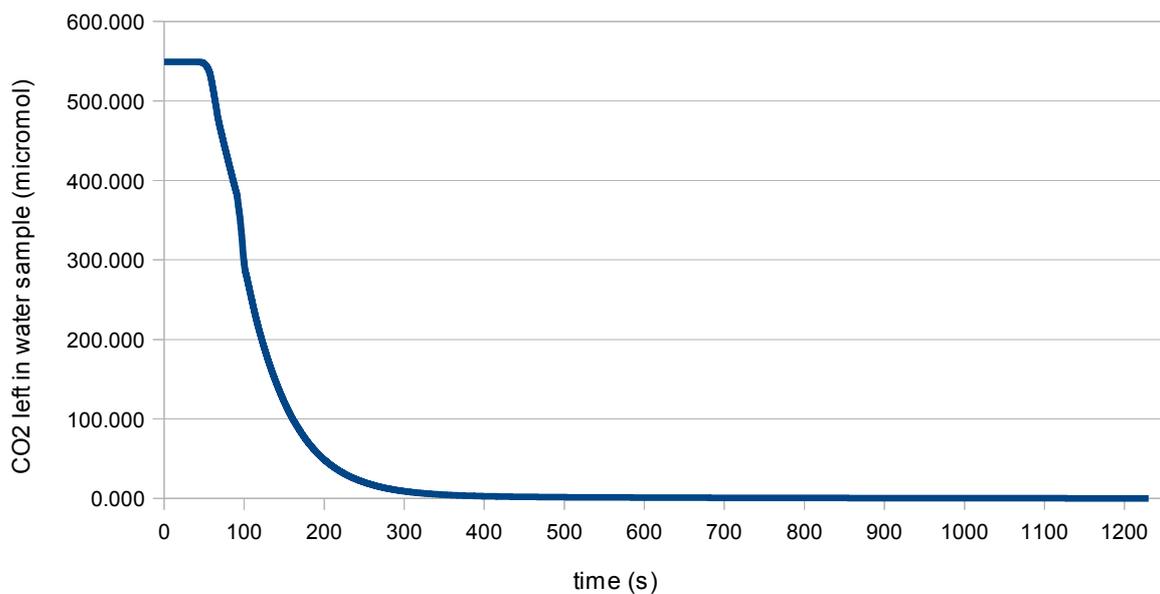
12 litres per hour.



Graph 7: 12 versus 20 liters per hour

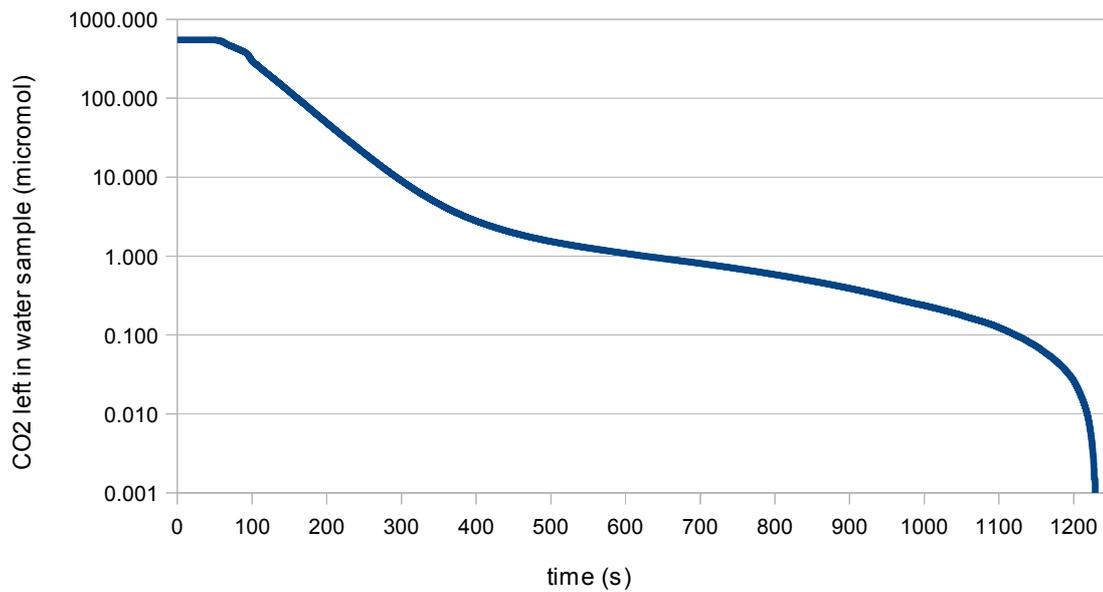
3.8.1 Progression of extraction at 12 l/h

Graph 8 shows the typical curve corresponding with the progression of extraction in time, starting with the amount to be extracted. Most of the CO₂ is extracted in the first 5 minutes of the process.



Graph 8: Progression of extraction at 12 l/h

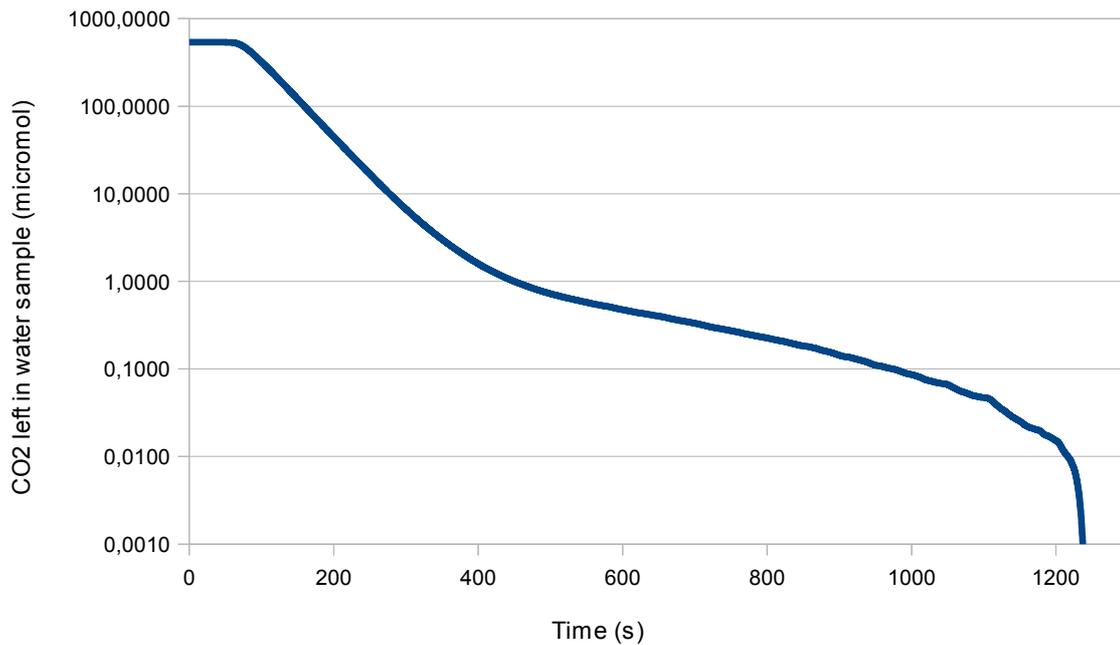
Graph 9 shows the same data, using a vertical logarithmic scale. Assuming 1 mol of nitrogen corresponds to 24.5 litres, the initial amount of CO₂ in the sample is calculated to be 0.55 millimol. This is close to the measured value of 0.6 millimol found later (see section 3.10). The curve demonstrates that sparging for more than 1200 seconds (20 minutes) is not meaningful. (Prior to the extraction the CO₂-detector baseline showed an average value of 6.27 ppm. This value was subtracted from all ppm readouts). 99.99% of CO₂ has been harvested after 816 seconds



Graph 9: Progression of extraction at 12 l/h - logarithmic vertical axis

3.8.2 Progression of extraction at 20 l/h

Graph 10 shows the data from the extraction at 20 l/h (no ultrasonic table). Prior to the extraction at 20 l/h the CO₂-detector baseline showed an average value of 7.7 ppm and was subtracted from all ppm readouts.



Graph 10: Progression of extraction - logarithmic

The initial amount in the water sample was calculated to be 0.54 millimol. When referring to the original data, 99.99 % of all CO₂ is harvested after 564 seconds (at 12 l/h: 816 seconds)

The logarithmic scale of Graph 9 and 10 reveals a change in slope, approximately 400 seconds in the process. At this time, more than 99% of the total CO₂ content in the water sample has already been extracted. Possibly the water sample was at this time depleted, while a low concentration of CO₂ gas was still residing in the trajectory between the water sample and the CO₂-detector. The extraction regime of this diffuse gas may differ from that of the CO₂ in the water sample.

The curves are obtained by second-to-second subtraction from the total yield. While nearing the end of the extraction time, the micromol value drops to zero, giving a sharp downward curve in the logarithmic graphs. The value drops to zero because the extraction was cut while a minimal amount of $0,2 \cdot 10^{-3}$ to $0,4 \cdot 10^{-3}$ mmol/s of CO₂ was still passing the CO₂-detector.

3.9 Extraction of CO₂ from tap water samples

To gain insight in the accuracy of the ACE setup, series of extractions were performed. Since

the samples used were all identical, the yields of CO₂ should be equal and isotope ratios should match. Table 2 shows the degree to which the yields agree in red.

date	only water gram	end pressure millibar	temp ° Celcius	per kg water sample: millimol/kg	zero point Vaisala ppm	Pa mbar	Pb mbar	remarks
15-05-12	263.73	628.70	21.48	3.406	6.14	786	17	Vaisala zero point taken after placing N2 DeWar
15-05-12	267.30	636.70	21.62	3.402	6.32	770	17	Vaisala zero point based on only 12 values
15-05-12	263.84	628.82	21.60	3.404	6.38	728	20	
16-05-12	264.17	625.40	21.61	3.381	6.00	817	23	Vaisala detects some CO2 during sparging
16-05-12	263.36	623.20	21.61	3.379	6.60	759	23	Vaisala detects some CO2 during sparging
16-05-12	261.80	617.80	21.66	3.369	6.12	780	23	Vaisala detects some CO2 during sparging

Table 2: Results sparging acidified tap water samples

Sparging was carried out at 12 litres nitrogen per hour. All samples were sparged for 900 seconds. Prior to each extraction, the baseline of the CO₂-detector was logged by flooding it with pure nitrogen.

Pa and Pb are the pressures in the left and right part of the setup. Monitoring Pb is important: increasing pressure leads to smaller path lengths of the molecules in the gas mixture. Since the CO₂ needs to be captured by the liquid nitrogen cold trap, each CO₂ molecule needs the longest possible free path to be able to reach the cold surface of the glass. The higher the concentration of gas molecules in the cold trap, the higher the chance of losing CO₂.

The last three extractions show a somewhat lower yield of CO₂ and the CO₂-detector detects CO₂ in the process. When calculating the actual loss in micromol each second, a total of 1 micromol turns out to be lost during each of the three last extractions, corresponding to 0.1 % of the yield from the water sample. The three last extractions are an average of 1.5 % lower than the first three. So, the loss of CO₂ does not account for the lower yield.

Another possibility is fluctuation of the Baratron itself (see section 3.13).

3.10 Extraction of CO₂ from seawater samples

Similar to the tap water extractions, several seawater extractions were performed as well, resulting in a number of highly equal yields, as can be seen in red in the table 3.

date	$\delta^{13}\text{C}$ code	water gram	N2 flow l/h	sparging time sec	end pressure millibar	temp ° Celcius	per kg water sample: millimol/kg	baseline Vaisala ppm	Pa mbar	Pb mbar	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$ VPDB-CO2/VPDB-CO2
05-23	ACE-1	276.86	12	1200	427.27	22.52	2.197	6.56	750	32	-3.181	1.274
05-23	ACE-2	274.50	12	1200	423.70	23.27	2.192	6.07	707	31	-3.133	1.308
05-23	ACE-3	275.83	12	1200	426.60	23.40	2.195	6.04	800	31	-3.174	1.232
05-23	ACE-4	275.34	12	1200	425.90	23.31	2.196	5.48	752	31	-3.136	1.202
05-23	ACE-5	272.96	12	120	307.90	23.56	1.600	5.48			-2.949	0.873
05-23	ACE-6	276.46	11	2100	427.66	23.64	2.194	6.86	772	31	-3.132	1.086
05-24	ACE-7	276.10	12	600	430.89	22.95	2.219	6.03	823		-3.182	1.233

Table 3: Highly consistent yields of CO₂ after extracting from identical seawater samples

The lower yield of 1.6 mmol/kg (ACE-5) was simply because that run was only sparged for 2 minutes. However, the last one in the list shows a total yield of 2.22 mmol/kg, which is unexpected. The sparging time was only 10 minutes, while the amount of CO₂ was significantly higher. Note that this last sample was taken a day later than the series in red. The previous series of samples, the tap water samples, also showed a consistent yield when extracted on the same day. But again, between the two days of extraction an unexplained difference can be observed.

3.11 Error considerations and analysis

Based on instrument specifications and the input from van Heuven, the following precision of the various instruments was adopted:

- weight of water sample m : $\sigma_m = \pm 0.1$ gram
- end pressure P : $\sigma_p = \pm 0.1$ mbar
- volume of calibration volume V : $\sigma_v = \pm 0.03$ ml
- temperature T : $\sigma_T = \pm 0.10$ K

The accuracy was not taken into consideration, since only the consistency of outcomes was explored and not the absolute yield. The errors were included in the calculation of the error in the final yield:

$$\sigma_n^2 = \left(\frac{V}{RTm}\right)^2 \cdot \sigma_P^2 + \left(\frac{P}{RTm}\right)^2 \cdot \sigma_V^2 + \left(\frac{-PV}{RT^2m}\right)^2 \cdot \sigma_T^2 + \left(\frac{-PV}{RTm^2}\right)^2 \cdot \sigma_m^2$$

Calculation produces an error of 2 μmol , which is in agreement with the standard deviation of the yield of the five CO_2 samples, being 2.2 μmol .

3.12 Calibration volume precision

In section 3.1, a precision of 0.08 ml was adopted from a similar device at MIT.

In the error analysis, the precision of the calibration volume is the main influence on the error in the CO_2 yield. The volume of the calibration volume should be approximately constant, due to the construction and the constant temperature in the lab. There is one possible variable: the valve which isolates the CO_2 yield after cryogenic transfer to the calibration volume. It may turn to a slightly different position after each extraction, thus changing the volume of the calibration volume. Observation of the piston shows no visible variation in the end position, which is supported by the highly consistent yields. A variation of more than 0.5 mm is not observed, which corresponds to an error 35 ± 0.03 ml.

Since the Baratron functions best at atmospheric pressure, a possibility is decreasing the volume of the calibration volume, thus increasing the final pressure. Drawback is a lowering of the relative precision of the calibration volume.

3.13 Possible Baratron fluctuations

The suspicion rises that one of the measuring instruments shows a considerable fluctuation. Because the calculation of the final yield only depends on the logged temperature and pressure, one of these instruments may malfunction in its readout in a degree that is not acceptable for the desired level of accuracy.



figure 12: the Baratron

The temperature sensor has been compared to a calibrated thermometer several times during the weeks of operation and no aberrations were found. Fluctuations in the calibration volume due to temperature variations and overnight accumulation of CO_2 in the head space of the sample bottles were excluded as cause. The Baratron (figure 12) thus becomes the only unknown factor. Specifications show that temperature fluctuations, hysteresis, non-linearity, and non-repeatability do not account for the observed fluctuations. The “old” sticker on the

device suggests the Baratron being unfit, although later extractions did not reveal problems with the Baratron.

3.14 ¹³C analysis

Several seawater samples were analysed for ¹³C and ¹⁸O, measurement using the MM10 Dual Inlet IR Mass Spectrometer of the CIO. The resulting values are displayed in the table.

date	$\delta^{13}\text{C}$ code	only water gram	N2 flow l/h	sparging time sec	end pressure millibar	temp ° Celcius	per kg water sample: millimol/kg	zero point Vaisala ppm	Pa mbar	Pb mbar	$\delta^{13}\text{C}$ VPDB-CO2 ‰	$\delta^{18}\text{O}$ VPDB-CO2
05-23	ACE-1	276.86	12	1200	427.27	22.52	2.197	6.56	750	32	-3.181	1.274
05-23	ACE-2	274.50	12	1200	423.70	23.27	2.192	6.07	707	31	-3.133	1.308
05-23	ACE-3	275.83	12	1200	426.60	23.40	2.195	6.04	800	31	-3.174	1.232
05-23	ACE-4	275.34	12	1200	425.90	23.31	2.196	5.48	752	31	-3.136	1.202
05-23	ACE-6	276.46	11	2100	427.66	23.64	2.194	6.86	772	31	-3.132	1.086
05-23	ACE-5	272.96	12	120	307.90	23.56	1.600	5.48			-2.949	0.873

Table 4: Isotope ratio's of CO₂ yields from sea water samples in red

The CIO states an error of 0.03 for the $\delta^{13}\text{C}$ values and an error of 0.06 for the $\delta^{18}\text{O}$ values. The obtained data has a standard deviation of 0.03 for the $\delta^{13}\text{C}$ values and 0.08 for the $\delta^{18}\text{O}$ values. The results show a constant ¹³C content, as expected when identical samples are extracted. The last two extractions were performed with shorter sparging times. As expected, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ value of the 120 second extraction deviates from those of the full extractions, since the heavier isotopes are harder to extract from the water sample. The 600 second extraction shows normal $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, which is expected, since 99.9% of all CO₂ is extracted in this particular run.

The $\delta^{13}\text{C}$ values do not correspond to typical values of seawater samples, which have values ranging from 0 to 2.5‰ [Mook, 2001]. As mentioned before, twenty year old samples were used for these extractions. Through the years the isotope ratios have changed, due to the exchange of CO₂ with the atmosphere. The current $\delta^{13}\text{C}$ for atmospheric CO₂ is -12 ‰, so depending on the rate of exchange, a lowering of the $\delta^{13}\text{C}$ is expected.

If a CO₂ sample would contain any water that escaped through the water trap, the $\delta^{18}\text{O}$ value would show a large deviation from the values in table 4.

3.15 Memory effect

Investigated was the possibility of a previous run polluting a subsequent run; traces of CO₂ could get trapped in the ice caught by the water traps. These traces could slowly be released in successive runs, possibly influencing yields and isotope ratios.

The described experiment was done rather hastily, repeating it in a more prepared setting is recommended.

Four water samples were prepared. Two of them were enriched by doubling the amount of ¹³C. For this, 50 mg of barium carbonate (BaCO₃) was added to a volume of 5 litres of tap water, which was stirred overnight. The BaCO₃ contains 60 percent ¹³C, when adding the mentioned amount to 5 litres of water, only a doubling of the usual ¹³C content is established, since not all BaCO₃ was dissolved. To avoid the mass spectrometer exceeding its scale maximum, larger concentrations are not desirable.

The two enriched samples were extracted first, thus flooding the system and especially the water trap with enriched ¹³C. The yield of each extraction was divided over two transport vessels for further analysis with the mass spectrometer.

Sample nr	δ ¹³ VPDB-CO ₂	δ ¹⁸ VPDB-CO ₂
ST1A	345.766	-2.646
ST1B	345.778	-2.671
ST2A	256.486	-5.708
ST2B	256.581	-5.676
ST3A	-9.579	-5.817
ST3B	-9.082	-4.909
ST4A	-8.760	-4.276
ST4B	-9.571	-5.829

Table 5: Memory effect

Subsequently the two standard tap water samples were sparged. Again, each yield was divided over two transport vessels. Each A/B combination originated from the same sample of CO₂, but still shows a considerable fluctuation (ST3A/B and ST4A/B in table 5). Possibly, some isotope fractionation occurred during the splitting process of the sample in the calibration volume. Splitting is performed by opening the calibration volume, thus distributing the gas over a larger volume. The calibration volume is then closed

again and the gas which is at that moment at the outside of the calibration volume is frozen into a transport vessel. After closing this vessel and opening another one, the process is repeated, resulting in two samples which should be identical in isotope composition. Uniform mixing of all isotopes combinations of CO₂ may take longer, meaning the valve of the calibration volume should have been open longer. Repeating this test is advisable. Note that the difference between each A/B combination is not related to the memory effect.

The first four δ¹³ correspond to the enriched samples, the last four to the standard tap water

samples. Despite the large ^{13}C contribution in the first samples, the ^{13}C values seem to return to normal in subsequent extractions, suggesting that previous runs do not influence later ones. However, since a run with standard, non-contaminated samples was omitted prior to the runs with the enriched samples, no actual $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of non-enriched water are known. Again, full certainty can only be established by repeating the procedure. In a new test, an extraction with standard tap water prior to the extraction of the enriched sample is recommended. This way, the $\delta^{13}\text{C}$ content before and after the enriched extraction can be compared.

4 Discussion & conclusions

Goal was to assess several elements of the Automatic CO₂ Extractor, to gain insight in performance of the setup. Also, precision of the CO₂ yield and consistency of isotope ratios was determined by extracting several identical samples of tap water and seawater. Generally, the Automatic CO₂ Extractor delivers according to specifications or even better. ACE provides precise data and thanks to the automated extraction process it relieves the work load, minimizes errors and speeds up the extraction process considerably.

Liquid nitrogen consumption by the large CO₂ trap is considerable. The largest possible Dewar is recommended or even topping halfway the sequence may be in order, possibly automated. Installing a second water trap of a different type solved the leak-through of water. Applying 1 ml of 85% orthophosphoric acid ensures complete release of CO₂ from carbonates in the (sea)water samples. Sparging at 20 litres/hour for 20 minutes ensures full extraction of CO₂. An extraction sequence with five identical seawater samples showed identical yields of 2.2 millimol each, with a standard deviation of 2 micromol. However, when comparing extractions which are a day apart while originating from the identical samples, inconsistencies in yields are found. Possible explanation is the Baratron which may show day to day variations. Further testing of this vital part of the setup is recommended.

Tests with enriched ¹³C water samples indicate that ACE is not affected by memory effect. However, given the large errors, repeating the test is recommended. The pressure of the CO₂ which is obtained after extraction is typically somewhere between 400 and 500 mbar. Since the Baratron has its best performance around atmospheric pressure, the plan is to reduce the current calibration volume. Drawback: the volume error increases. Ideally, a new Baratron should be installed, suitable for measuring lower pressures.

In some cases, the CO₂-detector did not return to its baseline value, even after prolonged extraction. Possibly the Dekabon tubing absorbs small quantities of CO₂, which are released again when the CO₂ flux from the water sample diminishes. This could be tested with an additional CO₂ detector. Baseline drift of the CO₂-detector during the course of an extraction doesn't seem likely. The CO₂-detector did not show drift during prolonged testing.

Currently, the setup is fully computer controlled: autonomous execution of full series of extractions and constant monitoring and logging of the entire process.

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7 Appendix A

Extraction procedure

Since the extraction process was not controlled by the computer yet, all operations were done manually. The step by step procedure is shown below. At present, valves, Dewars and pneumatics can be fully controlled by the computer, using Labview as control software.

Preparation prior to extraction

- Start computer logging
- Placing CO₂ ice / ethanol slurry around water traps
- Switch to small pump to be able to get zero ppm value of CO₂-detector
- Setting output pressure of N₂ cylinder slightly above lab pressure so N₂ can later flush spatter volume
- Important timestamps are logged manually, so computer logs can be interpreted easier

Extraction procedure

- N₂ over main line
- Placing N₂ Dewar around CO₂ trap
- Close main, open valve to spatter volume, flush spatter volume for 20 seconds
- Attach water sample while flushing continues. Make sure tube of spatter volume does not enter water surface in sample flask
- As soon as sample is in place, close valve above sample
- Nitrogen back along main channel
- Let CO₂-detector drop to its zero value
- Stop N₂ through main channel, switch to sparger
- Apply acid and open valve above water sample
- If necessary, adjust flow of nitrogen to desired level
- Let sample sparge
- Stop N₂ flow by closing BMV after needle valve
- Switch to large vacuum pump and pump down until Convectron no longer drops
- Disengage pump, make sure CO₂ is now in isolated system
- Remove left Dewar from large cold trap
- Ventilators on, wait until all ice has melted from CO₂ trap, CO₂ sublimates

- Ventilators off
- Place liquid nitrogen around calibration volume
- Close BMV above this volume after Convectron no longer drops
- Remove liquid nitrogen
- Ventilators on
- Wait several minutes for temperature to stabilize so pressure inside calibration volume can be correlated with temperature
- Store CO₂ for further analysis with another cryogenic transfer to a transport vessel
- Pump down with large pump
- Remove water sample

End of the day

- Stop computer logging, put CO₂ snow back in fridge and liquid nitrogen in big Dewar flask. Shut down pumps.