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Abstract

Copper has been suggested to be susceptible to water-induced corrosion under O_2-free conditions in the absence of external constituents affecting the process. The research behind this suggestion utilized stainless steel chambers with open glass vials for exposure of copper to water and mass spectroscopy for analysis of H_2 that was assumed to be a result of a corrosion process. An alternative method that utilizes glass vials and butyl rubber stoppers for exposure of copper to O_2-free water and gas chromatography for the analysis of H_2 was previously developed and reported 2013. Here, we report continued observations of the previously reported experiments that started 2012 and also results from new experiments that were started during 2013 and 2014.

Three consecutive series of experiments have been conducted. The first series covered the continued analysis of nine experiments, denoted N1 to N9, with five to ten glass vials containing copper rods in each experiment. The copper samples were obtained from test manufacturing of SKB's canisters and were of a similar material quality to that intended for use in SKB's final repository. These experiments were started during fall 2012 and H_2, O_2 and pressure were analysed for up to 850 days. The N4 and N5 experiments were stopped after 442 and 384 days, respectively, due to lack of space in the anaerobic jars and heat cabinets. The second series of experiments studied the influence of sodium chloride and pH, the effect of omitting water in the vials containing copper rods and the copper rod surface area on the emission of H_2. In the end of 2013 and during 2014, a third series of experiments were started with a combination of four copper types of different grades, and treatments including ultra-cleaning, electropolishing, heat treatment (400°C) and scratching of the copper materials. Finally, a method was set up to investigate if copper oxides could be detected on the copper rods before and after the experiments. Concurrently, a wet chemical method was developed for the analysis of copper in the vials after removal of the copper specimens. These methods were tested on copper specimens from a total of 5 experimental vials.

Sammanfattning

Koppar har föreslagits kunna korrodera i syrgasfritt, rent vatten i frånvaro av andra komponenter som allmänt anses behövas för att koppar ska korrodera. I forskningen som lett fram till denna slutsats har forskarna utnyttjat rostfria kammare med glasinsatser där kopparn utsatts för syrgasfritt vatten. En masspektrometer kopplades till kammaren via ett palladium membran och användes för analyser av vätgasutveckling vilken ansågs vara kopplad till en kopparkorrosionsprocess. En alternativ metod för studiet av vätgasutveckling från koppar i syrgasfritt vatten utvecklades under 2012 och rapporterades under 2013. I metoden placeras kopparbitar i vattenfyllda glasrör som sedan förseglas med butylgummikorkar. Vätgasutvecklingen analyseras med en gaskromatograf försedd med en detektor med mycket hög känslighet för vätgas och syrgas. Här rapporterar vi resultat från fortsatta mätningar av tidigare beskrivna och rapporterade experiment samt resultat från nya experiment vilka startades under 2013 och 2014.

Experimenten kan delas in i tre på varandra följande grupper. Den första gruppen omfattar fortsatta mätningar av nio tidigare startade experiment benämnda N1 till N9. Dessa experiment utformades med 5 till 10 glasrör med två kopparbitar varje rör. Kopparn kom från provtillverkning av SKB:s kapslar och var av liknande kvalitet som den som avses användas i SKB:s slutförvar. Experimenten startades under hösten 2012 och vätgas, syrgas samt total tryck i rören analyserade under upp till 850 dagar. Experimenten N4 och N5 avbröts dock efter 442 respektive 374 dagar på grund av platsbrist i anaerob-kammarna och värmeskåpen. Den andra gruppen experiment undersökte hur natriumklorid och surhetsgrad, samt avsaknad av vatten i rören och storleken på kopparytorna inverkade på vätgasutvecklingen. I slutet av 2013 och under 2014 startades en tredje grupp experiment där fyra olika typer av koppармaterial behandlades med ultrarengöring, elektropolering, värmebehandling (400 °C) samt repning av de rena metallytorna. Samtidigt utvecklades en metodik för våtkemisk mätning av kopparoxider på kopparytorna och förekomst av koppar i glasrören efter att kopparytorna tagits ut. Metoden testades på fem olika koppармaterial.

Contents

1 Introduction

Current models of copper corrosion indicate that copper is not subject to corrosion by water in itself, but that additional components, such as O_2 or sulphide are needed to initiate a corrosive process. Of late, however, a number of reports have suggested that copper may be susceptible to water-induced corrosion in the absence of external constituents affecting the process (Becker and Hermansson 2011, Hultquist et al. 1994, 2009, Szakálos et al. 2007). The process has been proposed to rely on the auto-dissociation driven presence of the hydroxide ions in pure water, and to result in the development of atomic hydrogen (H), with subsequent release of H_2 gas. A suggested equilibrium is reached at a partial pressure of H_2 of about 1 mbar (0.1 kPa) in 73°C, and the corrosion reaction is proposed to be rate-limited by the supply of hydroxide ions from the water, a process being slower than the proposed formation of water from a H_2–O_2 reaction. In consequence, the presence of O_2 in the system would result in no detectable release of H_2 until all O_2 was consumed, while the absence of O_2 would lead to water-driven corrosion of copper proceeding until the H_2 equilibrium is reached, at a partial H_2 pressure of about 1 mbar. The proposed mechanism presents a novel aspect on copper corrosion processes. By extension, the suggested corrosion process may have implications for proposed strategies for long-term storage of spent nuclear fuel (SNF), which in part rely on the long-term ($>10^5$ years) integrity of copper canisters stored in anoxic water-inundated environments (SKB 2010).

The development in three phases of a procedure that allows observation of the emission of H_2 from copper immersed in pure, O_2-free water in butyl rubber stoppered glass vials has been reported previously (Bengtsson et al. 2013). Although the basic procedure was adopted from methods in anaerobic microbiology, some new challenges had to be approached. The method needed improved control and removal of O_2 from the vial environments compared to the microbiological methods that rely on pH and redox buffers and on chemical O_2-scavengers (e.g. sulphide) in the media. Further, the relevant concentrations of H_2 and O_2 were very low and that put large demands on the analytical procedures for the gases. These challenges were dealt with stepwise until the required levels of a stable and reproducible glass vial environment, analytical precision and data variance were obtained.

The most important result obtained during the method development was that H_2 was emitted from copper in pure, anoxic water to partial pressures between 3 and 7 mbar depending on the experimental conditions. Further, it was observed that H_2 emission was inhibited when there were detectable amounts of O_2 in the gas phase of the vials. So far, it appeared as if copper may be susceptible to water-induced corrosion under O_2-free conditions in pure water. However, H_2 reached much higher partial pressures than predicted (Szakálos et al. 2007) and the H_2 emission rate and level were very dependent on the treatment of individual copper surfaces. Obviously, more research was needed to fully understand what variables influence the H_2 emission process.

The previous time of exposure to anaerobic conditions was generally not longer than 120–140 days, with exception for a few early experiments that lasted up to 420 days (Bengtsson et al. 2013). Steady states of the H_2 concentration were not observed because H_2 was either increasing or decreasing in the experiments at the time the latest reported readings were registered. There were consequently a need for long term observation until a steady state was established at some partial pressure of H_2 including nil. Further, it was also needed to repeat the treatment of copper surfaces, including the grinding step, to investigate if the initial rapid evolution of a high partial pressure of H_2 could be reproduced with the same copper surfaces. In this work, several of the previously reported experiments were followed for up to 850 days, and the effect from re-grinding during this time period was studied. Further, the integrity of the butyl rubber stoppers under various conditions such as new stoppers, used and penetrated stoppers, and wet and dry mounted stoppers was tested experimentally.

An inhibiting effect from O_2 on the H_2 emission process was observed previously, but the relation between time of exposure to O_2 and O_2 concentration and H_2 emission could not be established. Low concentrations of O_2 during short times appeared to have just a reversible effect; some data indicated that prolonged exposure to O_2 permanently shut down the H_2 emission process. Thus, the effect of an intermittent, significant exposure to O_2 on the H_2 emission process was investigated in the work presented here. The process(es) connected to the emission of H_2 would possibly be sensitive to the chemical and physical environment in the glass vials. A set of initial experiments were set up to test if addition of sodium chloride, change in pH, absence of water and also varying the surface area of the copper rods influenced the H_2 emission process.

All experiments introduced above were performed with ground and acid leached specimens produced from the SKB OFP canister 99.95% copper. The experiments were expanded to include other types of higher grade copper with various surface treatments such as electropolishing and heat treatments.

An H_2 emission from copper in the glass vials could originate from hydrogen atoms in the water molecules or from degassing of H_2 stored in the metal. The reduction to H_2 would need electrons and copper is the only possible source of electrons. Oxidized copper would need to react with concomitantly oxygen released from the water molecules to form copper oxides. Hence, a method was developed for the determination of copper oxides on the copper surfaces. A method for the analysis of copper in the water and vials of the experiments was also developed.

This report is mainly directed towards reporting of the outcome of the experiments presented above. In depth interpretation and evaluation of the results will be reported elsewhere since the competence, relevant to the problem at hand, of the authors of the present report is mainly in the area of method development and measuring technique.

2 Methodology

2.1 Preparations

Preparations of the vials followed the 'Micans method' as outlined in Chapter 3 in the report by Bengtsson et al. (2013) with modifications as given for each experiment in this report.

2.2 Evaluation of the integrity of the butyl rubber stoppers under various batch conditions

Bellco rubber stoppers were used to seal the glass vials containing copper specimens, water and gases. They are known to seal very well (Hungate et al. 1966), but because we previously occasionally observed unexpected pressure drops in the vials, we tested if there was any batch variation between new and old, used stoppers and if soaking the stoppers in water before mounting could improve sealing.

2.3 Method

Empty glass test vials were sealed with rubber stoppers from different batches. Some of the stoppers had been used previously in experiments and were already punctured with needles several times, but still of good overall quality. New stoppers were also used and tested dry as well as wet-mounted.

The sealed vials were evacuated and filled with pure N_2 to a final overpressure of 100 kPa. Then 50 µL of pure H_2 gas was added manually to each vial with a gastight Hamilton syringe through the stopper. It should be noted that it was difficult to add an exact amount of H_2 using this method, pure H_2 readily escapes from the syringe because of its low molecular weight. Because of this, addition had to be done swiftly causing variation between the vials. A start value of H_2 for each individual vial was analysed and compared with the final value after the end of incubation.

2.3.1 Material and stopper variables

- Empty glass test vials.
- Different stoppers, one type from a new batch and three types from older batches.
- Crimping equipment including aluminium rings.
- Hamilton gas-tight syringe, 250 µl.

Table 2-1. Detailed description of the five different stopper variables.

Sample ID	Stopper description	Replicates
ND1	New stoppers, dry mounted	2
ND2	New stoppers, wetted before mounting	2
ND3	Used stoppers, light blue, dry mounted	2
ND4	Used stoppers, dark blue, dry mounted	2
ND5	Used stoppers, dark blue, dry mounted, old and slightly dirty	2

2.3.2 Preparation

1. The stoppers were mounted on empty glass test vials using standard equipment.
2. The vials were evacuated and refilled with N_2 to a total pressure of 200 kPa (100 kPa overpressure vs atm. pressure) according to the Micans method (Bengtsson et al. 2013).
3. To each vial 50 µL pure H_2 was added as follows:
   - 3.1. A 250 µL syringe was flushed several times with pure H_2.
   - 3.2. The syringe was filled completely with H_2.
   - 3.3. The syringe was swiftly moved to the stopper of the respective glass vial.
   - 3.4. With the needle touching the stopper the H_2 volume was quickly adjusted to 50 µL and the needle pushed through the stopper in one rapid movement. This procedure flushed the syringe needle with 200 µL of H_2 at the very start of injection. The aim was to keep the plunger in a constant movement of displacement without stopping it at any moment, to avoid contamination and dilution.
   - 3.5. Before withdrawing the needle from the stopper it was flushed twice inside the glass vial.
4. A starting value for the H_2 content was analysed using a gas chromatograph (Section 2.4.1).
5. The vials with stoppers were placed in an anaerobic jar that was evacuated and filled with pure N_2 according to the Micans method (Bengtsson et al. 2013).
6. The anaerobic jar was stored in a heated cabinet at 70°C.
7. The amount of H_2 was analysed at regular intervals for three months.

2.3.3 Results

Four of the vials had starting partial pressures of H_2 that was significantly lower than the other six samples (Figure 2-1). This was probably due to variations in the addition of H_2 and N_2 because three of these vials also showed lower total pressures than the remaining vials (Figure 2-2).

During the three months period of sampling a slow trend of H_2 partial pressure loss through all of the stoppers could be detected. The loss in total pressure, and to some extent the loss in partial pressure of H_2, over time in the vials was caused by the sample extractions and not by any leakage. Each vial showed approximately constant total and partial pressures drops regardless of time between samplings, the start pressure and the stopper type.

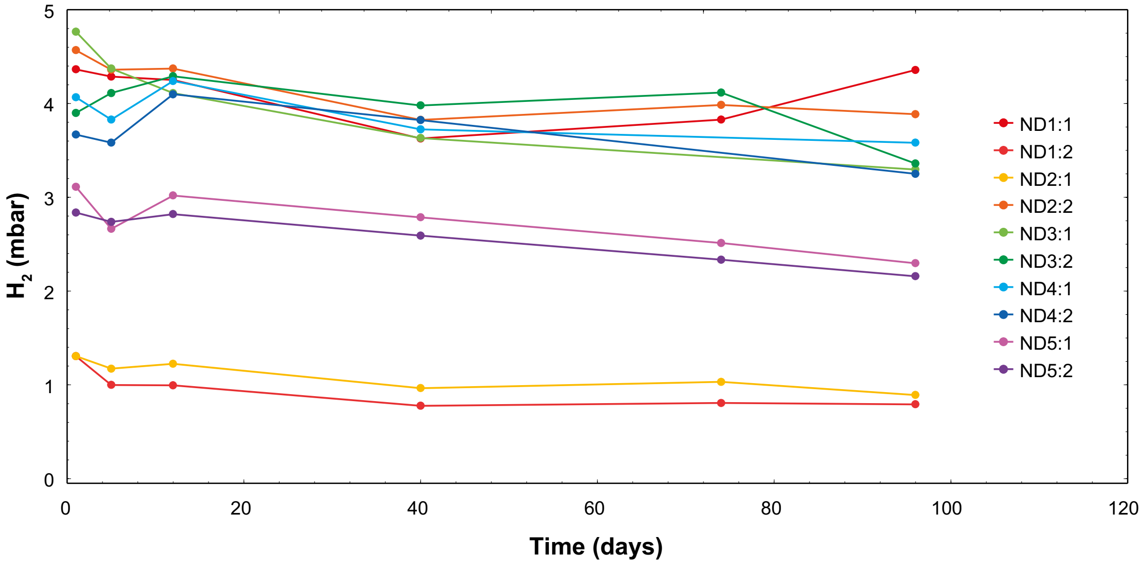

Figure 2-1. *The partial pressure of H_2 analysed for injections of 100 µL sample on the GC-450.*

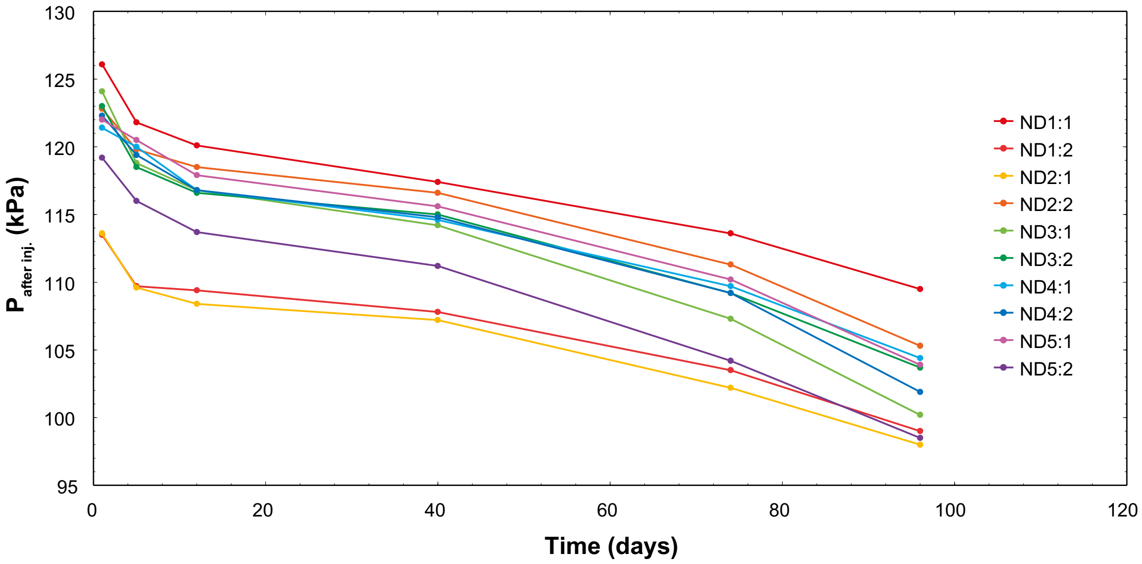

Figure 2-2. *The total pressure P in each vial of the stopper integrity test.*

The conclusion for this experiment is that over the three months period of testing no significant unexpected losses of total pressure and partial pressure of H_2 from the vials could be detected regardless of what stopper batch used, or if the stoppers had been pre-soaked in water or not. The test consequently confirms that the occasional pressure drops observed previously cannot be explained by variations in stopper quality. Rather, the large pressure drops occasionally observed previously were most likely due to artefacts caused during penetration such as syringe failure or a short period of gas outlet from the vial before the rubber material closed the penetration holes, particularly if the syringe was removed too fast.

It is also noted that these results, obtained with the vials filled with gas only, are compatible with the results of the calculations in Section A1.3.2 in Bengtsson et al. (2013). These suggest that 97% of the hydrogen gas in the smaller gas volume of 5 mL used in the copper experiments could be lost through outward diffusion through the vials in a matter of 420 days. The driving force for the outward diffusion depends only on the partial pressure of the gas in question and the diffusion properties of the stoppers, whereas the resulting pressure drop is inversely proportional to the gas volume in the vial. Hence, a 5 times smaller gas volume will experience a 5 times quicker pressure drop due to outward diffusion.

2.4 Analyses

2.4.1 Gas chromatography and pressure measurement

Gas sampling and analyses were initiated by allowing all vials to cool to room temperature. All vials, needles and equipment used were thoroughly flushed with Scientific or Instrumental He prior to attachment or insertion into experimental or control vials. All sampling was performed using an identical method. A Bruker 450 gas chromatograph equipped with a split column with a CP7355 PoraBOND Q 50 m×0.53 mm ID and a CP7536 MOLSIEVE 5A PLOT 25 m×0.32 mm ID and a Pulsed Discharge Helium Ionization Detector (PDHID) was employed for the H_2 and O_2 analyses (Bruker Daltonics Scandinavia AB, Vallgatan 5, SE-17067 Solna, Sweden). First, a sample volume of 50 or 100 µL was immediately injected into the GC-injector of the Bruker 450 chromatograph for H_2 and O_2 analysis. The injection volume was shifted from 100 to 50 µL and occasionally 25 µL when the H_2 partial pressures were larger than 3 mbar. Second, a pressure gauge-attached needle was inserted into the gas volume and the pressure after sampling was noted. The chromatograph was calibrated with CRYSTAL gas mixture from Air Liquid (Bataverstr. 47, 47809 Krefeld, Germany) containing H_2, 0.0987 mole %; O_2, 1.036 mole %; Ar 1.030 mole %; Ne 0.977 mole %; N_2O, 0.993 mole %; rest N_2. In October 2014, the injection liner volume was reduced and the split ratio could be reduced from 4-1 to 1-1 which increased detector sensitivity and response.

2.4.2 H_2 limit of detection

The PDHID detector is very sensitive for H_2. The limit of detection (LOD) for H_2 was 0.1 nL.

2.4.3 O_2 limit of detection and report levels

The PDHID detector is very sensitive for O_2. The LOD for O_2 was 0.1 nL

During the development of the method (Bengtsson et al. 2013) it was found that air could be captured in the syringe needle during transfer of the sample from the vial to the injector on the gas chromatograph which resulted in O_2 data not related to the gas phase in the vials. Therefore, at regular intervals, carrier gas (He) was injected for determination of this injection error. It was found that between 0.2 and 0.5 µL air i.e. between 0.04 and 0.1 µL O_2 were captured during injection which corresponds to approximately 0.8 and 4 mbar O_2 depending on the pressure in the vial gas phase and the volume injected, usually 50 or 100 µL. The exact amount of O_2 contamination depended on the skills of the respective technician and we started specific injection training during the method development Phase II that became fully developed during method validation. In several of the result figures there is an undulating trend in O_2 values from 0 up to a couple of mbar O_2. These values consequently represent O_2 contamination during injection and not O_2 in the vials. Occasionally there were problems with air leakages during sampling that introduce O_2 in the vials if the pressure in the vial was at or below atmospheric pressure. It can consequently be concluded that O_2 was present in the vial if the partial pressure of O_2 was significantly above 4 mbar. Values below this partial pressure generally reflect air capture during injection of the samples. Values above this partial pressure suggest that there has been a contamination of the vial gas environment due to leakages during sampling. It is not possible to set an exact cut-off partial pressure for when the vial was contaminated because there is a variation in how well the injections proceed and there is also a relation between a fixed volume of air contamination and the total pressure in the vial; the higher the total pressure in the vial, the lower the partial pressure from a fixed amount of contaminating air will be.

3 Overview of performed experiments

3.1 Continuation of the N1–N9 experiments

There were nine experiments, N1 to N9, with five to ten glass vials containing copper rods started during fall 2012 and reported previously after exposure to anaerobic conditions for 120–140 days (Bengtsson et al. 2013). Measurements of H_2, O_2 and pressure were continued for up to 850 days as outlined in Table 3-1. The N4 and N5 experiments were stopped after 442 and 374 days, respectively, due to lack of space in the anaerobic jars and heat cabinets. An overview of each experiment is given in Table 3-2.

3.2 The chemical and physical treatment experiments

During 2013, four new experiments were initiated that studied the influence of sodium chloride, pH, absence of water and copper surface area on the emission of H_2. Periodic measurement of H_2, O_2 and pressure for these experiments were as outlined in Table 3-1. An overview of each experiment is given in Table 3-2.

3.3 The copper type and treatment experiments

In the end of 2013 and during 2014, new experiments with a combination of copper of different grades and treatments were designed by the Swedish Nuclear Fuel and Waste Management Company (SKB) in cooperation with the Department of chemistry at Uppsala University. Periodic measurement of H_2, O_2 and pressure for these experiments were as outlined in Table 3-1. Microbial Analytics laboratory made some preparation steps on the different copper types, as outlined in the respective descriptions of preparation. An overview of each experiment is given in Table 3-2.

3.4 Appendix information

All data for H_2, O_2 and pressure in the tables are listed in an Appendix at the end of this report.

Table 3-1. A scheme showing the total length of each experiment and when it was performed. The scheme also indicates the months when major actions were undertaken for each experiment. Each experiment is briefly described in Table 3-2 and explained in detail in the text. Colours indicate:

▒ The total length of the experiment.
🟥 Copper surfaces were acid leached and transferred to new glass vials with new stoppers and water and filled with N_2
◈ The vials were evacuated from H_2 and filled with pure N_2.
🟩 The vials were evacuated from H_2 and filled with pure N_2 after replacement of the stoppers.
🟦 The vials were pH adjusted before evacuation from H_2 and filled with pure N_2 after replacement of the stoppers.
🟨 Copper surfaces were ground again before acid leach and transferred to new glass vials with new stoppers and filled with N_2.
🟧 Copper surfaces were acid leached and transferred to new glass vials with new stoppers and filled with N_2.
🟪 Copper surfaces from one of the vials were transferred to a new glass vial with a new stopper and water and filled with N_2.

		2012				2013												2014												2015	
No	**Experiment**	**9**	**10**	**11**	**12**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**1**	**2**
	Continuation of the N1–N9 experiments																														
1	N1	▒	🟥	▒	▒	▒	▒	◈	▒	▒	🟩	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒		
2	N2	▒	▒	▒	▒	▒	▒	🟦	▒	▒	🟩	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
3	N3	▒	🟦	▒	▒	▒	▒	▒	▒	🟦	▒	🟩	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
4	N4	▒	▒	▒	▒	▒	▒	🟦	▒	▒	🟩	▒	▒	▒	▒	▒	▒														
5	N5	▒	▒	▒	▒	▒	▒	▒	▒	🟦	▒	🟩	▒	▒	▒																
6	N6	▒	▒	▒	▒	▒	▒	🟦	▒	▒	🟩	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒		
7	N7	▒	▒	▒	▒	▒	▒	◈	▒	▒	🟩	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒		
8	N8	▒	▒	▒	▒	▒	▒	◈	▒	▒	🟥	▒	▒	▒	🟨	▒	▒	▒	▒	▒	🟨	▒	▒	▒	▒	▒	▒	▒			
9	N9	▒	▒	▒	▒	▒	▒	🟦	▒	▒	🟩	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒		
	The chemical and physical treatment experiments																														
10	NN Sodium chloride							▒	▒	▒	▒	🟥	▒	▒	▒	▒	▒														
11	NpH											▒	▒	▒	▒	▒	▒														
12	NCD							▒	▒	▒	▒	🟧	▒	▒	▒	▒	▒														
13	NCS							▒	▒	▒	▒	🟥	▒	▒	▒	▒	▒														

		2012				2013												2014												2015	
No	**Experiment**	**9**	**10**	**11**	**12**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**1**	**2**
	The copper grade type and treatment experiments																														
15	NUK											▨	▨	▨	▨	▨	▨														
16	UK														▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨						
17	A																		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨			
18	B																		▨	▨	▨	▨	▨	▨	▨	▨	■	▨	▨	▨	
19	C																		▨	▨	▨	▨	▨	▨	▨	▨	■	▨	▨	▨	
20	D																		▨	▨	▨	▨	▨	▨	▨	▨	■	▨	▨	▨	
21	E																		▨	▨	▨	▨	▨	▨	▨	▨					
22	F																		▨	▨	▨	▨	▨	▨	▨	▨					
23	G																			▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		
24	H																			▨	▨	▨	▨	▨	▨	▨	▨	▨			
25	I																			▨	▨	▨	▨	▨	▨	▨	▨	▨			
26	J																						▨	▨	▨	▨	▨	▨			
27	K																						▨	▨	▨	▨	■	▨	▨	▨	
28	L																					▨	▨	▨	▨	▨	▨	▨	▨	▨	
29	M																						▨	▨	▨	▨	■	▨	▨	▨	
30	Q																											▨	▨	▨	
31	Controls B–C; E–F																		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨			
32	Controls G–I																			▨	▨	▨	▨	▨	▨	▨	▨	▨			
33	Controls L																			▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
34	Controls J, K, M																						▨	▨	▨	▨	▨	▨	▨	▨	
35	Controls Restarts																											▨	▨	▨	
36	Controls Q																												▨	▨	

Table 3-2. Overview of experiments.

No	Dates	Days	Experiment name	Treatment summary	No of vials with Cu/ H_2O/N_2	No of evacuations	Reference to text
1	2012-09-10–2014-12-30	841	N1	O_2 treatment; evacuation and acid leach; pH adjustment and two more consecutive evacuations	10/0/0	3	4.1
2	2012-09-11–2015-01-05	846	N2	O_2 treatment and two consecutive evacuations	10/0/0	2	4.2
3	2012-09-13–2015-01-07	846	N3	N_2 treatment and H_2 removal, two more consecutive evacuations	5/5/0	3	4.3
4	2012-09-17–2013-12-03	442	N4	O_2 treatment and two consecutive evacuations	5/5/0	2	4.4
5	2012-09-24–2013-10-03	374	N5	N_2 treatment and H_2 removal, stoppers in contact with water, and two more consecutive evacuations	10/0/0	3	4.5
6	2012-10-01–2015-01-05	826	N6	N_2 treatment, stoppers contact water, increased pressure and two consecutive evacuations	10/0/0	2	4.6
7	2012-10-09–2015-01-07	820	N7	N_2 treatment, stoppers contact water, pH adjustment and two consecutive evacuations	10/0/0	2	4.7
8	2012-10-15–2014-12-30	806	N8	Acid leach effect; evacuation, pH adjustment, evacuation and acid leach and two consecutive evacuation, grinding and acid leach cycles	14/5/0	4	4.8
9	2012-11-08–2015-01-05	788	N9	pH adjustments and two consecutive evacuations	15/0/0	2	4.9
10	2013-03-21–2013-12-13	267	NN Sodium chloride	Sodium chloride treatment, evacuation and acid leach	15/15/0	1	4.10
11	2013-07-09–2013-12-12	156	NpH	pH treatment	15/15/0	0	4.11
12	2013-03-15–2013-12-05	261	NCD	Dry exposure in the absence of water, evacuation	15/0/5	1	4.12
13	2013-03-26–2013-12-06	255	NCS	Copper surface area, evacuation and acid leach	10/0/0	1	4.13
14	2013-07-10–2013-12-10	153	NUK	99.9999% Cu-OF (Alfa Aesar) Uppsala method and treatment	2/3/0	0	4.16
15	2013-10-07–2014-08-15	312	UK	99.9999% and 99.9% Cu-OF (Alfa Aesar) Uppsala method and treatment	4/5/0	0	4.16, 4.17
16	2014-02-07–2014-11-21	286	A	99.95% Cu-OFP (SKB), Micans method, heat treatment 400°C in anoxic environment	2+2/0/0	0	4.14
17	2014-02-21–2015-01-16	> 350	B	99.95% Cu-OFP (SKB), Uppsala metod	2/0/0	1	4.14
18	2014-02-21–2015-01-16	> 350	C	99.9999% Cu-OF (Alfa Aesar), Uppsala method, scratched in anoxic environment	2/0/0	1	4.17
20	2014-02-07–2015-01-21	> 370	D	99.9999% Cu-OF (Alfa Aesar), no treatment	2/0/0	1	4.16
21	2014-02-21–2014-08-13	173	E	99.9999% Cu-OF (Alfa Aesar), Micans method	2/0/0	0	4.16
22	2014-02-21–2014-08-13	173	F	99.9999% Cu-OF (Alfa Aesar), heat treatment 400°C in anoxic environment	2/0/0	0	4.16
23	2014-03-24–2014-11-28	249	G	99.95% Cu-OFHC, temper:hard (Goodfellow), Uppsala method	2/0/0	0	4.15
24	2014-03-24–2014-11-28	249	H	99.95% Cu-OFHC, temper:hard (Goodfellow), heat treatment 400°C in anoxic environment	2/0/0	0	4.15
25	2014-03-24–2014-11-28	249	I	99.95% Cu-OFHC, temper:hard (Goodfellow), no treatment	2/0/0	0	4.15

No	Dates	Days	Experiment name	Treatment summary	No of vials with Cu/ H_2O/N_2	No of evacuations	Reference to text
26	2014-06-03–2014-11-28	178	J	99.95% Cu-OFP (SKB), Uppsala metod	2/0/0	0	4.14
27	2014-06-03–2015-01-16	>250	K	99.9999% Cu-OF (Alfa Aesar), Uppsala method, scratched in anoxic environment	2/0/0	1	4.17
28	2014-04-25–2015-01-21	271	L	99.95% Cu-OFP (SKB), Micans method	2/0/0	0	4.14
29	2014-06-03–2015-01-16	>250	M	99.95% Cu-OFP (SKB), heat treatment 400°C in anoxic environment	2/0/0	1	4.14
30	2014-11-11–2015-01-21	> 80	Q	99.9999% Cu-OF (Alfa Aesar), Uppsala method, scratched in anoxic environment	2/3/3	0	4.17
31	2014-02-21–2014-11-12	264	Controls B–C; E–F	Micans method	0/5/5	0	4.14, 4.15.1, 4.17
32	2014-03-24–2014-12-01	252	Controls G–I	Micans method	0/3/3	0	4.15
33	2014-04-25–2015-01-22	272	Controls L	Micans method	0/3/3	0	4.14
34	2014-06-03–2015-01-15	227	Controls J, K, M	Micans method	0/3/3	0	4.17
35	2014-10-23–2015-01-21	>100	Controls Restarts	Micans method	0/3/3	0	4.14
36	2014-11-11–2015-01-22	>90	Controls Q	Micans method	0/3/3	0	4.17

4 Experiments

4.1 N1 – O_2 treatment, acid leach, add H_2O+N_2 and repeated evacuations

4.1.1 Description of experiment

A series of 10 vials with two copper rods in each vial was prepared as described previously (Bengtsson et al. 2013). Briefly, after the last evacuation in the gas bench, approximately 240 nmol of O_2 was allowed to enter all vials. Analyses were performed weekly until day 43. Then the vials were opened in the anaerobic chamber and the copper rods were acid leached and placed back into the vials which were filled with water, added with new stoppers and N_2. Thereafter measurements continued for 841 days with repeated evacuations at days 188 and 288 according to Table 3-1. pH was adjusted to approximately 7 with NaOH at day 188.

4.1.2 Results

The results for the first 155 days have been discussed previously (Bengtsson et al. 2013). Briefly, there was a significant average H_2 emission in the experiment which reached an average partial pressure of 0.4 mbar after 43 days (Figure 4-1). After the change of gas environment and repeated leaching with the acid, H_2 was produced in all vials but one after 14 days and the partial pressure was 2.2 mbar after 111 days. The vial N1:9 lost all overpressure after 240 days, possibly due to a bad stopper or a sample withdrawal error, or a micro-fracture in the glass vial, and became contaminated with air. This exposure to O_2 in air darkened the copper surfaces significantly (Figure 4-10) and stopped further emission of H_2 in that vial. The N1 experiment suggested that H_2 emission will not start in the presence of O_2. The experiments also showed that the initially added O_2 disappeared from the gas phase which may have been due to reactions with the copper, dissolution in the water, or due to diffusion into the stopper or combinations thereof. When there was no detectable O_2 in the gas phase (confer 2.4.3), the H_2 emission started, unless the O_2 exposure was large and prolonged as in N1:9 which darkened the copper surfaces significantly and a brown ring formed on the glass wall at the gas/water interface as described previously (Bengtsson et al. 2013). H_2 emission generally commenced after each evacuation, albeit with decreasing rates and pressures that levelled out at between 1 and 2 mbar.

4.2 N2 – O_2 treatment and repeated evacuations

4.2.1 Description of experiment

A series of 10 vials with two copper rods in each vial was prepared as described previously (Bengtsson et al. 2013). After the last evacuation in the gas bench, approximately 300 nmol of O_2 was allowed to enter all vials. This experiment was denoted N2. The vials were evacuated from H_2 and filled with pure N_2 after 183 and 280 days. The old stoppers were changed to new stoppers at day 280 and analysis continued until day 846 (Table 3-1).

4.2.2 Results

The results for the first 155 days have been discussed previously (Bengtsson et al. 2013). Briefly, the addition of O_2 at day 0 was approximately 50 nmol mL^{-1} which corresponded to 300 nmol per vial. The concentration of O_2 was below detection after 15 days when several vials started to produce H_2. The N2 experiment results reproduced the N1 experimental results well and showed that H_2 emission will not proceed in the presence of O_2. The experiments also showed that O_2 disappeared from the gas phase which may have been due to reactions with the copper, dissolution in the water, or due to diffusion into the stopper or combinations thereof. This was discussed in more detail previously (Bengtsson et al. 2013). When there was no detectable O_2 in the gas phase, H_2 emission started. H_2 emission generally commenced after each evacuation, albeit with decreasing rates and pressures that levelled out at between 1 and 2 mbar. The N2:6 vial lost pressure and became air contaminated after the first evacuation. The H_2 emission in this vial consequently stopped, the copper surfaces became slightly darkened and a brown ring appeared on the glass wall at the gas/water interface (Figure 4-11). The darkening can be difficult to see on the images, but if the vials indicated here to have stopped produce hydrogen are carefully inspected, the darkening is hopefully visible in comparison with vials with ongoing H_2 emission. In other words, the H_2 emission was halted by a limited amount of copper oxides on the copper rods.

4.3 N3 – N_2 treatment and repeated evacuations

4.3.1 Description of experiment

A series of 5 vials with two copper rods in each vial and 5 vials with only water was prepared as described previously (Bengtsson et al. 2013). Analyses were performed weekly until day 40. The measurements were continued and the gas environment in the vials was again replaced with pure N_2 at 244 and 288 days. New stoppers were inserted days 40 and 288 (Table 3-1). The experiment was latest analysed after 846 days.

4.3.2 Results

There was no H_2 emission in the absence of copper in vials and H_2 emission started after day 5 in vials with copper surfaces (Figure 4-3). There was a linear, continuous increase in emission of H_2 in vials with copper for the first 40 days this experiment lasted. When the vials were evacuated of H_2 and supplied with N_2 again, H_2 emission continued in all five vials with copper rods at all three gas exchange occasions. Although there was a large variability in the data between vials, each vial seemed to have its own, specific H_2 emission rate. The order of vials with respect to H_2 emission rates and amounts was withheld almost exactly after each gas exchange occasion. Just as found in experiments N1 and N2, it appeared likely that each set of two copper rods had unique characters that determined how much H_2 could be produced over time. H_2 emission generally commenced after each evacuation, albeit with decreasing rates and pressures that levelled out at between 1 and 2 mbar after 846 days. The copper surfaces stayed shiny and there were no brown rings at the gas/water interfaces (Figure 4-12).

4.4 N4 – O_2 treatment and repeated evacuations

4.4.1 Description of experiment

A series of 5 vials with two copper rods in each vial and 5 vials with only water was again prepared as described previously (Bengtsson et al. 2013). After the last evacuation in the gas bench, approximately 180 nmol of O_2 was allowed to enter all vials. The measurements were continued for 442 days. The gas environment in the vials was replaced with pure N_2 at days 178 and 274 and new stoppers were inserted at day 288 (Table 3-1).

4.4.2 Results

The addition of O_2 at day 0 to vials with copper rods was approximately 30 nmol mL^{-1} which corresponded to 180 nmol per vial. The concentration of O_2 was below detection after 15 days when all five vials with copper rods started to produce H_2. The emission of H_2 increased linearly for the first 65 days where after the H_2 pressure started to decrease in 4 of the vials (Figure 4-4). The N4 experiment, like the N1 and N2 experiments, again showed that the H_2 pressure started to increase when there was no detectable O_2 in the gas phase. H_2 emission commenced in 3 of the vials after each evacuation, albeit with decreasing rates and pressures that levelled out at approximately 1.5 mbar. There were 2 vials that stopped to give off H_2 after 211 days, N4:7 and N4:10. These two vials experienced leakage of air during between 40–60 days of pressure drop approaching atmospheric pressure and the copper surfaces were exposed to O_2, possibly during withdrawal of samples (confer 2.4.3) which seems to have stopped the H_2 emission process permanently during the time frame of the experiment. After O_2 was removed at day 281, H_2 production did not commence. Although the total pressure was recovered in vials N4:7 and N4:10 after 281 days, the vial N4:9 lost pressure and O_2 was detected in the vial concomitant with a reduced emission rate of H_2.

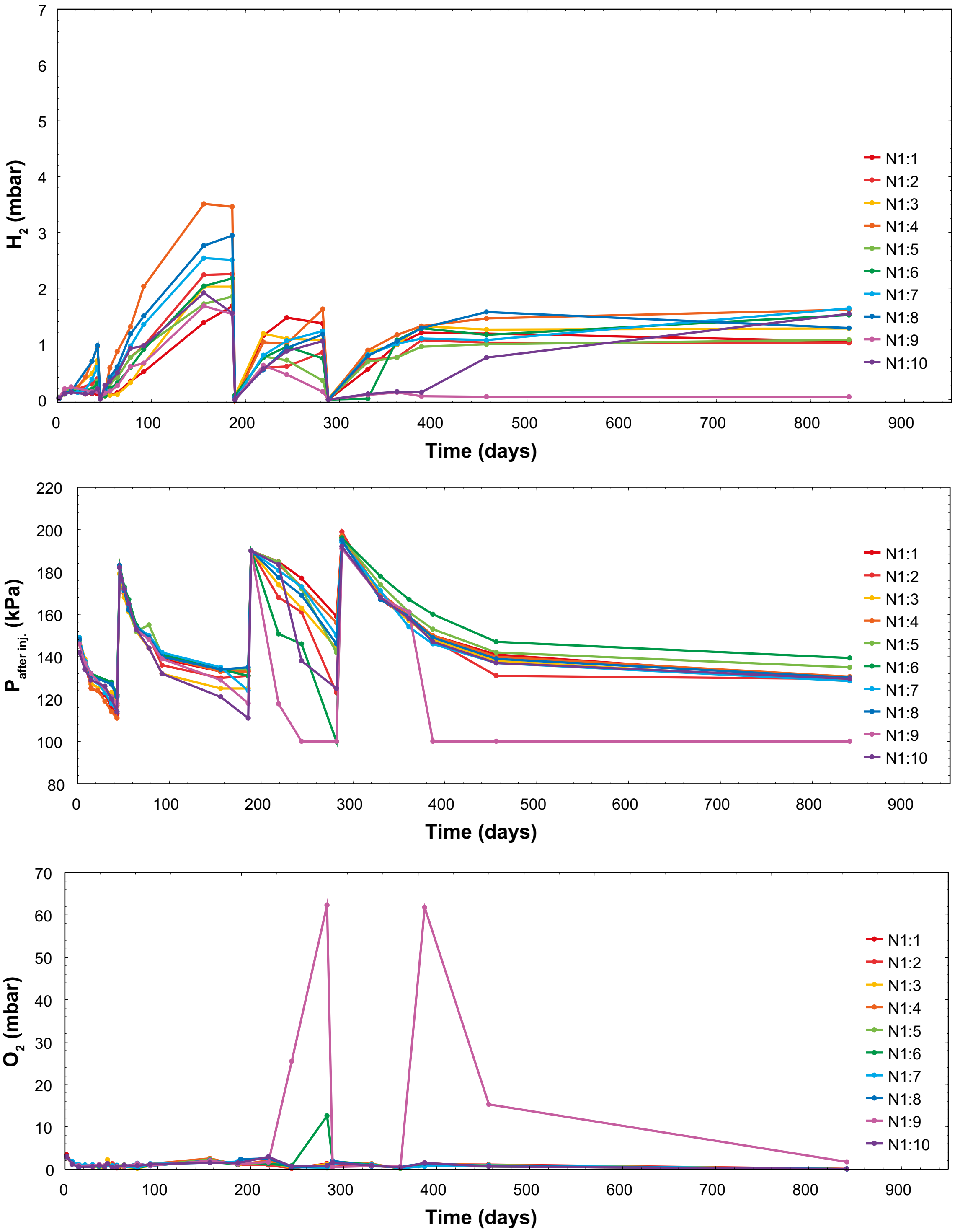

Figure 4-1. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the N1 experiment.*

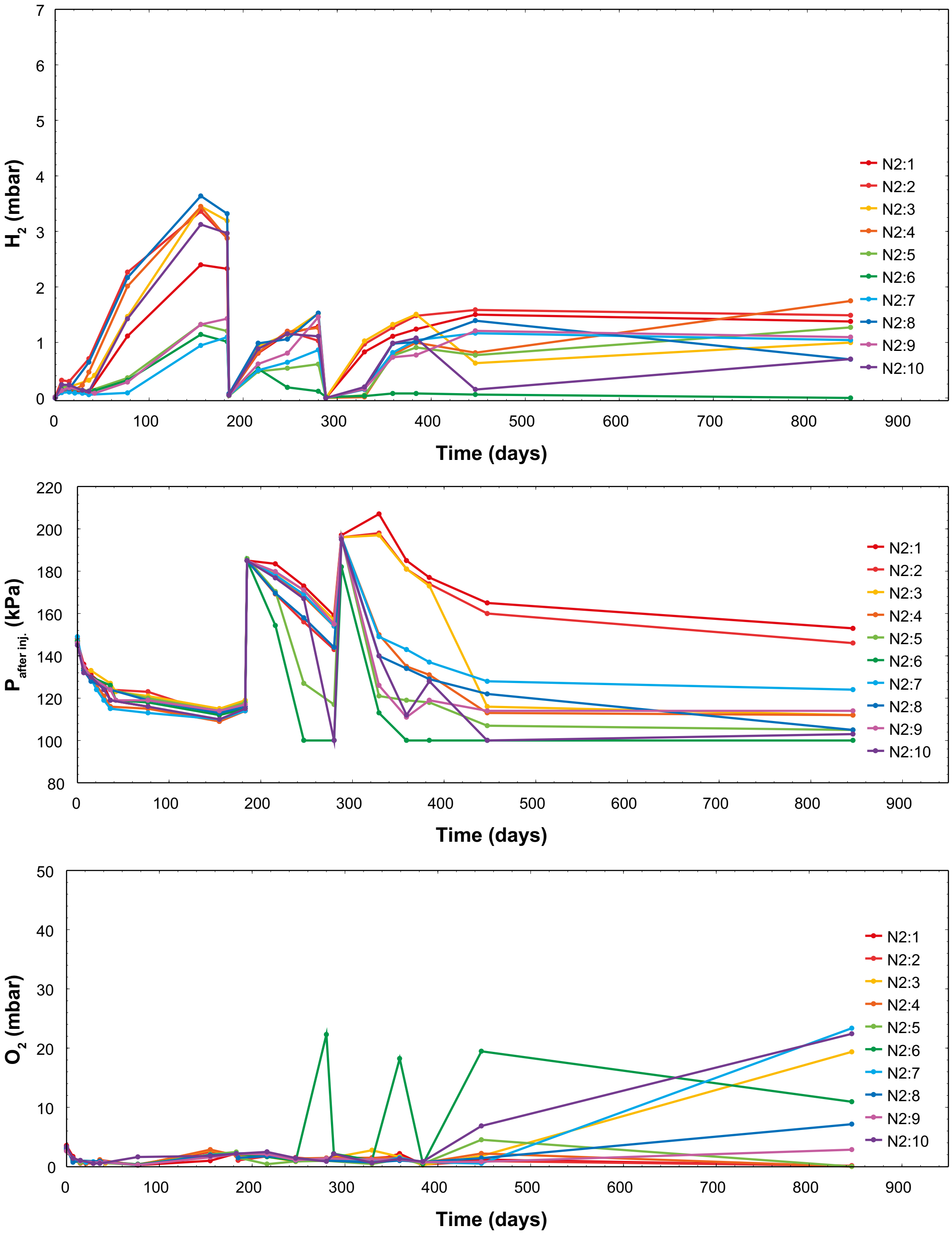

Figure 4-2. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the N2 experiment.*

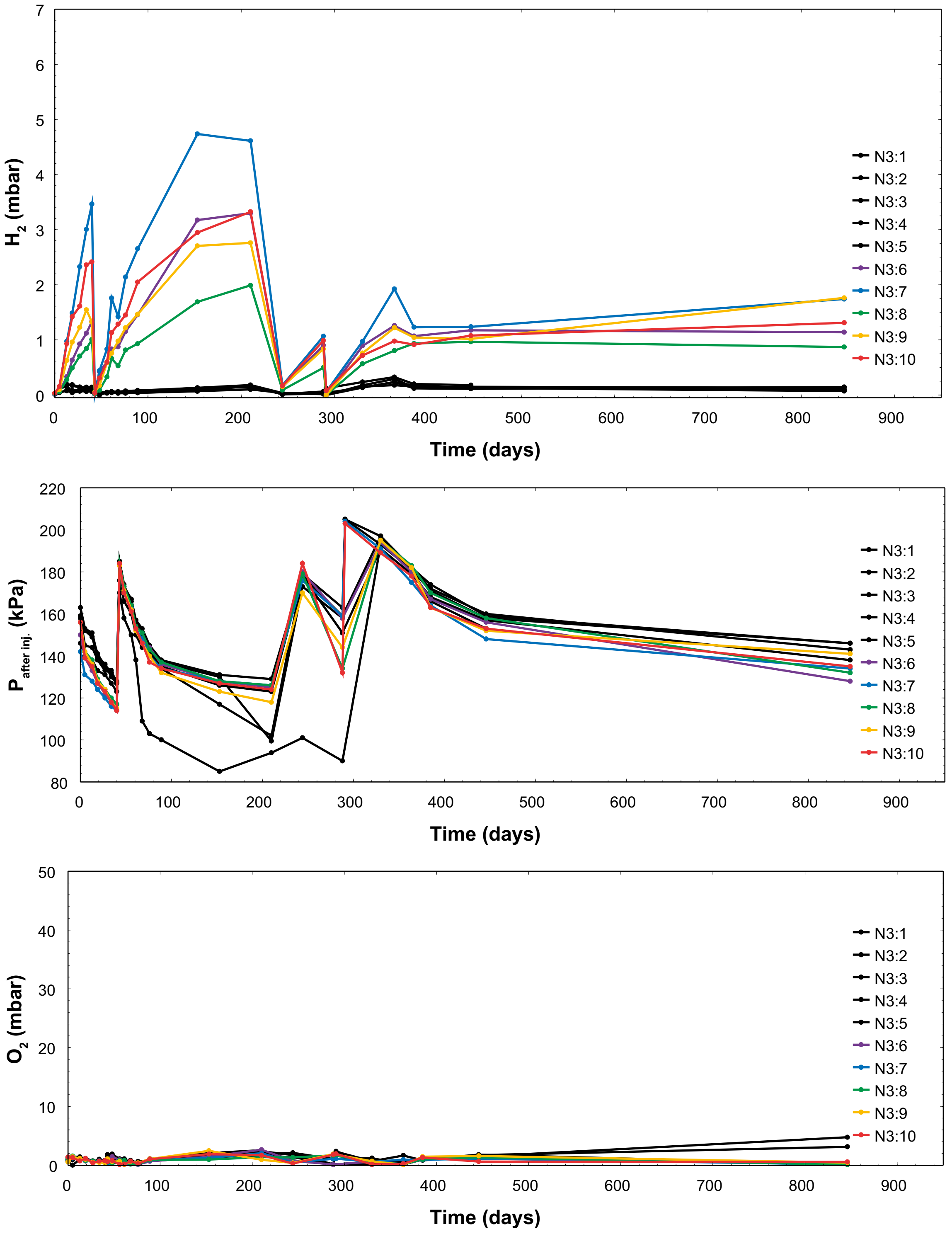

Figure 4-3. The total pressure P and the partial pressures of H_2 and O_2 in each vial of the N3 experiment. Black symbols and lines show control vials with water but without copper surfaces.

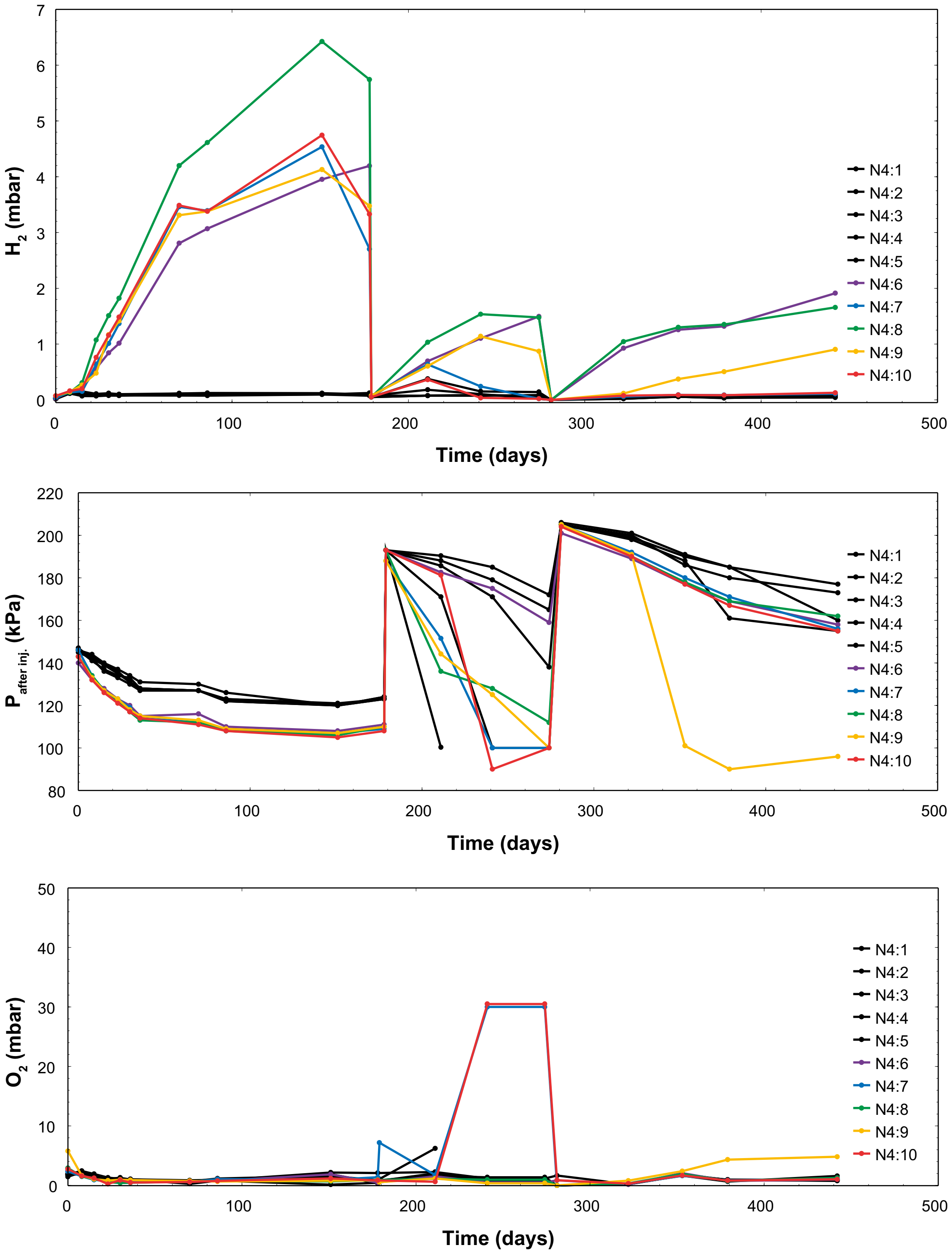

Figure 4-4. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the N4 experiment. Black symbols and lines show control vials with water but without copper surfaces.*

4.5 N5 – N_2 treatment and repeated evacuations, stoppers in contact with water

4.5.1 Description of experiment

A series of 10 vials with two copper rods in each vial was prepared as described previously (Bengtsson et al. 2013). Five of these vials were incubated upside down with water on the stoppers and five with the stoppers and gas phases up. Analyses were performed weekly until day 42. Then the gas in the vials was replaced with pure N_2, and all vials were left with the stopper upwards and measurements were performed for 374 days. The gas environment in the vials was again replaced with pure N_2 at days 233 and 280 and new stoppers were inserted at day 280 (Table 3-1). N5:1 was removed for copper analysis after 199 days, see Section 5.3.1.

4.5.2 Results

All vials emitted H_2, but vials with the stoppers in contact with water produced, on average, a little less H_2 than did vials without contact during the first 42 days as discussed elsewhere (Bengtsson et al. 2013). After the second exchange of gas environment, there were no difference in H_2 pressure between vials (except for N5:7) with stoppers initially positioned upwards or downwards. H_2 emission commenced after each evacuation, albeit with decreasing rates and pressures that levelled out at approximately 1.5 mbar.

One vial (N5:7) had a "stopper problem" that resulted in a faster pressure drop compared to all other vials. That vial behaved differently during the remaining time of the experiment despite change of gas environment and stoppers (Figure 4-5). The vial stopped to give of H_2 after 144 days. Possibly, the copper surfaces in N5:7 were exposed to O_2 during a period of pressure drop below atmospheric pressure which seems to have influenced the H_2 emission process permanently during the remaining time frame of the experiment. The last evacuation did remove all O_2 but H_2 emission did not begin again.

4.6 N6 – N_2 treatment, repeated evacuations and increased pressure

4.6.1 Description of experiment

A series of 10 vials with two copper rods in each vial was prepared as described previously (Bengtsson et al. 2013). Five of these vials were again incubated upside down and five with the stopper up as previously for N5. The start pressure of N_2 was increased from 150 kPa used in N1–N5, to >180 kPa in this and the following experiments in the N-series. Analyses were performed weekly until day 164. Then the gas in the vials was replaced with pure N_2, and all vials were left with the stopper upwards and measurements were performed until day 826. The gas environment in the vials was again replaced with pure N_2 and new stoppers at day 261 (Table 3-1).

4.6.2 Results

Having stoppers downwards was introduced to reduce problems with the pressure drops which was indeed effective because in this experiment there were pressure drops in several of the vials with stoppers up, while vials with stopper down did not have pressure drops larger than what was caused by sampling (Figure 4-6). Possibly, there was a problem with the stopper batch first used for this experiment. However, it cannot be excluded that the observed pressure drops were due to leakage during stopper penetration. The reasons behind the pressure drop in N6 are consequently not clear and it only occurred in large scale until new stoppers were introduced at days 261. As repeatedly found in the experiments N1–N5, pressure drops below atmospheric pressure introduced air in the vials and prolonged exposure to O_2 seems to permanently have shut down H_2 emission during the remaining experimental time (Figure 4-6). In experiment N6, H_2 emission stopped completely in the vials N6:3, N6:6, N6:8 and N6:9 after long periods of O_2 exposure. The copper surfaces in these four vials became darkened and a brown ring appeared on the glass wall at the gas/water interface (Figure 4-13). H_2 emission did not begin again in these vials during the remaining 559 days despite removal of all O_2 after day 267. Remaining vial partial H_2 pressures levelled out at approximately 1.5 mbar.

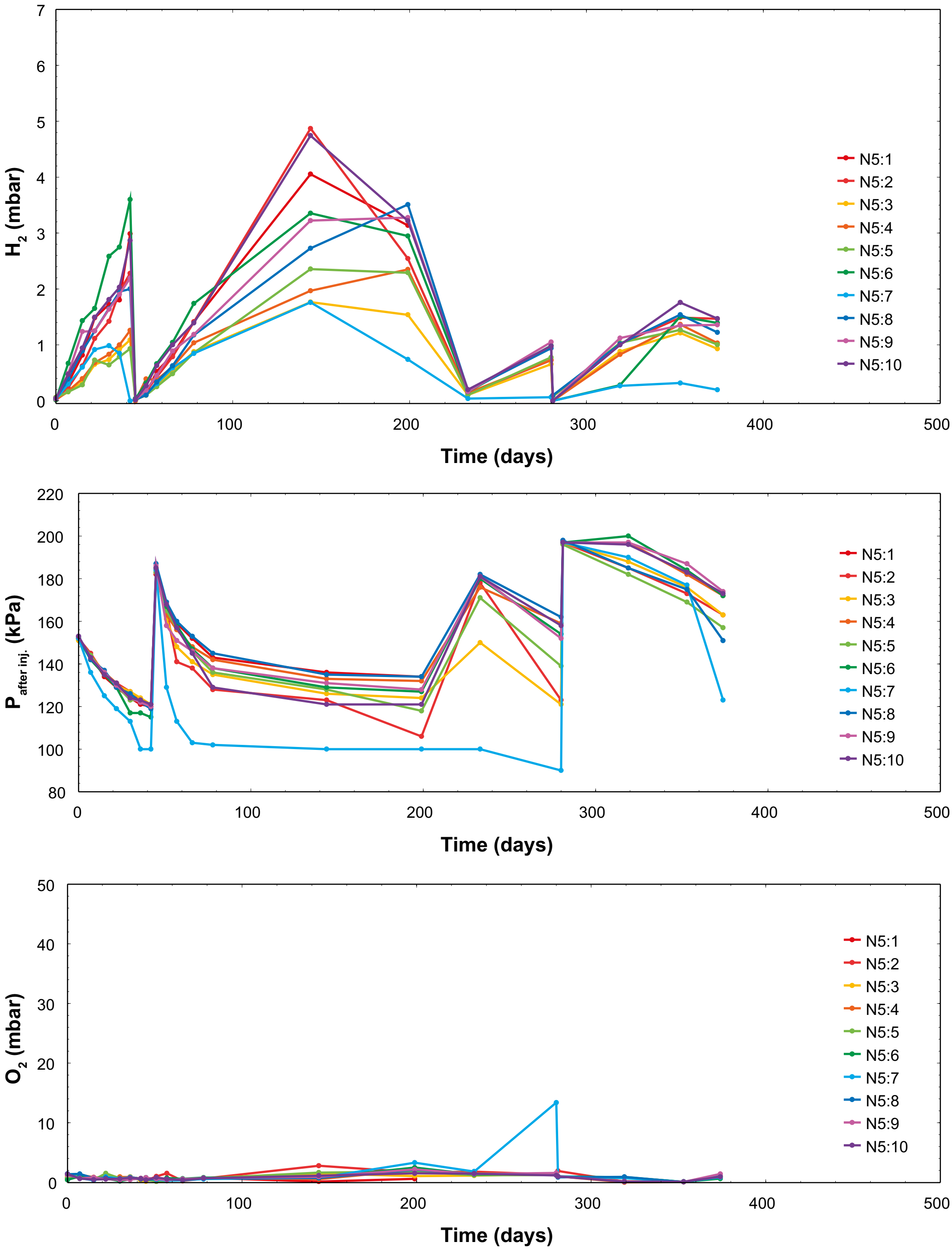

Figure 4-5. *The total pressure P and the partial pressures of* H_2 *and* O_2 *in each vial of the N5 experiment. Vials N5:1 to N5:5 were incubated with the stoppers down in contact with the vial water and vials N5:6 to N5:10 were incubated with stoppers up the first 42 days.*

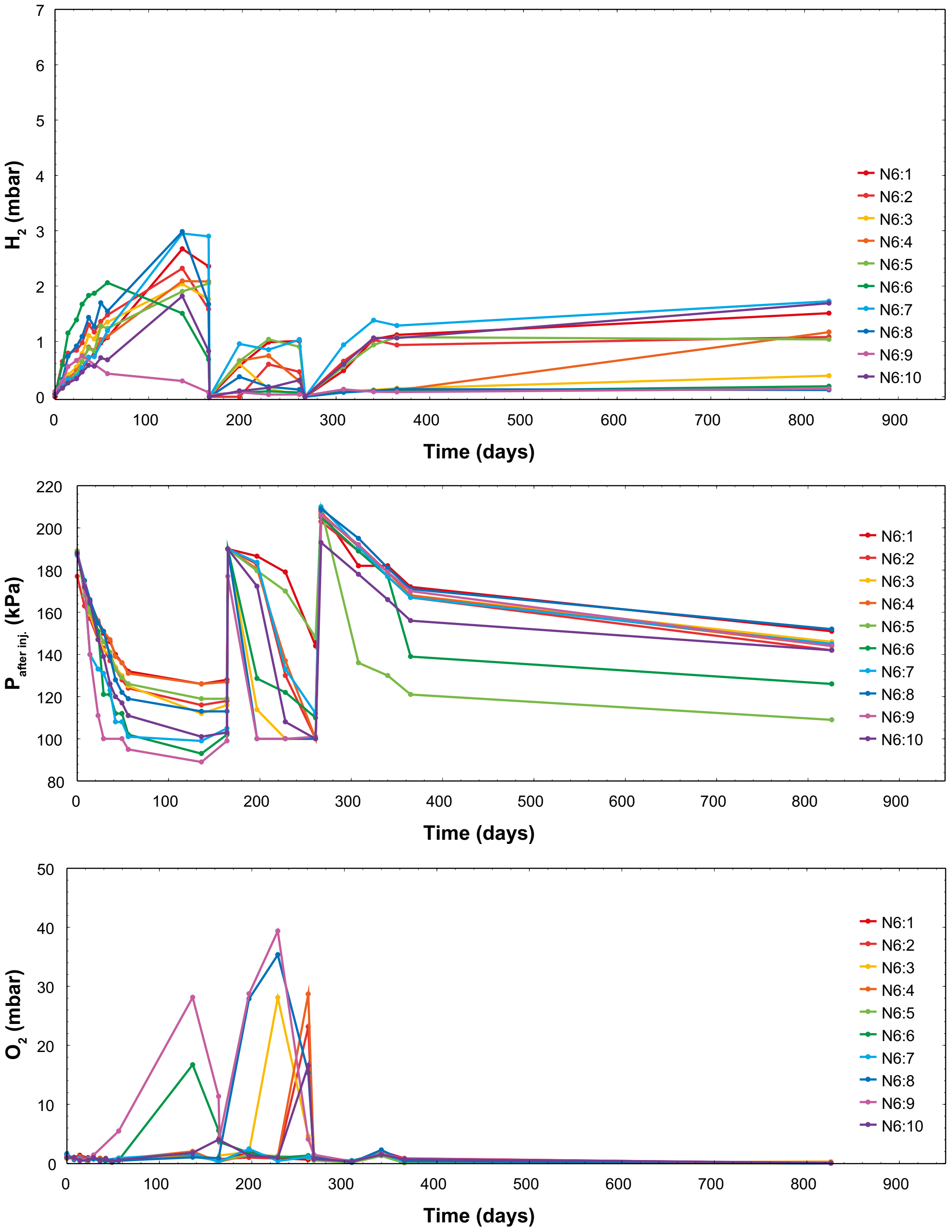

Figure 4-6. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the N6 experiment. Vials N6:1 to N6:5 were incubated with the stoppers down in contact with the vial water and vials N6:6 to N6:10 were incubated with stoppers up until day 164.*

4.7 N7 – N_2 treatment, and repeated evacuations and stoppers in contact with water

4.7.1 Description of experiment

Because we encountered problems with pressure drops in some vials in experiment N6, a new experiment was set up with the same conditions as in N6. Five of these vials were incubated upside down and five with the stopper up during the first 156 days. The start pressure of N_2 was 190 kPa. Analyses were performed weekly until day 357. pH was adjusted with NaOH to approximately 7.5±0.5 after 156 days and the old stoppers were replaced with new stoppers after 253 days. Evacuations were preformed days 156 and 253 and measurements were continued until day 820 (Table 3-1).

4.7.2 Results

This experiment reproduced the conditions in N6 and this time, there were three pressure drops that introduced air in vials N7:1, N7:6 and N7:8 (Figure 4-7). The copper surfaces in these three vials became darkened and a brown ring appeared on the glass wall at the gas/water interface (Figure 4-14). Again, H_2 emission stopped permanently for the remaining duration of the experiment, also after removal of O_2 at day 260. The glass of the N7:7 vial was cracked at day 156 and therefore lost. Remaining vial partial H_2 pressures levelled out at approximately 1 mbar except for N7:2 that approached 3 mbar.

4.8 N8 – Acid leach, repeated grinding and evacuations

4.8.1 Description of experiment

A series of 14 vials with two copper rods in each vial was prepared as described previously (Bengtsson et al. 2013) with the following change. Five control vials with only water was prepared as well. Seven of these vials were not passed through the acid leach steps, while seven of the vials were leached as done previously. First one rod was placed in each vial in the washing (with water after leaching) order in vial 1 to 7. Then the wash water was replaced and one more rod was placed in each vial in washing order in vial 7 to 1. This was done to even out any possible remaining effect from the acid step on pH and surface characteristics. N8:1–N8:7 rods were not acid leached, N8:8–N8:14 rods were acid leached. Analyses were performed weekly until day 151 when the gas was exchanged to pure N_2 and pH was adjusted to between 7 and 8 with NaOH in all vials. The vials were opened in the anaerobic chamber on day 252 and the copper rods in all vials were acid leached and placed back into the vials which were filled with water, added with new stoppers and filled with N_2. Thereafter measurements continued until day 383 when all surfaces were ground again before acid leach and transferred to new glass vials with new stoppers and filled with N_2. All but three surfaces where then analysed intermittently until day 806. At day 557, the copper rods in vials N8:7, N8:10 and N8:12 were ground again before acid leach and transferred to new glass vials with new stoppers and filled with N_2. The H_2 emission in these three vials was followed until day 806.

4.8.2 Results

This experiment basically failed for the first 252 days due to uncontrolled pressure drops in vials N8:1, N8:6, N8:11, N8:12 and N8:14 with concomitant air exposure of the copper rods. The reasons for these drops are not clear. The most likely cause for the observed pressure drops is leakage during stopper penetration. The experience from experiment N8 again demonstrated that when an experimental vial fails and becomes O_2 contaminated, H_2 emission stops permanently, even if the O_2 is removed. However, when these contaminated rods were ground again, H_2 emission commenced at pressures that levelled out at approximately 1 mbar (Figure 4-8). It should be noted that although grinding did induce H_2 emission from all ground surfaces again, also those that were exposed to O_2, the partial H_2 pressure did not reproduce the high partial H_2 pressures obtained after 100 days from the start of the N8 series.

The initial pressure drops were biased towards the non-acid leached copper rods. This may explain why the average partial pressure of H_2 was lower compared to the vials with acid leached copper rods. The two vials with highest partial pressures of H_2 had non-acid leached copper rods. This experiment, dealing with how surface treatments may influence H_2 emission, needed to be repeated flawless for proper conclusions. Because surface treatment with or without acid appeared to exert an effect on H_2 emission, a new experiment was started with pH adjustments, i.e. the experimental series N9. There was no visible staining of the copper surfaces as exemplified by the surfaces not re-ground after start (Figure 4-15).

4.9 N9 – pH adjustments

4.9.1 Description of experiment

A series of 15 vials with two copper rods in each vial was prepared as described previously (Bengtsson et al. 2013). pH was analysed and adjusted in three steps. In the first step, 30 µL 1 M NaOH was added to 2,000 mL anaerobic water to pH 7 and 5 vials (N9:1–N9:5) were filled with approximately 16 mL water (exact weight was registered for each vial). Thereafter, 45 µL 1 M NaOH was added to the remaining 1,920 mL water to pH 9–10 (N9:6–N9:10) and five more vials were filled. Finally, 7 mL of a 1 M HCl was added to the remaining 1,840 mL water to pH 2–3 (N9:11–N9:15) and five more vials were filled. Consequently, vials N9:11–N9:15 also contained 3.8 mM Cl^-. The start pressure of N_2 was 190 kPa. This experiment was denoted N9. Analyses of pH 7 vials were stopped at day 126. The remaining vials were evacuated and filled with N_2 at days 137 and 231. New stoppers were applied day 231 and measurements continued until day 788.

4.9.2 Results

The vials adjusted to pH 7 with a small amount of NaOH rapidly produced H_2 at the fastest rate of all experiments N1–N9. The H_2 emission in the five pH 7 vials was coherent with a standard deviation of $< 10\%$ after 21 days and 20% after 32 days. The average H_2 emission in the pH 9 treatment closely followed that of the pH 7 treatment but with a somewhat larger standard deviation. Lowering the pH to 2–3 resulted in a much slower average initial H_2 emission rate compared to pH 7 and 9–10. The O_2 content was below the detection limit and all but five vials had excellent pressure curves day 21. Thereafter, there were pressure drops in several vials and the most likely cause for the observed pressure drops is a leaking syringe used during stopper penetration day 21. The average partial pressures of H_2 was 4.5 mbar in pH 7, 2.7 mbar in pH 9–10 and 3.1 mbar in pH 2–3 after 101 days. Evacuation and filling with pure N_2 day 126 was not very successful with regard to the pressure. Five vials soon lost most pressure and became exposed to O_2. It was assumed that the stoppers were leaky and needed replacement. After this stopper replacement at day 231 all pressures were flawless and there was no O_2 contamination. The copper rods that were exposed to O_2 before this day (N9:6, N9:7 and N9:10), did not produce any H_2 for the remaining 557 days of the experimental time despite documented O_2-free conditions. The copper surfaces in these three vials became darkened and a brown ring appeared on the glass wall at the gas/water interface (Figure 4-16). Again, this experiment corroborated the conclusion from several of the N1–N8 experiments that prolonged exposure to O_2 with concomitant oxidation of the copper surfaces blocked the H_2 emitting process.

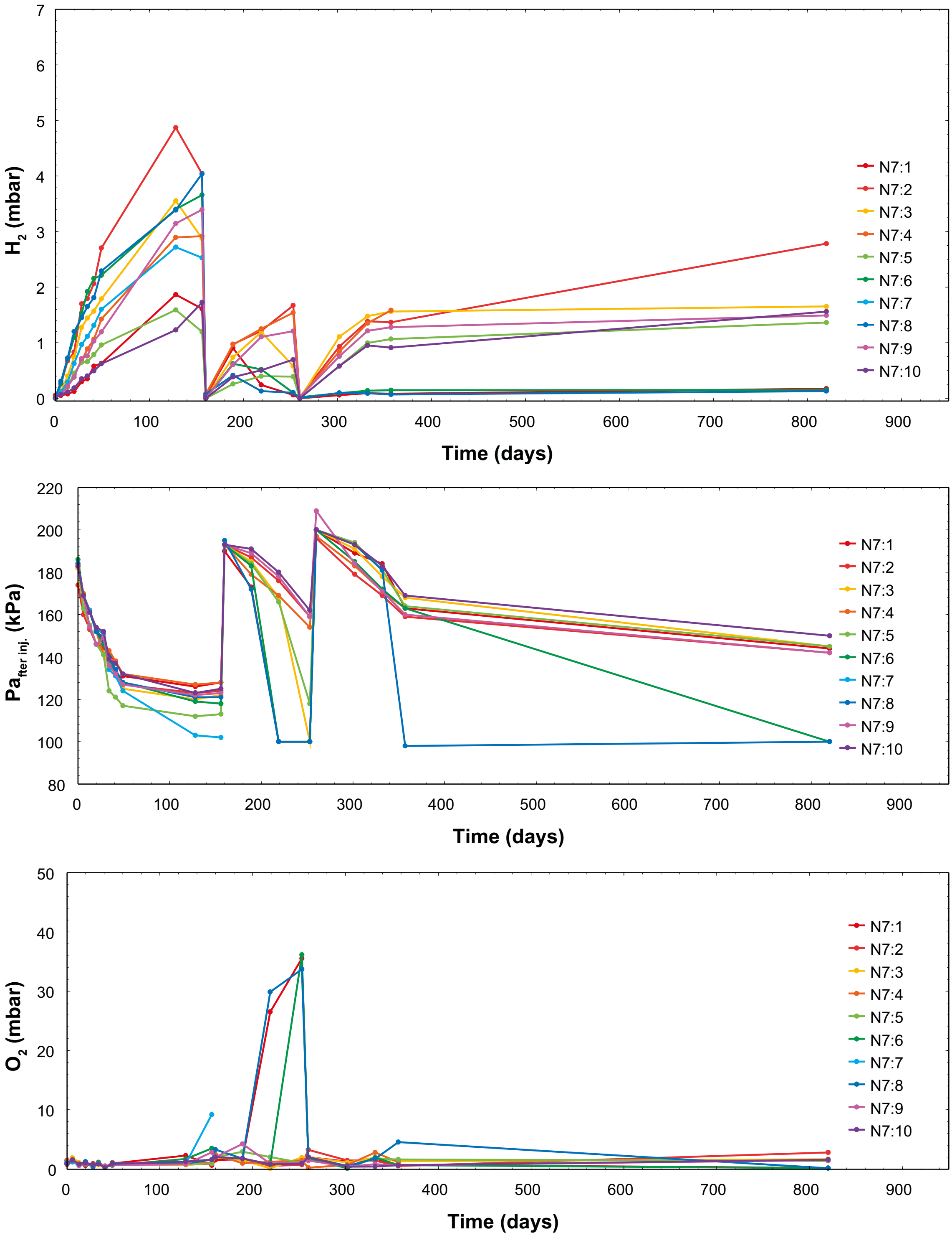

Figure 4-7. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the N7 experiment. Vials N7:1 to N7:5 were incubated with the stoppers down in contact with the vial water and vials N7:6 to N7:10 were incubated with stoppers up until day 156.*

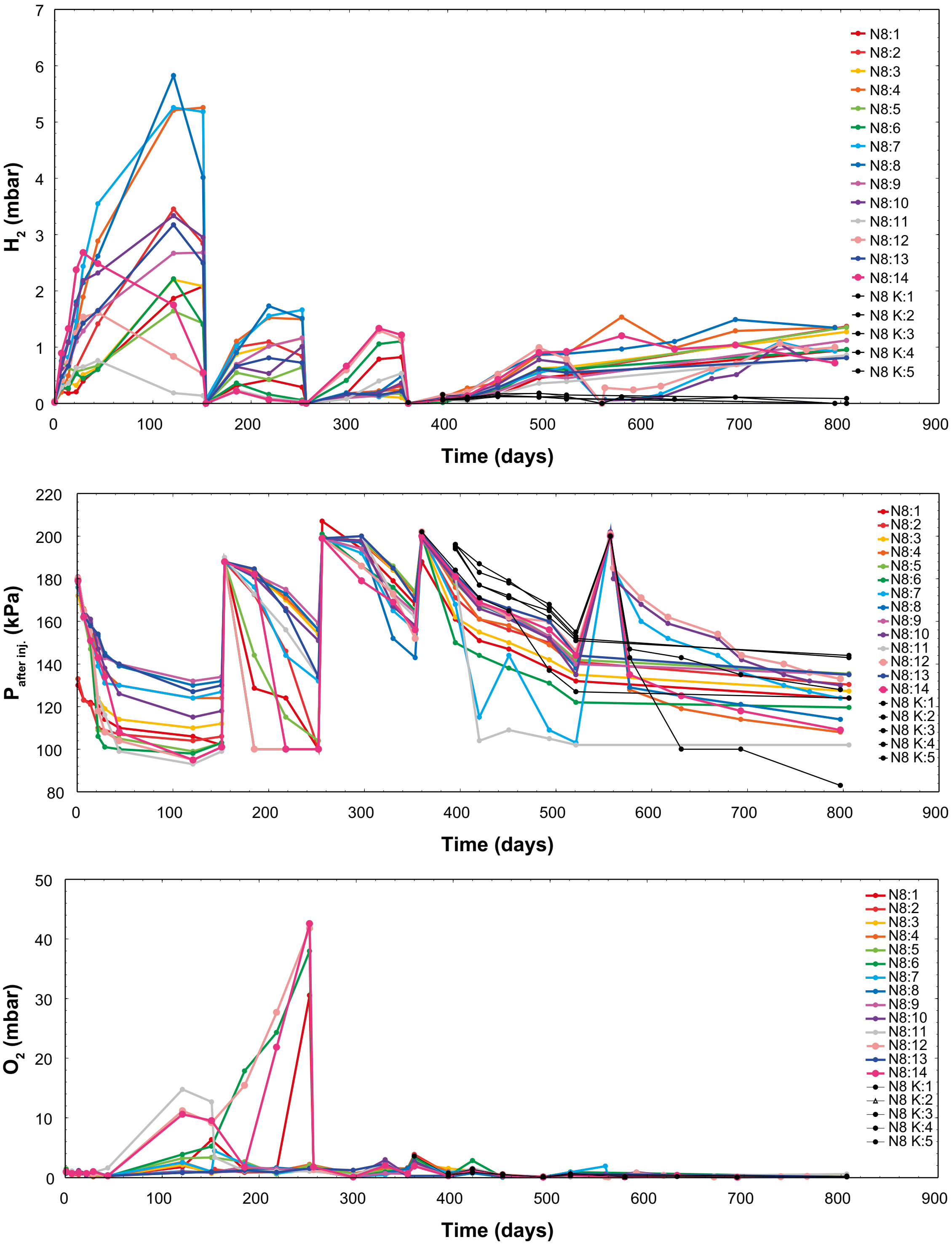

Figure 4-8. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the N8 experiment. See text for details.*

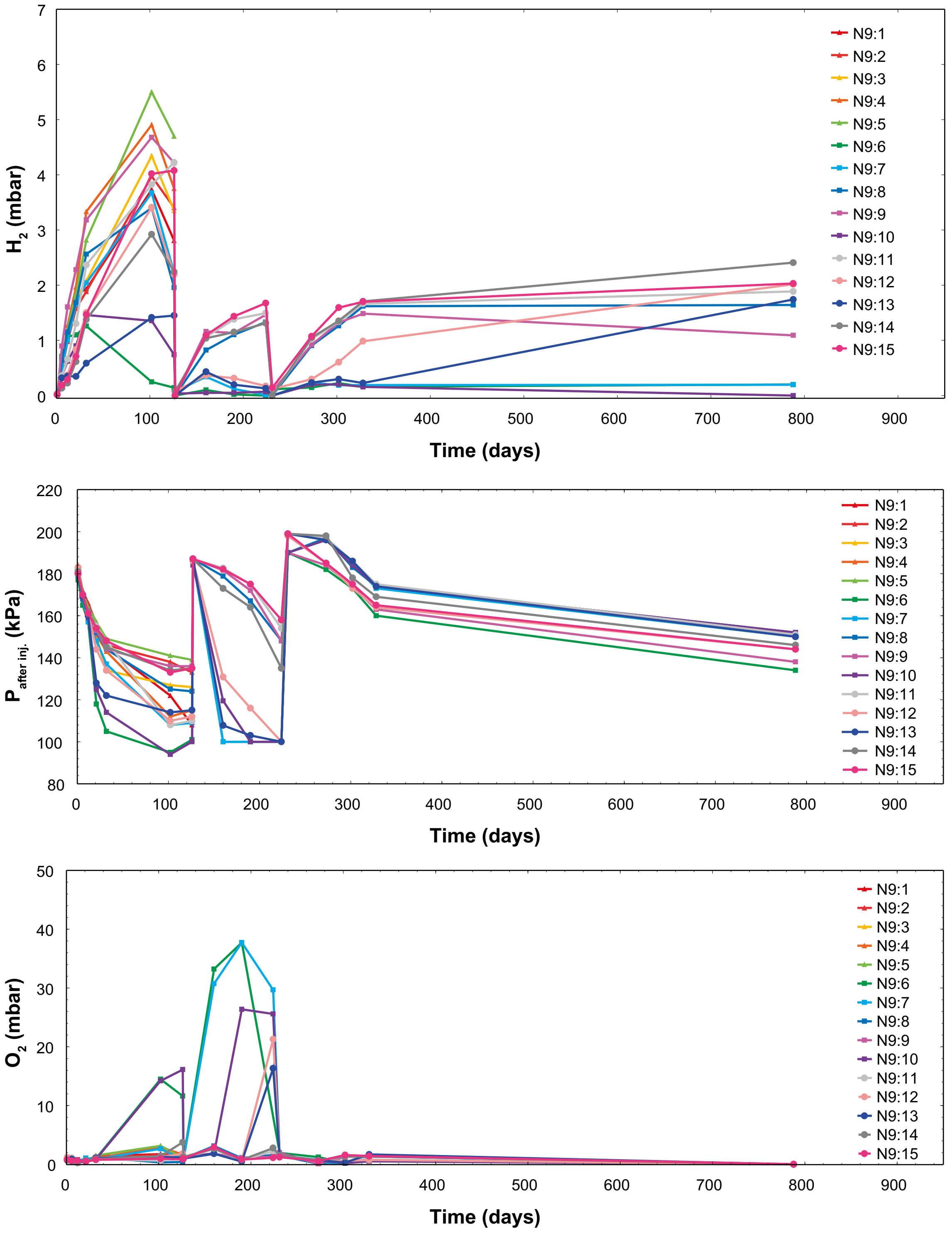

Figure 4-9. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the N9 experiment. See text for details. Symbols, ▲ N9:1–N9:5, pH 7; ■ N9:6–N9:10, pH 9–10; ● N9:11–N9:15, pH 2–3.*

Figure 4-10. Image of N1 vials after 841 days. N1:1 to N1:10 are shown from left to right.

Figure 4-11. Image of N2 vials after 846 days. N2:1 to N2:10 are shown from left to right.

Figure 4-12. *Image of N3 vials after 846 days. N3:6 to N3:10 with copper and water and N3:2 to N3:5 with water only are shown from left to right.*

Figure 4-13. *Image of N6 vials after 826 days. N6:1 to N6:10 are shown from left to right.*

Figure 4-14. *Image of N7 vials after 820 days. N7:1 to N7:10 (with exception for lost vials N7:4 and N:7) are shown from left to right.*

Figure 4-15. *Image of N8 vials after 806 days. Vials N8:1, 2, 3, 5, 8, 9, 11, 13 are shown from left to right plus two vials with water only.*

***Figure 4-16.** Image of N9 vials after 788 days. N9:6 to N9:15 are shown from left to right.*

4.10 NN sodium chloride

4.10.1 Description of experiment

Three experiments (NN1–NN3) consisting of five vials with two copper rods in each vial were prepared with water containing two different concentrations of sodium chloride and one control without sodium chloride. The NN-experiments were prepared as described previously (Bengtsson et al. 2013) except that a calculated amount of sodium chloride (reagent grade, Scharlau) was added to the sterilised and anoxic water before sample vials were filled with water. As controls, five vials with only water containing desired concentrations of sodium chloride were prepared at the same time. The vials NN1_6 and NN1_7 in the control experiments were removed from the experiment at the start and sent to the Department of chemistry at Uppsala University for their analysis as reported elsewhere. After 45 days, the concentrations were determined to 0.07 M and 0.2 M sodium chloride and the experiments was repeated with a higher concentration of NaCl prepared all over again. The vials were opened in the anaerobic chamber and the copper rods were acid leached again and placed back into the new vials. Then, the experiments were carried out as described previously (Bengtsson et al. 2013) except that this time, the sterilised anoxic water was prepared with the sodium chloride concentrations of 0.2 and 0.5 M.

4.10.2 Results

There were hydrogen emissions in all vials except for the control vials (Figure 4-17) also after the evacuation and change of water and sodium chloride concentrations. With exception for one control vial, there was no O_2 contamination in this experiment. The removal of two copper rod vials (NN1_6 and NN1_7) hampered the significance level for the statistical evaluation using the Student's t-test because it gave an unbalanced data set. Still, there was a significant difference ($p<0.05$) compared to the control vials, with the largest H_2 emission from vials with 0.2 M sodium chloride (Table 4-1). There was also a significant difference ($p<0.05$) between the 0.07 and 0.2 M vials, again with the largest H_2 emission from vials with 0.2 M sodium chloride. Although the graphs suggest that these differences were repeated after evacuation, and the means clearly differ in (Table 4-2), the differences were not significant in the second t-test from day 105 and onwards due to the large standard deviations observed for each sodium chloride treatment (in particular the 0.5 M vials) and due to the unbalance in the data set. Despite these uncertainties, it seems possible that H_2 emission correlate positively with increasing sodium chloride concentrations.

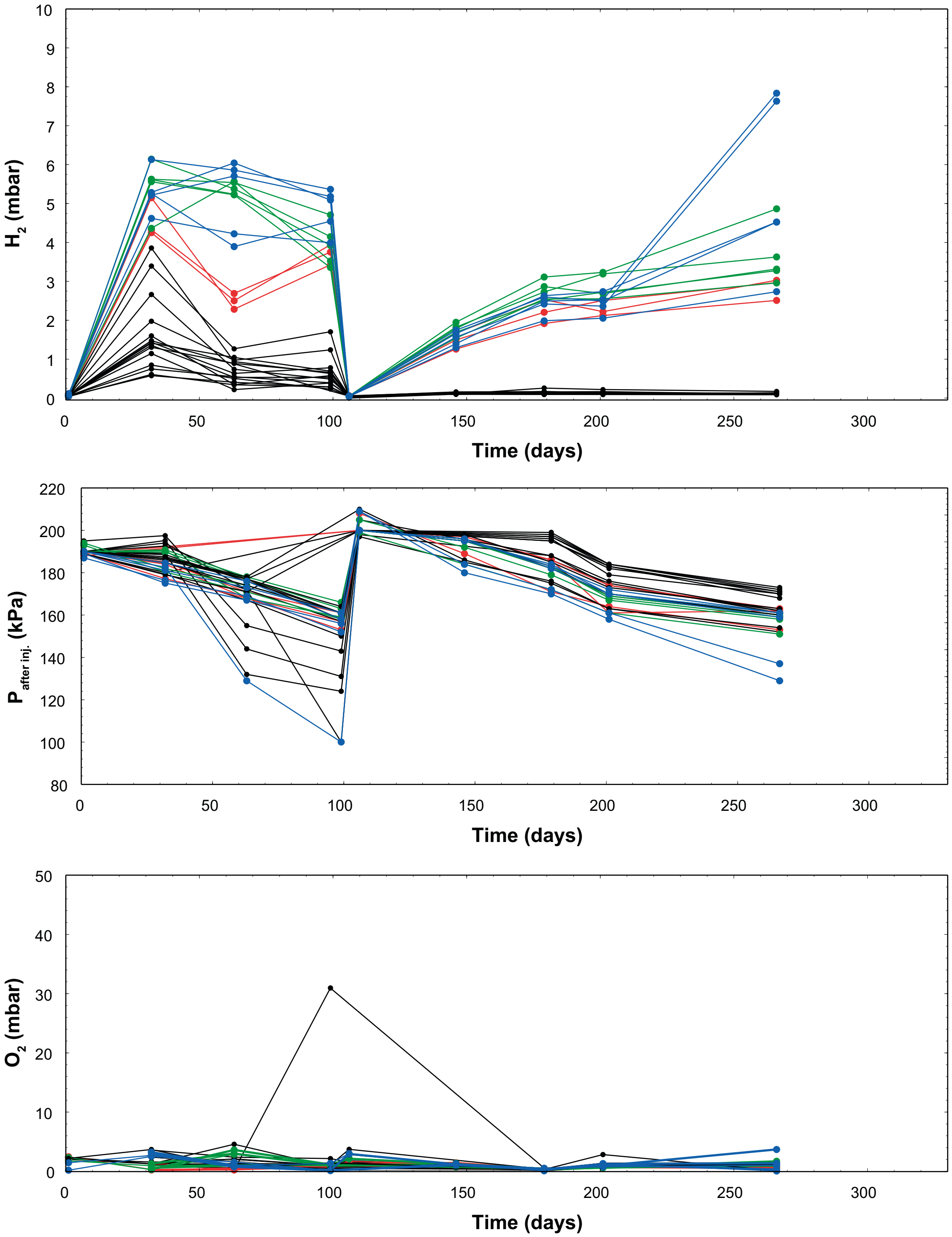

Figure 4-17. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the NN sodium chloride experiment. Symbols: black, vials with water and sodium chloride only; red, vials with 0 M sodium chloride; green, vials with 0.1/0.2 M sodium chloride; blue vials with 0.2 (days 0–105) or 0.5 M (days 106–266) sodium chloride.*

Table 4-1. Student's t-test for independent samples by variables. The variables were over sodium chloride concentrations 0, 0.07 and 0.2. The means of H_2 partial pressures (mbar) in the vials at day 99, before evacuation, are shown.

Treatment A–B	Mean A	Std. Dev. A	Mean B	Std. Dev. B	t-value	df	p	F-ratio Variances	p Variances
0–0.07	3.706	0.260	3.934	0.536	–0.672	6	0.5263	4.2572	0.3983
0–0.2	3.706	0.260	4.836	0.560	–3.212	6	0.0183	4.6532	0.3693
0.07–0.2	3.934	0.536	4.836	0.560	–2.602	8	0.0315	1.0930	0.9334

Table 4-2. Student's t-test for independent samples by variables. The variables were over sodium chloride concentrations 0, 0.2 and 0.5. The means of H_2 partial pressures (mbar) in the vials at day 266, are shown.

Treatment A–B	Mean A	Std. Dev. A	Mean B	Std. Dev. B	t-value	df	p	F-ratio Variances	p Variances
0–0.2	2.836	0.284	3.608	0.739	–1.690	6	0.1418	6.79106	0.264903
0–0.5	2.836	0.284	5.450	2.210	–1.975	6	0.0956	60.68249	0.032556
0.2–0.5	3.608	0.739	5.450	2.210	–1.767	8	0.1152	8.9356	0.056702

4.11 NpH

4.11.1 Description of experiment

Two series (NpH 2–3 and NpH 9–10) consisting of five vials with two copper rods in each vial was prepared with citrate buffer (0.01 M) and carbonate buffer (0.01 M). Before the pH experiment was started, buffers were prepared at given pH values and stored over night at 70°C to confirm that the buffer solutions were stable under the given experimental conditions. Buffer solutions with pH 3 and pH 10 dropped 0.1–0.2 and 0.9–1.3 pH-units, respectively. The NpH-experiments were prepared as described previously (Bengtsson et al. 2013) except that instead of water, sterilised, anoxic buffers solutions were prepared as described below before addition to vials.

Citrate buffer (0.01 M) was prepared from stock solutions of 1.05 g citric acid ($C_6H_8O_7 \times H_2O$) and 1.47 g sodium citrate ($C_6H_5O_7Na_3 \times 2H_2O$), each added to 500 mL analytical grade water (AGW). A volume of 90 mL sodium citrate (0.01 M) was added to a 500 mL volumetric flask and then diluted with citric acid (0.01 M) to the final volume of 500 mL before sterilised according to the method protocol (Bengtsson et al. 2013).

Carbonate buffer (0.01 M) was prepared from stock solutions of 0.53 g sodium carbonate (Na_2CO_3) and 0.42 g sodium bicarbonate ($NaHCO_3$) each added to 500 ml AGW. A volume of 250 mL sodium carbonate (0.01 M) was added to a 500 mL volumetric flask and dilute with the sodium bicarbonate (0.01 M) to the final volume of 500 mL before sterilised according to the method protocol (Bengtsson et al. 2013).

All chemicals used were of analytical grade. As controls, five vials with buffer solution only, no copper, were prepared at the same time to each experiment.

4.11.2 Results

There were hydrogen emissions in all vials except for the control vials (Figure 4-18). There was an unexplained drop in the H_2 partial pressures for pH 9–10 at day 70 that had recovered at next analysis occasion. There were no O_2 contaminations or leakages in pressure in this experiment. Therefore, a likely explanation is an occasional problem with the analysis on the GC, e.g. a leaky syringe or septum. There was a significant difference ($p<0.05$) between pH 2–3 that showed the largest H_2 emissions compared to the emissions from the pH 9–10 vials that averaged at a 1.65 mbar lower partial pressure (Table 4-3). Lowering the pH consequently initially increased the rate of the H_2 emitting process.

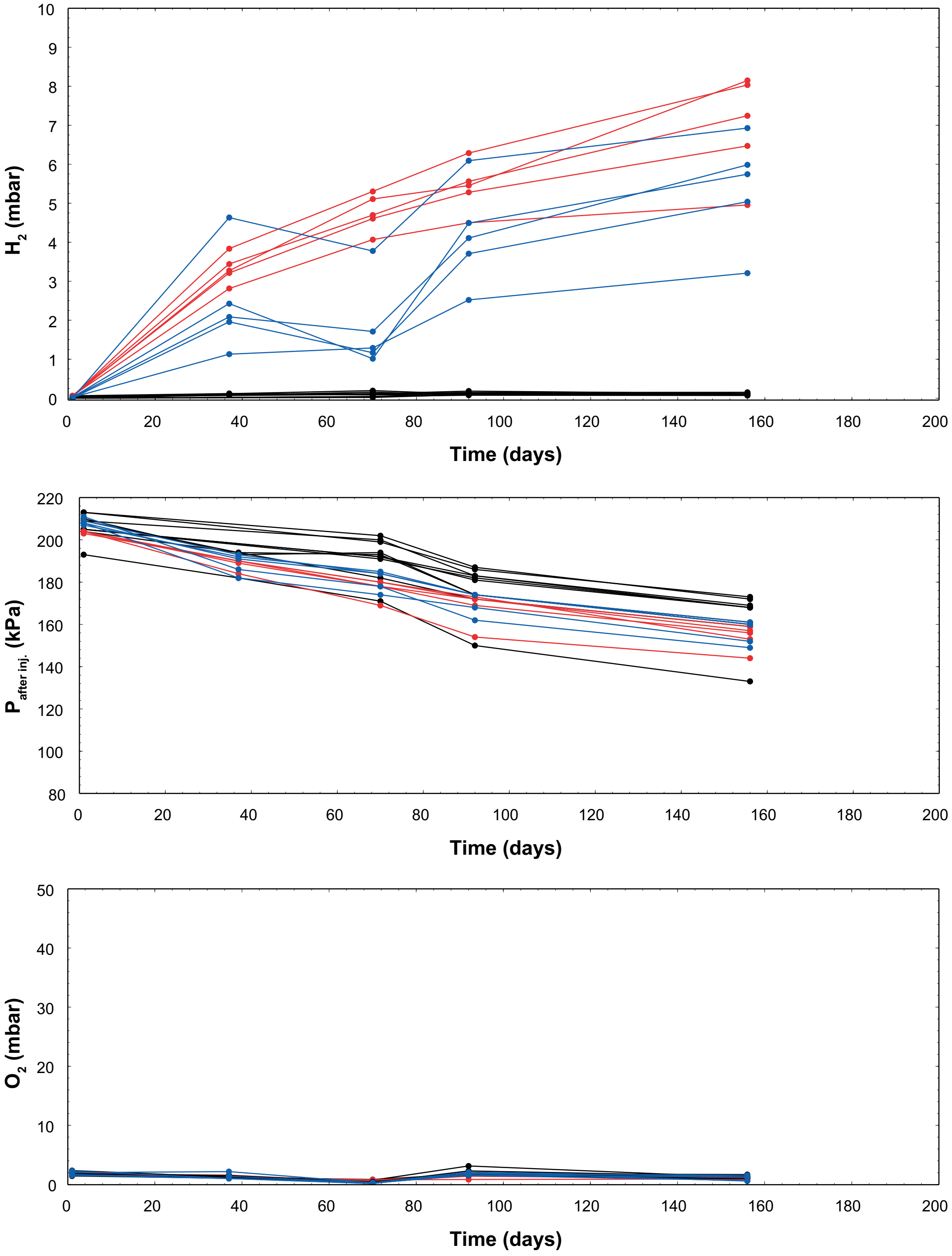

Figure 4-18. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the NpH experiment. Symbols: black, vials with buffer solution only; red, vials with pH 2–3; blue vials with pH 9–10.*

Table 4-3. Student's pair-wise t-test for independent samples by variables. The variable was pH treatment as outlined in the text. The means of H_2 partial pressures (mbar) in the vials at day 156 are shown.

Mean pH 2–3	Std. Dev. pH 2–3	Mean pH 9–10	Std. Dev. pH 9–10	t-value	df	p	F-ratio Variances	p Variances
6.97	1.31	5.381	1.390	–1.859	8	0.100017	1.1214	0.9142

4.12 NCD

4.12.1 Description of experiment

In the first copper-dry experiment, three experiments (NCD2–NCD4) consisting of five vials with two copper rods but without water were prepared in different ways for each experiment as follows:

Treatment 1: Raw copper as received, i.e. the copper surface was not ground or acid leached (NCD2)

Treatment 2: Ground copper surface but not acid leached (NCD3)

Treatment 3: Ground copper surface and acid leached (NCD4) according to Micans method (Bengtsson et al. 2013).

As controls, five vials containing only nitrogen were prepared (NCD1). After different treatments, according to Micans method, samples were prepared as described previously (Bengtsson et al. 2013). It was decided after 112 days to do a second copper-dry experiment with the experiments NCD3 and NCD4, due to the suspicion of moisture in the samples with copper, not visible for the eye during sample preparation. Before preparation of the second experiment, the copper rods from the first experiment were placed in an ultrasonic bath and subsequently acid leached for two days to remove impurities on the surfaces, such as copper oxides. These samples were then prepared with subsequent treatments according to Micans method (Bengtsson et al. 2013), except that the NCD3 was prepared dry, without water and NCD4 was prepared with 0.5 mL sterilised and anoxic water. As controls, five new vials containing only nitrogen were prepared (NCD1).

4.12.2 Results

Hydrogen was emitted from all surfaces despite the absence of a water phase in the vials (Figure 4-19). There was also a significant difference ($p<0.05$) in the partial pressure of H_2 between the vials with non-treated copper surfaces compared to the ground copper surfaces (Table 4-4). The ground and acid leached vials were not significantly different on the $p>0.05$ level due to a large standard deviation (SD) of the acid leached surfaces. The treatments 2 and 3 were continued for 265 days after evacuation at day 112. There were no significant differences between these two treatments in any of the two time series (Table 4-4 and Table 4-5). There was no O_2 contamination in this experiment, possibly with one exception. The levels of dry conditions in the vials are not known exactly. Although there was no visible humidity on the glass walls and on the copper rods, the presence of very small amounts of water on the rods cannot be conclusively ruled out. Grinding consequently increased the initial rate of the H_2 emitting process compared to surfaces not ground. It is important to understand that the gas volume in this experiment was approximately 5 times larger compared to experiments with water. Consequently, the mean values of H_2 partial pressures in Table 4-4 and Table 4-5 were diluted 5 times compared to what the corresponding partial pressures would be in vials with water, assuming similar emission rates. That would correspond to almost 10 mbar in a vial with water which is more than observed in any other experiments. The addition of 0.5 mL water did not influence the H_2 emission in the second experiment.

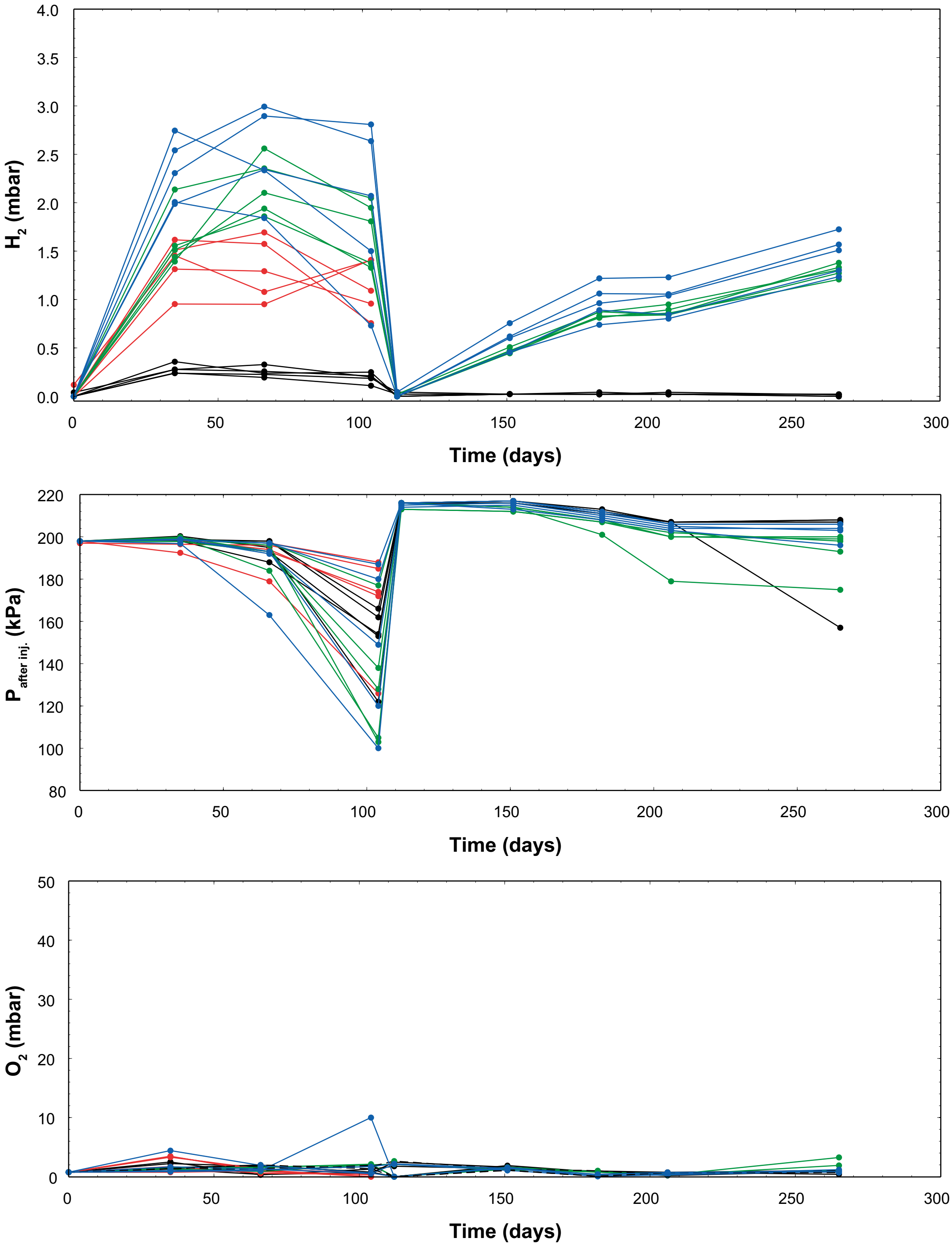

Figure 4-19. *NCD. The total pressure P and the partial pressures of H_2 and O_2 in each vial of the NCD experiment. Symbols: red, vials raw copper surfaces, denoted treatment 1; green, vials with ground but not acid leached copper surfaces denoted treatment 2; blue, vials with ground and acid leached surfaces, denoted treatment 3; black, control vials with N_2. Blue vials were added with 0.5 mL water after evacuation, see text for more details.*

Table 4-4. Student's pair-wise t-test for independent samples by variables. The variable is copper treatments as outlined in the text. The means of H_2 partial pressures (mbar) in the vials at day 104, before evacuation, are shown.

Treatment A–B	Mean A	Std. Dev. A	Mean B	Std. Dev. B	t-value	df	p	F-ratio Variances	P Variances
1–2	1.124	0.285	1.701	0.330	–2.957	8	0.01824	1.34019	0.78349
1–3	1.124	0.285	1.949	0.853	–2.050	8	0.07446	8.93670	0.05669
2–3	1.701	0.330	1.949	0.853	–0.605	8	0.56172	6.668260	0.09317

Table 4-5. Student's pair-wise t-test for independent samples by variables. The variable is copper treatments as outlined in the text. The means of H_2 partial pressures (mbar) in the vials at day 265, are shown.

Treatment	Mean 2	Std. Dev. 2	Mean 3	Std. Dev. 3	t-value	df	p	F-ratio Variances	P Variances
2–3	1.300	0.0646	1.467	0.201	–1.777	8	0.11339	9.629	0.04979

4.13 NCS

4.13.1 Description of experiment

Two series consisting of five vials each were prepared in the copper-surface experiment as described previously (Bengtsson et al. 2013) except that the surface ratio were 1 to 4. The series were:

NCS1: One copper rod, with dimension (50×10×2) mm and no angle.

NCS2: Two copper rods with the dimensions (100×10×2) mm and 15 degree angles.

After 100 days, the samples were opened in an anaerobic chamber. The copper rods were etched with acid and placed back into the new vials before sealed with new (newly bought) butyl rubber stoppers.

4.13.2 Results

Hydrogen was emitted from all surfaces (Figure 4-20). In the beginning of the experiment a very large dispersion of H_2 partial pressure values was observed which made a statistical evaluation blunt. This dispersion was likely due to an equally large dispersion in the total pressures. After evacuation, the treatments showed more coherent results. There was no O_2 contamination at any time in this experiment. At day 255, there were a 3.37 times higher average partial pressure of H_2 in the vials with the larger surface area (Table 4-6). This difference was highly significant at p=0.00009. Both the surface area and the mass of copper were approximately 4 times larger in the vials with rods of the size used in all of the experiments described above compared to the vials with smaller rods. The 4 times larger copper surface agrees well with the 3.37 times higher partial pressure of H_2. The initial H_2 emitting process consequently was dependent on the surface area and the mass of copper but the experiment cannot resolve the effect from each of these two variables.

Table 4-6. Student's pair-wise t-test for independent samples by variables. The variable is copper surface area as outlined in the text. The means of H_2 partial pressures (mbar) in the vials at day 255 are shown.

Mean 12.4 cm^2	Std. Dev. 12.4 cm^2	Mean 48.8 cm^2	Std. Dev. 48.8 cm^2	t-value	df	p	F-ratio Variances	p Variances
0.879	0.193	2.97	0.618	–7.196	8	0.00009	10.254	0.04456

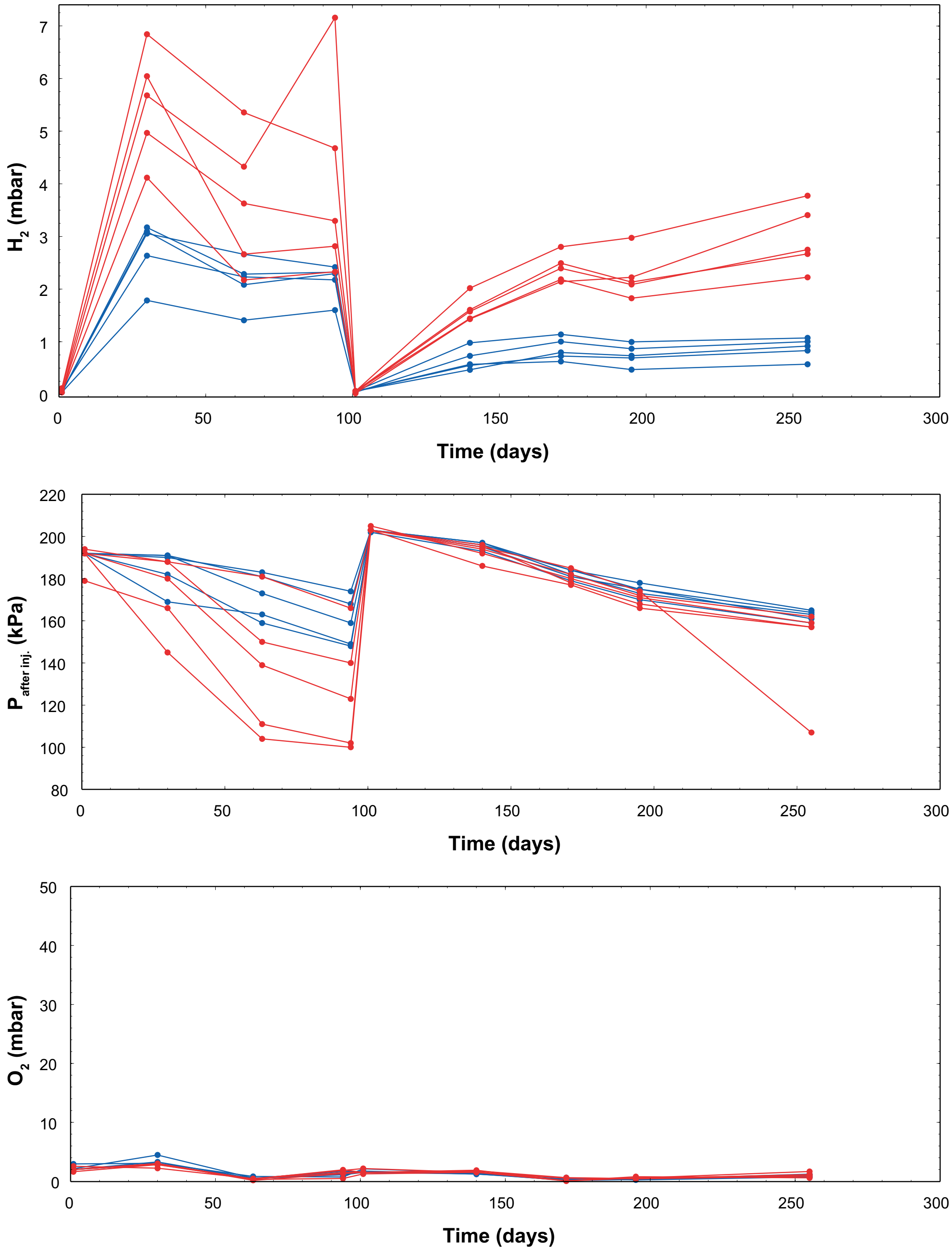

Figure 4-20. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the NCS experiment. Symbols: red, vials with two copper surfaces with dimensions as in all other N-experiments (100×10×2 mm); blue, vials with one copper surface with dimension 50×10×2 mm.*

4.14 99.95% Cu OFP, (SKB-canister Cu), experiments A, B, J, L and M

4.14.1 Description of experiments

Five different, new experiments were completed with canister copper (99.95% Cu-OFP, SKB). Each of the five experiments consisted of two vials, except experiment A that comprised four vials, with two copper rods in each vial. They were prepared in different ways as follows:

- **Experiment A**: The copper surfaces were ground and acid leached according to Micans method (Bengtsson et al. 2013) before anoxic heat treatment at 400°C in Uppsala. For Uppsala method details, see Boman et al. (2014).
- **Experiment AC**: The copper surfaces were ground and acid leached according to Micans method (Bengtsson et al. 2013).
- **Experiment B**: Raw copper rods, i.e. copper as received from the machine work shop was treated in an anoxic atmosphere according to the Uppsala method that includes electropolishing followed by reduction in H_2 and heat treatment at 400°C. For Uppsala method details, see Boman et al. (2014).
- **Experiment J**: This experiment was a repetition of experiment B, except that the copper was from a different canister lid. The new copper rods were cut out from a copper canister lid (TX183) that had been heat treated at 400°C. For description of preparation details, see experiment B.
- **Experiment L**: The copper surfaces (copper rods from the lid TX183) were ground and acid leached according to Micans method (Bengtsson et al. 2013).
- **Experiment M**: Raw copper rods, i.e. copper as received from the machine work shop (copper rods from the lid TX183) were anoxic heat treated at 400°C in Uppsala. For the Uppsala method details, see Boman et al. (2014).

After the sample preparations described above, the copper rods were placed into vials in an anaerobic chamber and sealed with new butyl rubber stoppers. Sample vials were filled with sterilised and anoxic water and were completed with subsequent treatments, according to Micans method (Bengtsson et al. 2013). Ten vials (5+5) containing water and nitrogen, respectively were prepared as controls to experiment B. Six vials (3+3) containing water and nitrogen, respectively, were prepared as controls to experiments J, L and M.

The samples B:1 and M:2 were re-started after 244 and 142 days, respectively, by opening the vials in an anaerobic chamber. The copper rods were placed back into the new vials and sealed with new butyl rubber stoppers before subsequent treatments as described previously. Six vials (3+3) containing water and nitrogen, respectively were used as controls to re-started samples.

4.14.2 Results

The results are presented in Figure 4-21. There was no O_2-contamination or uncontrolled pressure drops in the vials. The copper rods that were not heat treated, rods L and AC, emitted H_2 in the same range as previously observed, while the heat treated rods, A and M did not. There was a small H_2 emission from one of the electro-polished rods, B:1, but not from the heat treated electro-polished rods, J. Likewise, no H_2 emission could be observed after evacuation of the vials B:1 and M:2.

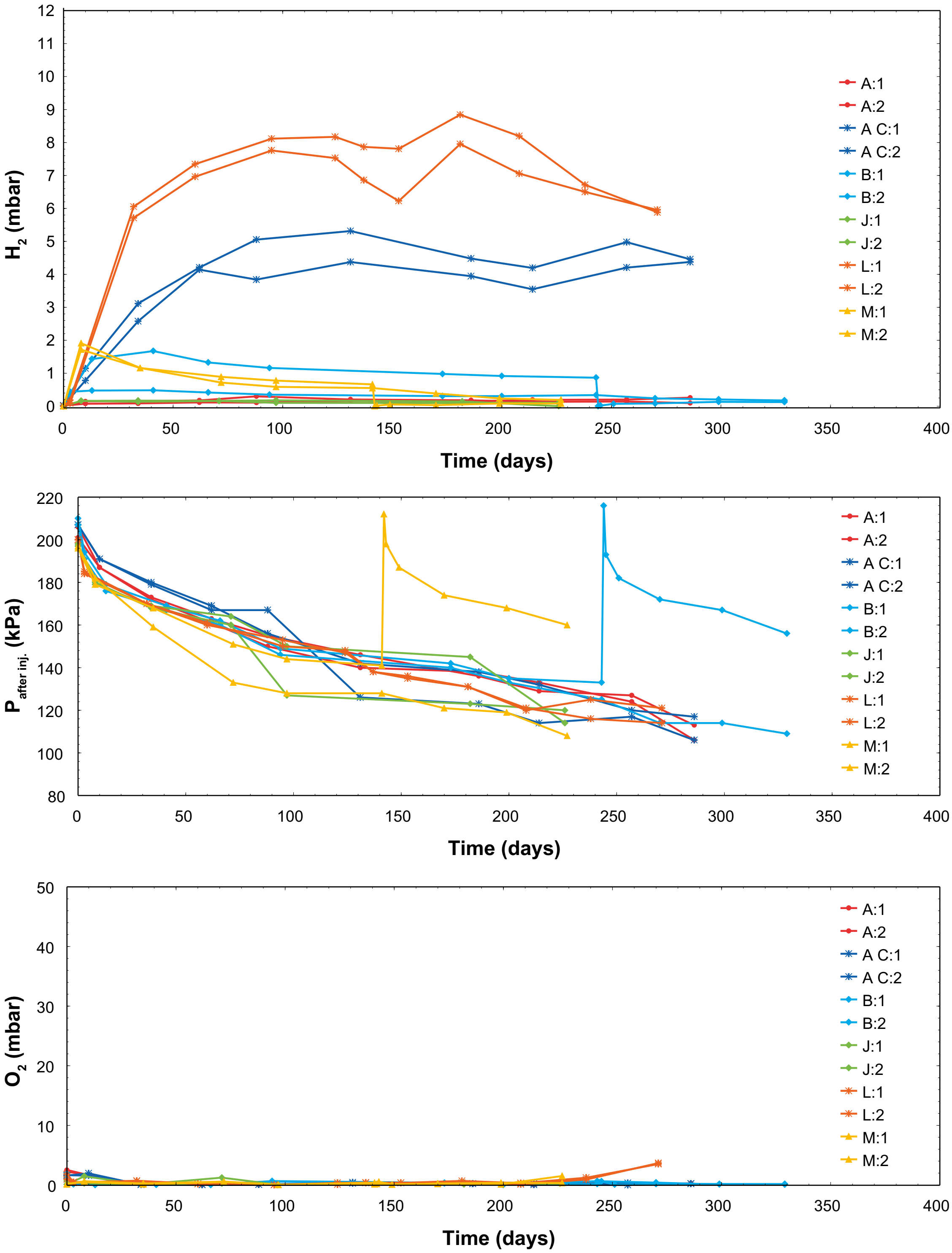

Figure 4-21. The total pressure P and the partial pressures of H_2 and O_2 in each vial of the experiments A, A C, B, J, L and M containing Cu-OFP, 99.95%, SKB (canister-Cu). Symbols show: (●) copper surface was ground and acid leached according to Micans method and then anoxic heat treated at 400°C in Uppsala, (✳) copper surface was ground and anoxic acid leached according to Micans method, (♦) copper surface treated in anoxic atmosphere according to the Uppsala method (electropolishing, reduction in hydrogen and heat treatment at 400°C and (▲) copper surface heat treated at 400°C in Uppsala. For details, see text for each experiment.

4.15 99.95% Cu OF, Goodfellow, experiments G, H and I

4.15.1 Description of experiments

Three different types of experiments were performed with this type of copper material (99.95% Cu OF, Goodfellow), of the same copper quality as used in other long-term experiments (e.g. Hultquist et al. 2009). The three experiments consisted of two vials with two copper sheets (100×10×0.25 mm) in each vial and they were prepared as described below:

- **Experiment G**: The raw copper sheets, i.e. copper as received, were treated in anoxic atmosphere according to the Uppsala method that includes electropolishing, followed by reduction in H_2 and heat treatment at 400°C. For the Uppsala method details, see Boman et al. (2014).
- **Experiment H**: The raw copper sheets, i.e. copper as received, were anoxic heat treated at 400°C in Uppsala. For the Uppsala method details, see Boman et al. (2014).
- **Experiment I**: The raw copper sheets, i.e. copper as received, were placed into vials without any preparation and sealed with new butyl rubber stoppers in an anaerobic chamber.

After the sample preparations described above, the copper sheets were placed into vials in an anaerobic chamber and sealed with new butyl rubber stoppers. Sample vials were filled with sterilised and anoxic water and were completed with subsequent treatments, according to Micans method (Bengtsson et al. 2013). Six vials (3+3) containing water and nitrogen, respectively, were prepared for comparisons with experiments G, H and I.

4.15.2 Results

The results are presented in Figure 4-22. There was no O_2-contamination or uncontrolled pressure drops in the vials. There was no H_2 emission above the background of 0.1–0.2 mbar H_2 in any of the experiments.

4.16 99.9999% Cu-OF (Alfa Aesar), unscratched, experiments D, E, F, NUK and UK

4.16.1 Description of experiments

Five experiments were studied with ultrapure copper (99.9999% Cu-OF, Alfa Aesar). The sheets measured 100×10×0.25 mm, except for sheets in NUK that measured approximately 15×10×0.25 mm. The five experiments consisted of two vials with two copper sheets in each vial. The raw copper surfaces were prepared as described below:

- **Experiment D**: The raw copper sheets, i.e. copper as received, were placed into vials without any preparation and sealed with new butyl rubber stoppers in an anaerobic chamber.
- **Experiment E**: The copper surfaces were acid leached (but not ground) according to Micans method (Bengtsson et al. 2013).
- **Experiment F**: The copper surfaces were heat treated under anoxic conditions at 400°C in Uppsala (For Uppsala method details, see Boman et al. 2014) and acid leached according to Micans method (Bengtsson et al. 2013).
- **Experiment NUK and UK1**: The copper surfaces were treated in an anoxic atmosphere according to the Uppsala method that includes electropolishing followed by reduction in H_2 and heat treatment at 400°C. For Uppsala method details, see Boman et al. (2014).

After the sample preparations described above, the copper sheets were placed into vials in an anaerobic chamber and sealed with new butyl rubber stoppers. Sample vials were filled with sterilised and anoxic water and were completed with subsequent treatments, according to Micans method (Bengtsson et al. 2013). Six vials (3+3) containing water and nitrogen, respectively were used as controls to re-started samples.

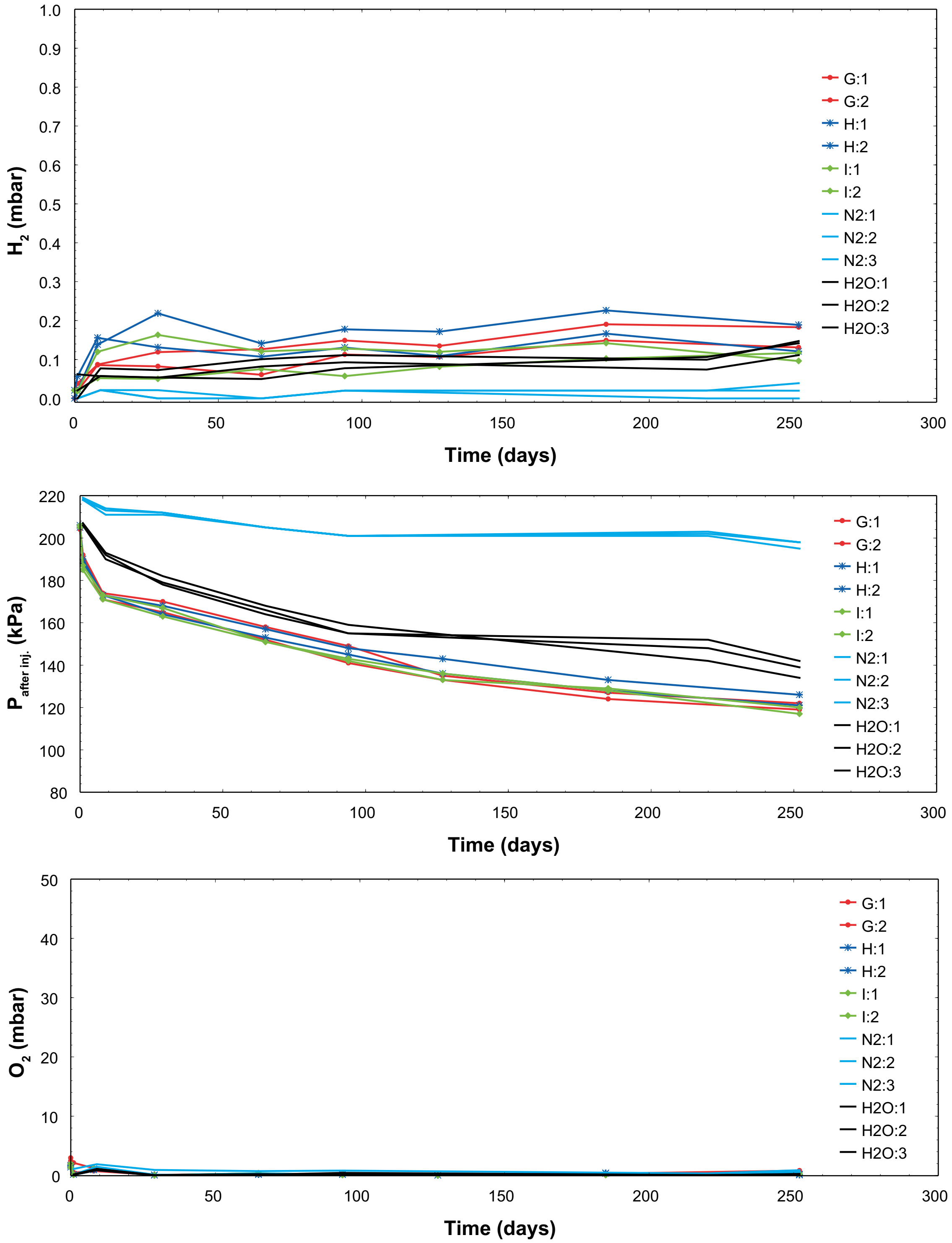

Figure 4-22. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the experiments G, H and I containing Cu-OF, 99.95%, Goodfellow. All experiments have been treated differently ways. Symbols show (●) copper surface was treated in anoxic atmosphere according to the Uppsala method (electropolishing, reduction in hydrogen and heat treatment at 400°), (✳) copper rod heat treated at 400°C in Uppsala and (♦) copper surface untreated. Blue and black lines show control vials with nitrogen and water, respectively, but without copper surfaces. For details, see text for each experiment.*

The sample D:1 was re-started after 258 days, by opening the vial in an anaerobic chamber. The copper sheets were placed back into the new vials and sealed with new butyl rubber stoppers with subsequent treatments as described previously. Ten vials (5+5) containing water and nitrogen, respectively were prepared as controls to experiments E and F. Five and three vials respectively containing water was prepared as controls for experiment NUK and UK. For NUK it was no H_2 emission (Figure 4-24).

4.16.2 Results

The results are presented in Figure 4-23 and Figure 4-24. There was no O_2-contamination or uncontrolled pressure drops in the vials except for the final analyses of a few samples that showed signs of O_2-contamination. There was possibly an initial weak H_2 emission in the D:2 vial, else, the H_2 emission values were within the background range of 0.1–0.2 mbar for all experiments. If there was a H_2 emission it was too slow to be registered during the time of observation. After the evacuation of H_2 there was some emission of H_2 but the values did not increase above the background range during the time of observation.

4.17 99.9999% Cu-OF (Alfa Aesar), scratched in anoxic environment, experiments C, K, Q and unscratched UK

4.17.1 Description of experiments

Four experiments were studied with ultrapure copper (99.9999% Cu-OF, Alfa Aesar). The sheets were measuring 100×10×0.25 mm. The four experiments consisted of two vials with two copper sheets in each vial. The copper specimens in all experiments were surface treated in anoxic atmosphere according to the Uppsala method (electropolishing, reduction in H_2 and heat treatment at 400°C) with subsequent anoxic scratching of some copper surfaces as described below: For Uppsala method, see Boman et al. (2014). For copper surfaces scratched details with SiC and diamond powder, see SKBdoc 1470267, Section 3.1.

- **Experiment C**: The surfaces were scratched anoxic with silicon carbide (SiC).
- **Experiment K**: The surfaces were scratched anoxic with silicon carbide (SiC).
- **Experiment Q**: The surfaces were scratched anoxic with diamond powder.
- **Experiment UK1**: The copper surfaces were unscratched and added for comparison with experiments C, K and Q.

After the sample preparations described above, the copper sheets were placed into vials in an anaerobic chamber and sealed with new butyl rubber stoppers. Sample vials were filled with sterilised and anoxic water and were completed with subsequent treatments, according to Micans method (Bengtsson et al. 2013). Ten vials (5+5) containing water and nitrogen, respectively were prepared as controls to experiment C. Six vials (3+3) containing water and nitrogen, respectively were prepared as controls to K and Q. Five vials containing water was prepared as controls for experiment UK.

After 244 and 142 days, respectively, the samples C:2 and K:1 were re-started by opening the vials in an anaerobic chamber. The copper sheets were placed back into the new vials and sealed with new butyl rubber stoppers with subsequent treatments as described previously. Six vials (3+3) containing water and nitrogen, respectively were used as controls to re-started samples.

4.17.2 Results

The results are presented in Figure 4-25 and Figure 4-26. There was no O_2-contamination or uncontrolled pressure drops in the vials except for the final analyses of a few samples that showed signs of O_2-contamiantion. The scratched copper surfaces, vials C and K, rapidly developed high partial pressures of H_2 after a very short time that linearly declined towards zero after 200–300 days. The vials Q with scratched copper sheets that had “rested” a couple of days before start of the experiment did not show any H_2 emission. There was no H_2 emission in the vials C:2 and K:1 after evacuation.

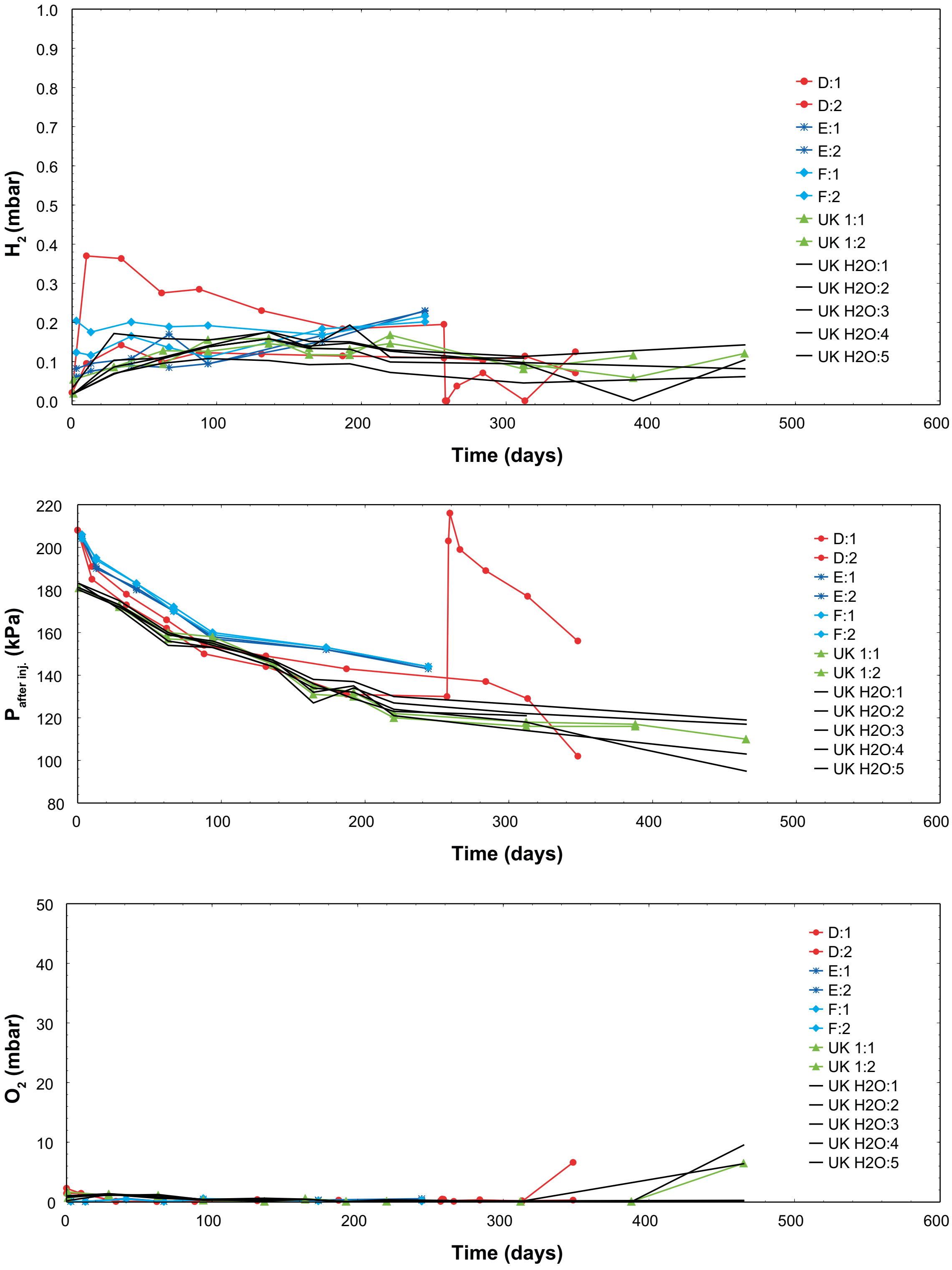

Figure 4-23. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the experiments D, E, F, UK1 containing Cu-OF, 99.9999%, Alfa Aesar. All experiments have been treated differently ways. Symbols show (●) copper surface untreated, (✳) copper surface acid leached according to Micans method, (♦) copper surface was heat treated at 400°C in Uppsala and anoxic acid leached according to Micans method and (▲) copper surface treated in anoxic atmosphere according to the Uppsala method (electropolishing, reduction in hydrogen and heat treatment at 400°C). Black lines show control vials with water but without copper surfaces. For details, see text for each experiment.*

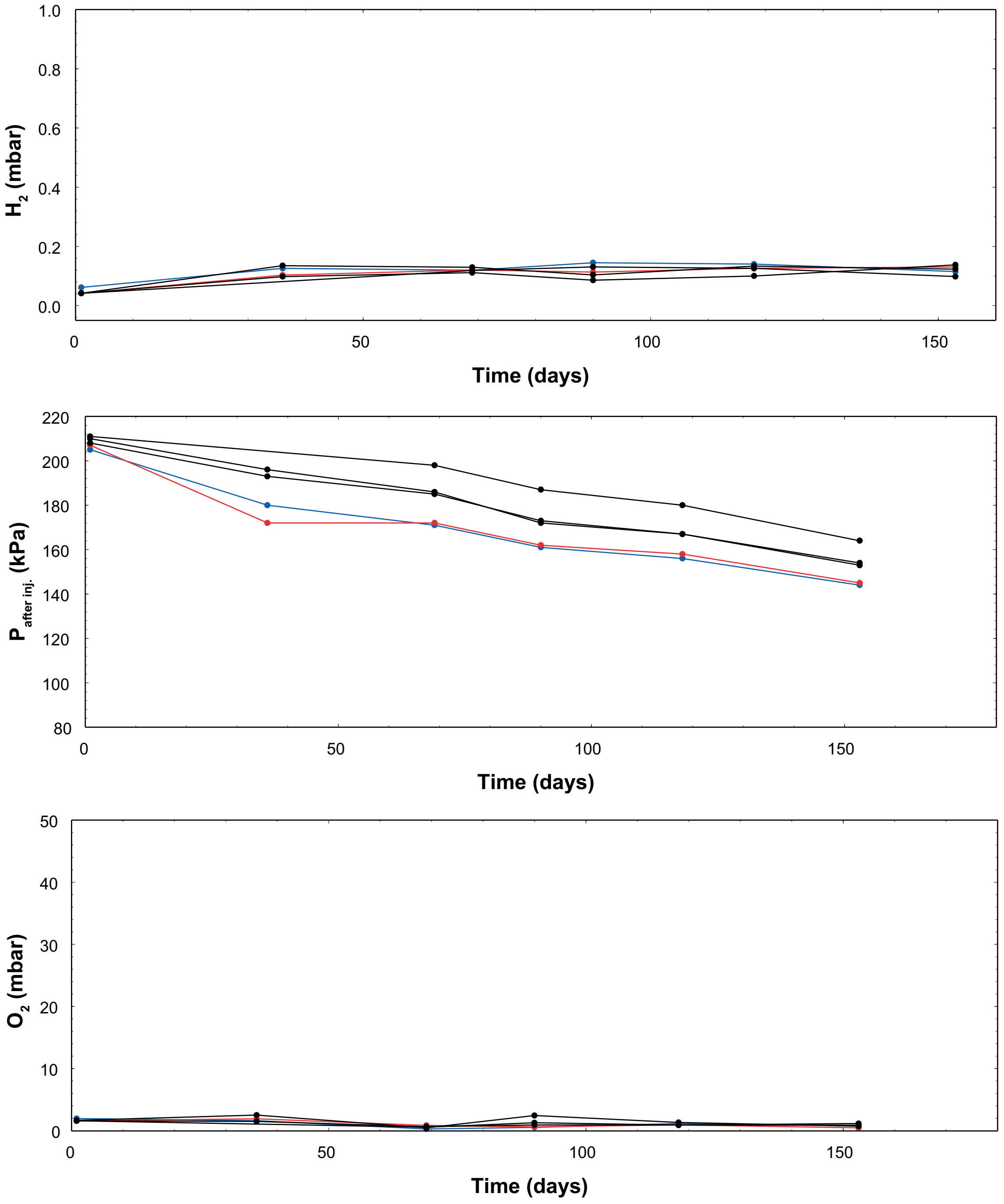

Figure 4-24. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the NUK experiment. Blue (NUK:1) and red (NUK:2) symbol and line show vial with ultrapure copper (Cu-OF, 99.9999%, Alfa Aesar). Copper surface treated in anoxic atmosphere according to the Uppsala method (electropolishing, reduction in hydrogen and heat treatment at 400°C). Black symbols and lines show control vials with water, but without copper surfaces. See text for details.*

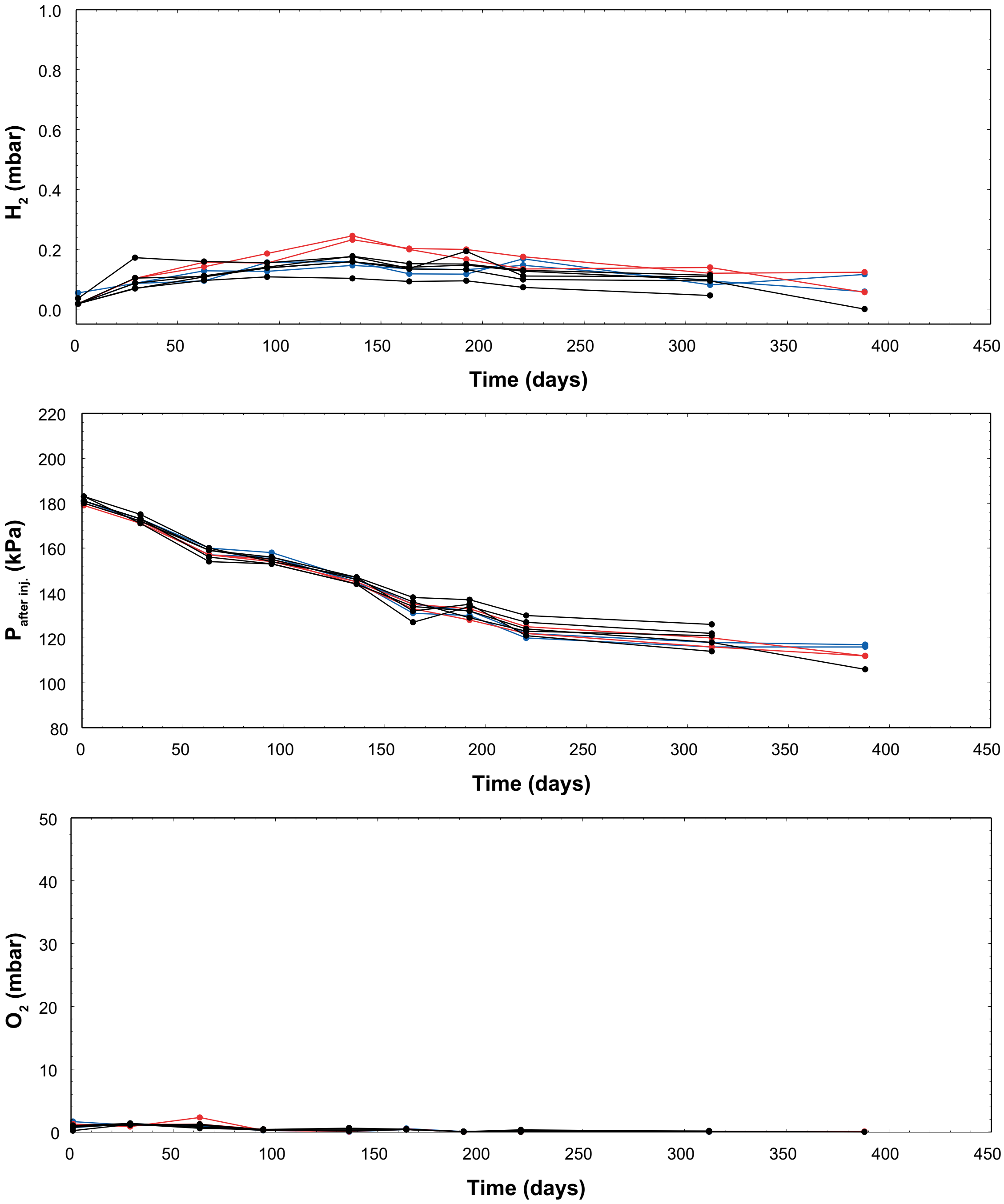

Figure 4-25. *The total pressure P and the partial pressures of* H_2 *and* O_2 *in each vial of the UK experiment. Blue (UK1, Cu-OF, 99.9999%, Alfa Aesar) and red (UK2, Cu-OF, 99.9%, Alfa Aesar) symbols and lines show vials with ultrapure copper of different quality. Copper surface treated in anoxic atmosphere according to the Uppsala method (electropolishing, reduction in hydrogen and heat treatment at 400°C). Black symbols and lines show control vials with water, but without copper surfaces. See text for details.*

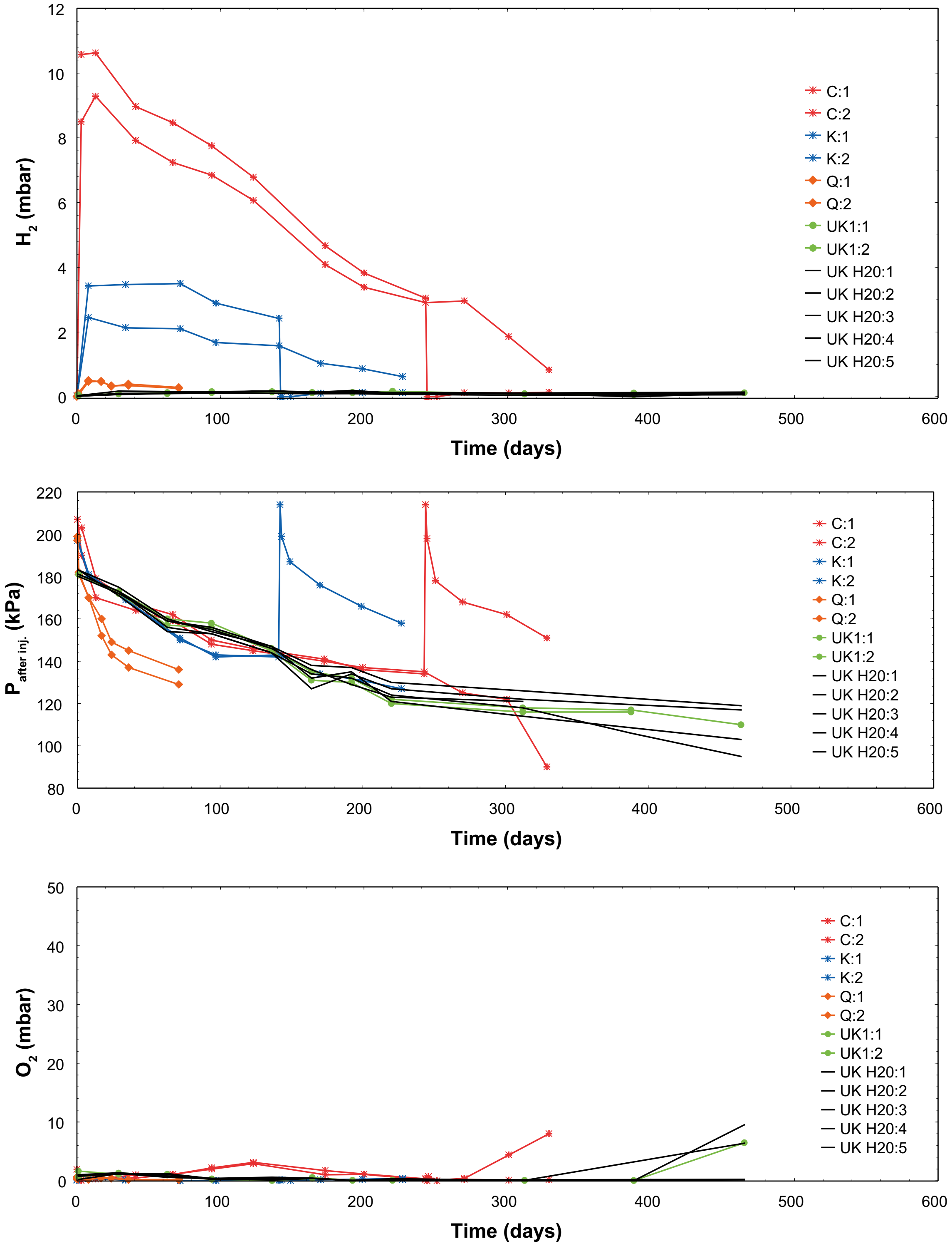

Figure 4-26. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the experiments C, K, Q and UK1 containing Cu-OF, 99.9999%, Alfa Aesar. All experiments have been surface treated in anoxic atmosphere according to the Uppsala method (electropolishing, reduction in hydrogen and heat treatment at 400°C) with subsequent anoxic scratching of some copper surfaces. Symbols shows: (✳) copper surface scratched with silicon carbide (SiC), (♦) scratched with diamond and (●) unscratched copper surface. Black lines show control vials with water, but without copper surfaces. For details, see text for each experiment.*

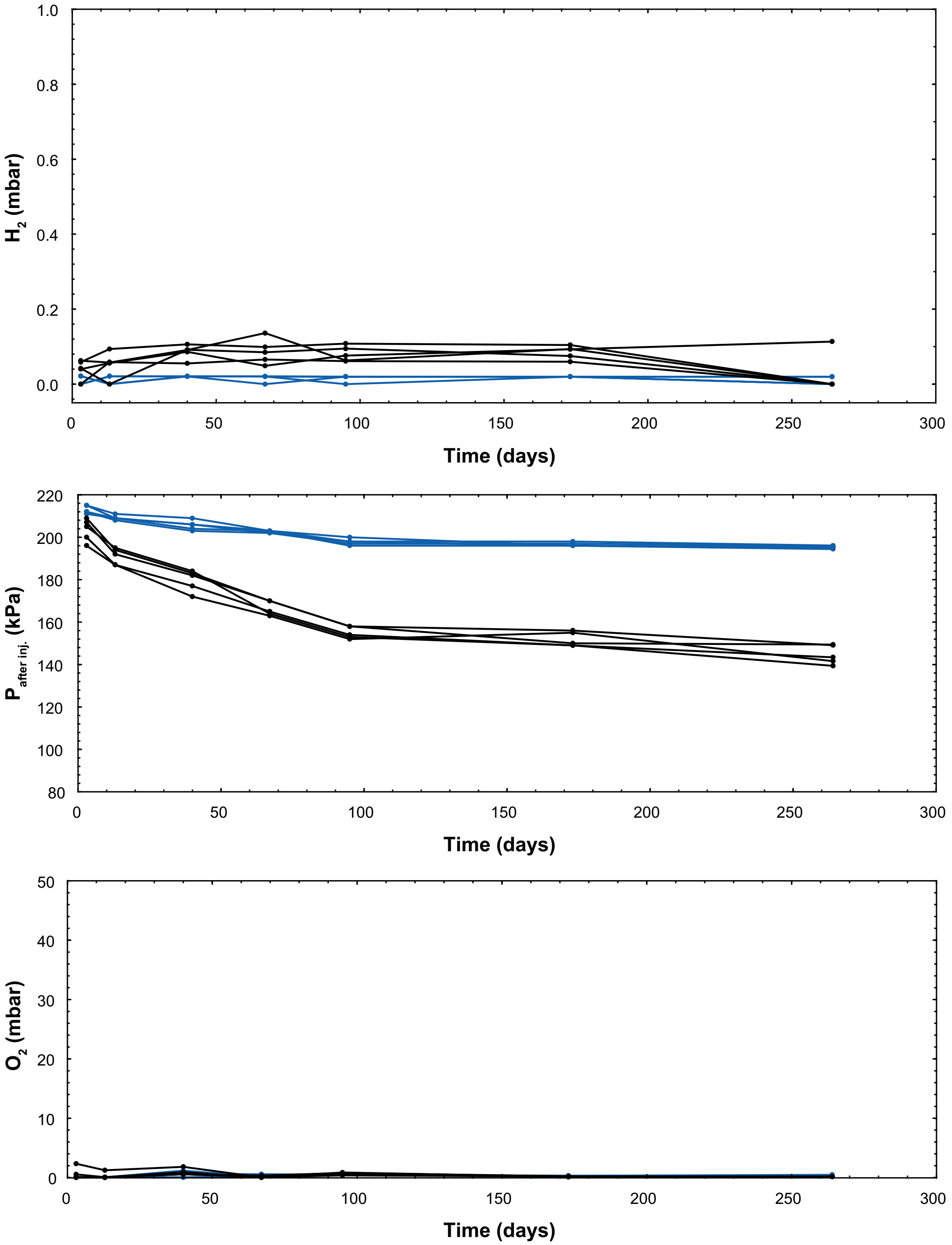

Figure 4-27. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the controls to experiments B–C and E–F. Black and blue lines show control vials with nitrogen and water, respectively.*

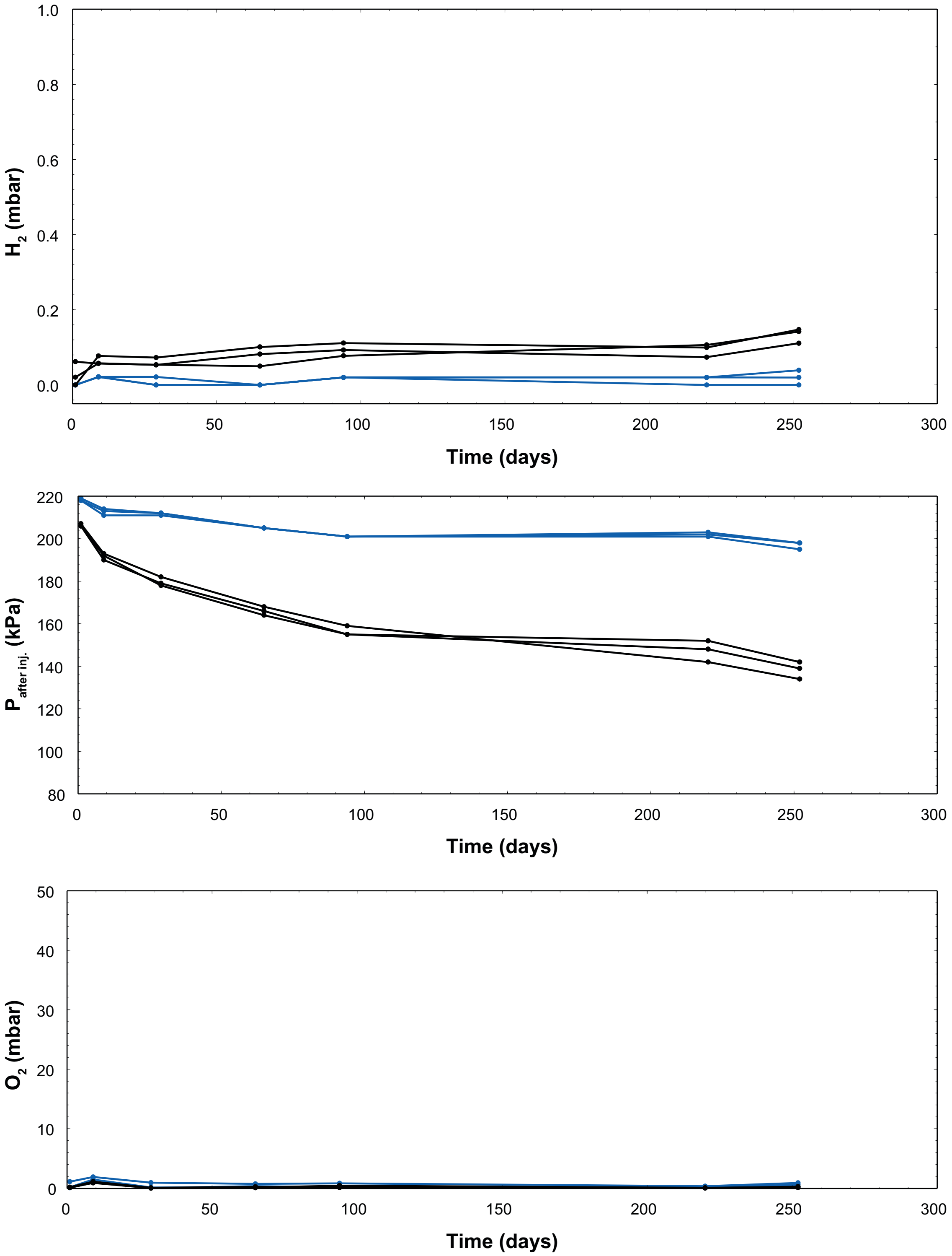

Figure 4-28. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the controls to experiments G–I. Black and blue lines show control vials with nitrogen and water, respectively.*

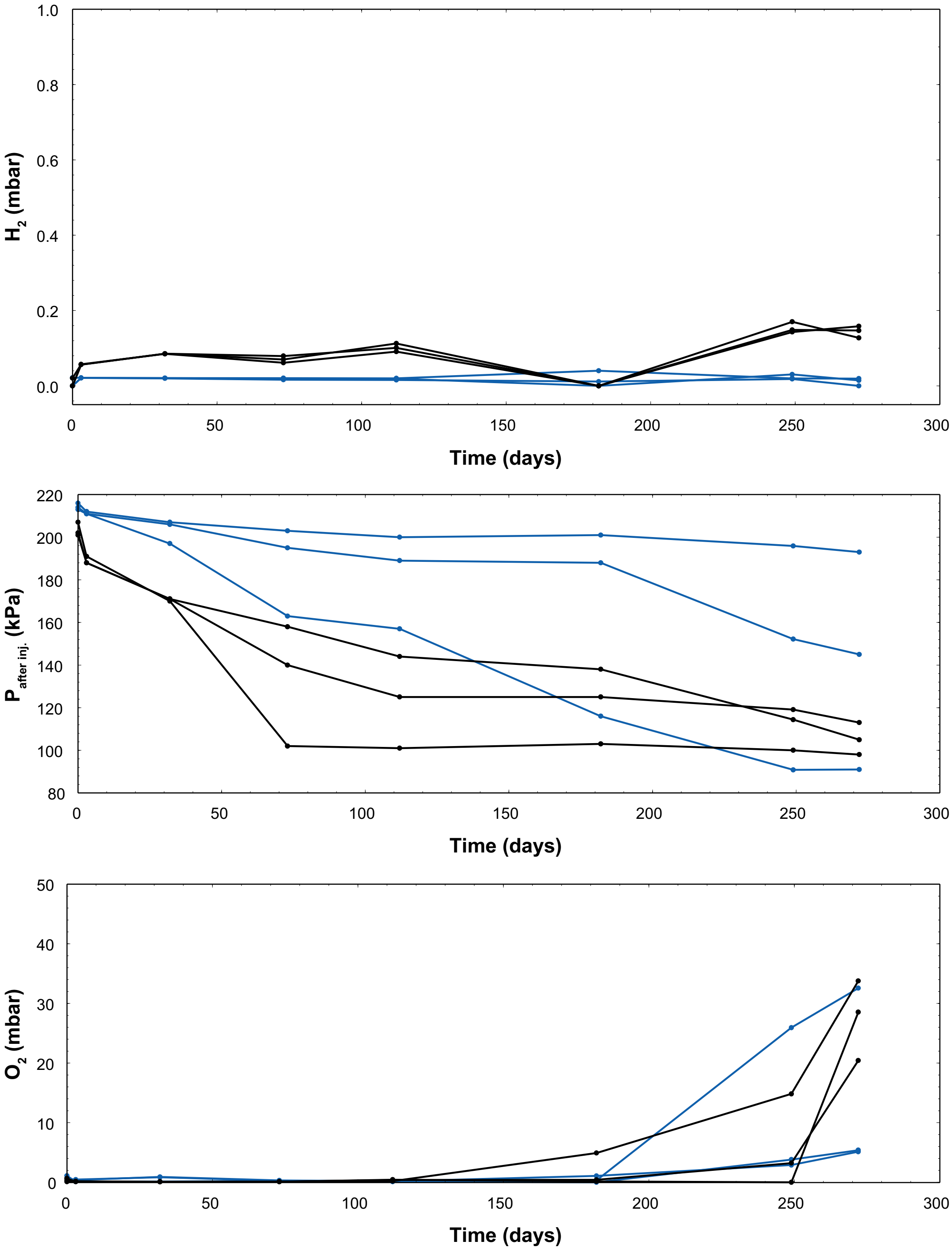

Figure 4-29. *The total pressure P and the partial pressures of* H_2 *and* O_2 *in each vial of the controls to experiment L. Black and blue lines show control vials with nitrogen and water, respectively.*

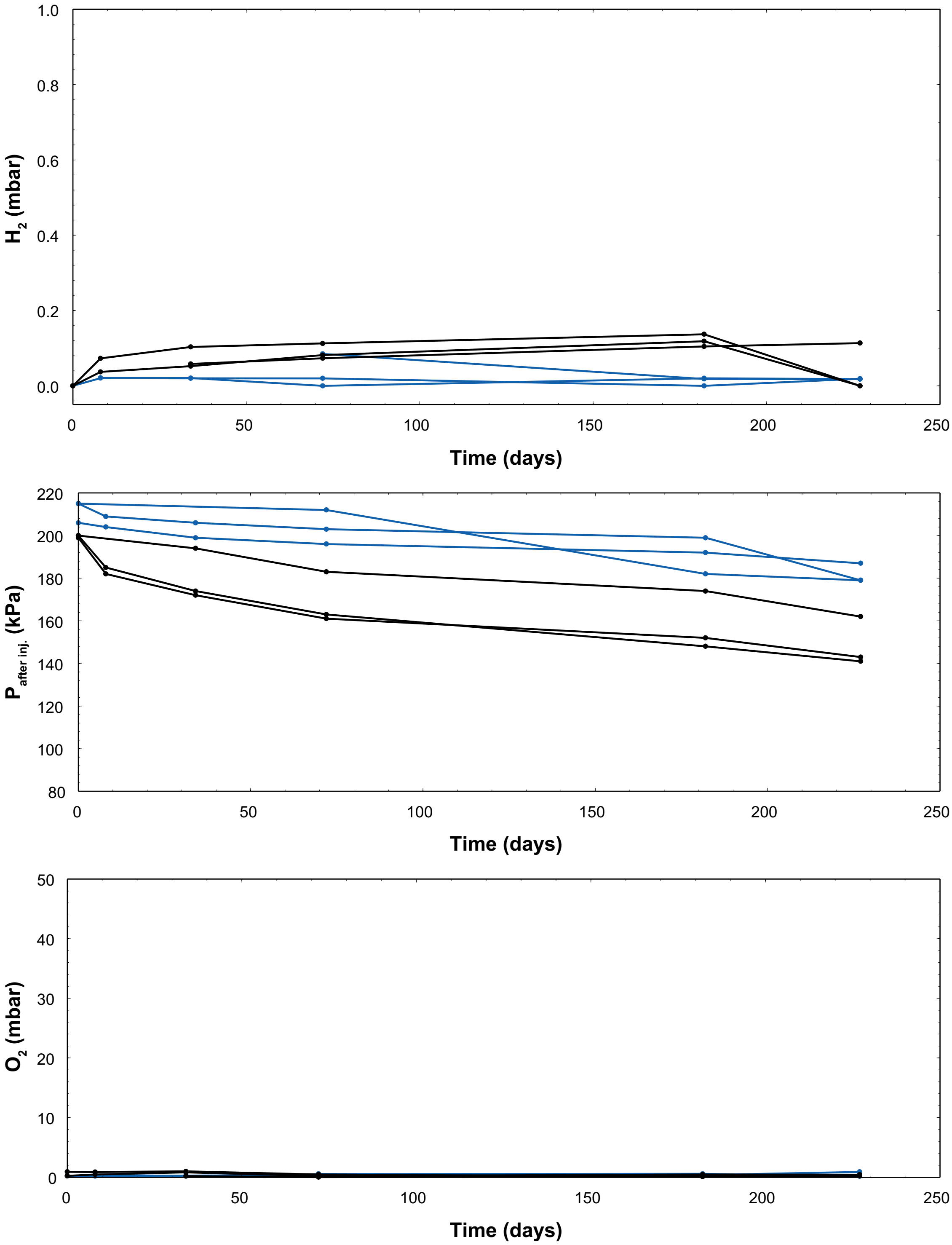

Figure 4-30. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the controls to experiments J, K and M. Black and blue lines show control vials with nitrogen and water, respectively.*

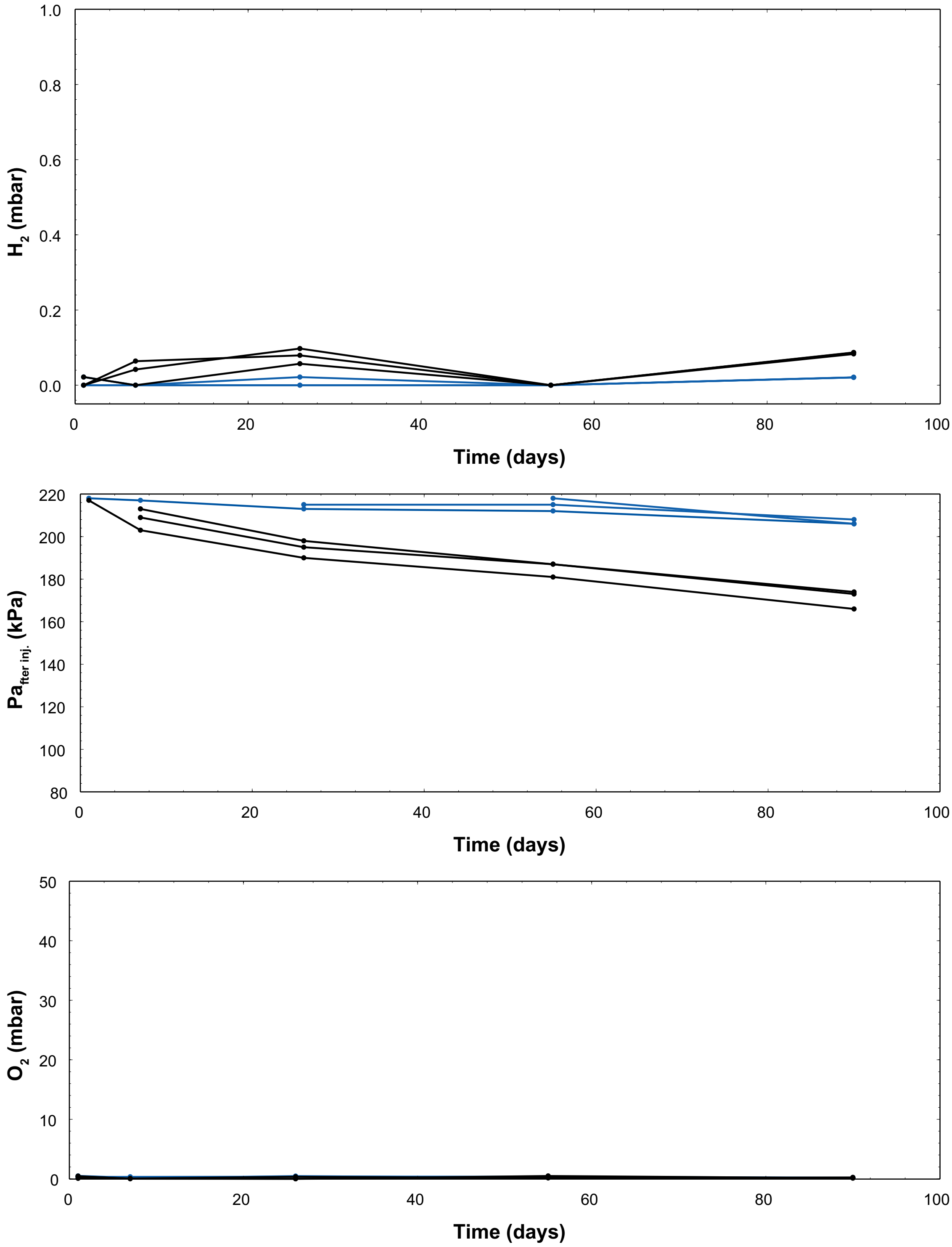

Figure 4-31. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the controls to restarted experiments B–D, K and M. Black and blue lines show control vials with nitrogen and water, respectively.*

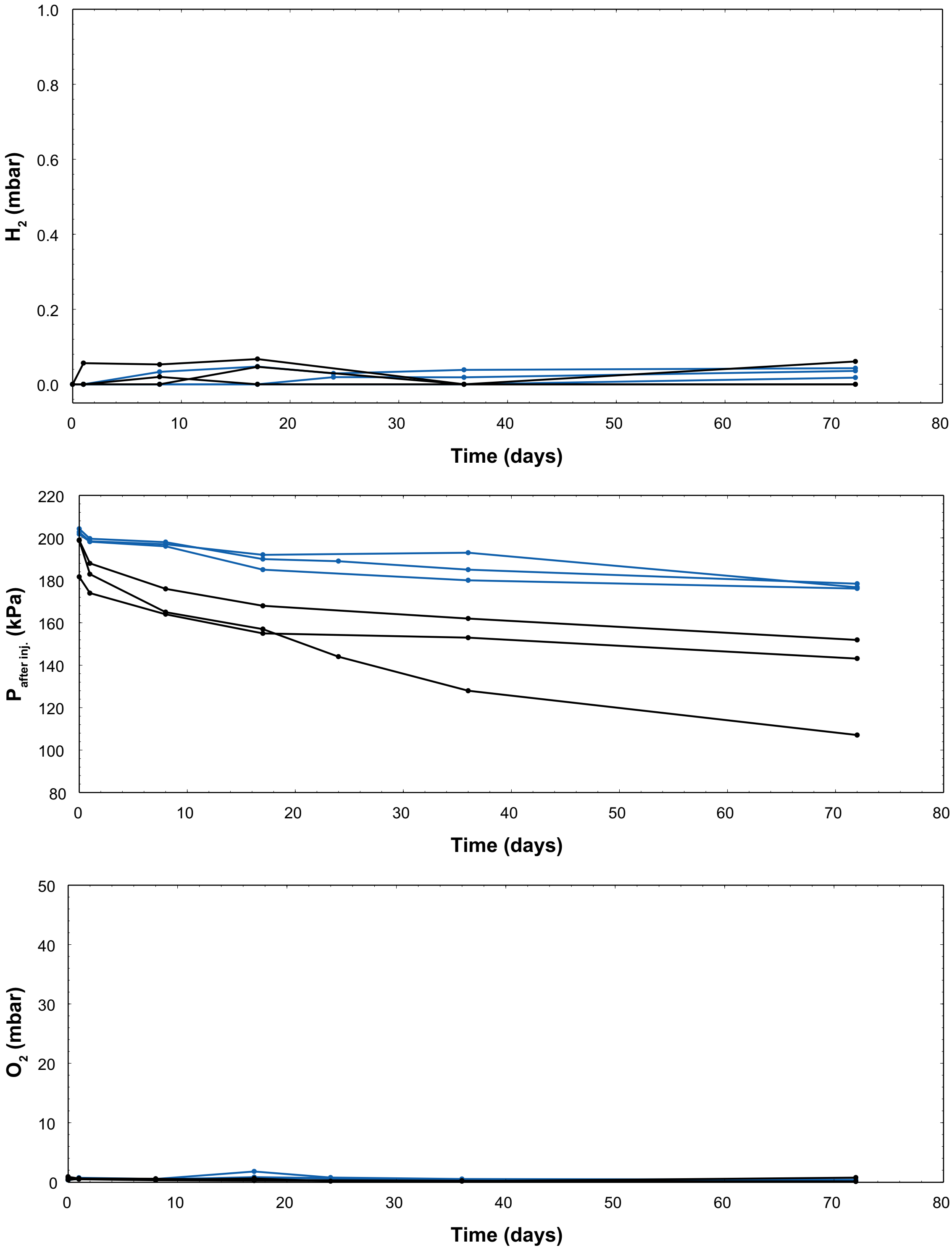

Figure 4-32. *The total pressure P and the partial pressures of H_2 and O_2 in each vial of the controls to experiment Q. Black and blue lines show control vials with nitrogen and water, respectively.*

5 Method development for the analysis of copper content of surface layers on pure copper metal and copper in glass vial water

5.1 Background

This method was set up to investigate if copper oxides could be detected on the copper rods before and after the experiments. The method development was performed in June 2013. Later the method was tested on 4 copper surfaces as described in Section 5.4. Concurrently, a method was developed for the analysis of copper in the vials after removal of the copper specimens.

5.2 Copper analysis methodology

All samples were sent for analysis by ICP-MS at VA Syd under supervision of Mats From, working for SWEDAC with accreditation of testing laboratories using ICP-MS.

The samples were analysed on ICP-MS (Perkin-Elmer Elan DRCe) after addition of internal standard (^{72}Ge) to correct for fluctuations in the pump and possible ion suppression. The samples were quantified against external standards prepared to concentrations 1, 10 and 100 µg L^{-1} of each metal (confer Table 5-10). The external standards were prepared by dilution of a certified stock solution (Perkin-Elmer Multi3) using calibrated and controlled automatic pipettes. As quality control (QC), a separate standard with a concentration of 10 µg L^{-1} was prepared using another batch of starting material (P-E Multi3, different batch) and diluted with other controlled pipettes. This QC sample was analysed repeatedly throughout the analysis experiments together with blank solutions made at the laboratory using high-grade metal-free water.

All calibration curves were plotted linear and forced through zero. The instrument is known to be linear in response also over a greater range of concentrations but results above 100 µg L^{-1} were reanalysed after dilution to fit the calibration range. The method used was VA Syd SOP 072 utg. 15-01-08 based on standard method SS-EN ISO 17294-2:2005 and all results are accredited. The uncertainty of measurement is evaluated specifically for this analysis based on results from the QC, the dilution principle and used equipment. Accuracy for copper is in the range of 5% relative with a coverage factor of 95%, two standard deviations.

Normally results are reported to two significant digits, but considering the improved accuracy in these tests, values are reported as obtained from the raw data. Care should be taken when evaluating the results, keeping the uncertainty of measurement in consideration. For the diluted samples (results above 100 µg L^{-1}) this is especially important since the extra dilution step could not be accounted for by the analysed QC control sample. It was, however performed using best available procedures. In all cases where dilutions were necessary the samples were diluted 100 times to give a final concentration in the range of the QC sample. Also, an even 100 times dilution was technically preferred to minimise possible errors.

5.3 Outline of the method for leachable copper analysis

The method was based on information from Möller (2012, Sections 4.6.6 and 4.6.7). Sulphamic acid is aggressive against cuprous oxides but shows only limited aggressiveness against pure copper metal. It is normally used to clean the copper surface from formed oxides according to method SS-ISO 8407:2010.

In this method development, a repeated leaching in four cycles with sulphamic acid was used to determine leachable amounts of copper from selected copper rods. The origin of this copper was predominantly oxides but since the base metal also shows some leachability a blank test with freshly polished copper had to be added to the test experiments. The amount of copper leached from the clean surface was compared with the amounts obtained from the surfaces that may show presence of cuprous oxides. Blank samples for all the used chemicals, like the sulphamic acid solution, the water used for dilutions and the nitric acid used for stabilization of the samples, were also included.

One sample vial, N5:1 (Figure 4-5), was chosen for the method development and removed from the experiment at day 199. This vial showed a normal behaviour for the experiments regarding H_2 production and showed no signs of O_2 contamination. It was the first vial from a test experiment that had been evacuated once during the test run, showing H_2 production both before and after evacuation. In the first part of the test a total amount of 663 nmol H_2 was evolved in the vial, and after evacuation another 847 nmol H_2 was produced giving a total amount of 1,510 nmol of H_2. This value was not corrected for any diffusion of H_2 out of the vial. The actual amount of H_2 evolved during the tests was probably slightly higher than 1,510 nmol.

Since formed oxides possibly could be detected not only on the surface of the copper but also as sediment particles in the vial itself, tests were also made on the copper content in the water inside the vial after an addition of 2% nitric acid and sonication in an ultrasonic bath. This measurement should include copper in the water and also dissolved copper from sediment oxide particles, and also copper leached from the vial itself. Soda glass is known to contain small amounts of copper.

As a reference blank sample a piece of copper was ground and polished in the same way as the N5 samples and stored in ethanol inside an anaerobic box before the experiment. Unlike the test samples it was not leached in sulphamic acid before the experiment.

5.3.1 Experimental procedure

1. The glass vials with copper rods were opened inside an anaerobic box. The two rods of copper were transferred to two separate centrifuge tubes (Sarstedt 50 mL) inside the anaerobic box. Remaining water inside the vial was acidified with p.a. nitric acid to a final concentration of 2%. The water was left in the vial for leaching during 24 hours, 1 hour of this time the tubes were sonicated in an ultrasonic bath.
2. In parallel, a newly cleaned rod of copper was placed in a centrifuge tube to be used as reference.
3. The tubes with copper rods from the opened vial were marked “A” and “B”, the tube with a new, clean, reference sample of copper metal was marked “C”.
4. To the three tubes containing copper samples 10 mL of sulphamic acid was added with a pipette and they were immediately placed on a shaking table to be leached for exactly 5 minutes. The leaching took place inside the anaerobic box and the prepared solution of sulphamic acid was deoxygenated with nitrogen gas before the tests.
5. After five minutes the fluid from the tubes was decanted to a smaller test tube (15 ml Sarstedt). A new addition of 5 mL of sulphamic acid was added to the tubes containing copper samples and the leaching procedure was repeated for another five minutes. After four cycles, giving a total leaching time of 20 minutes, the procedure was stopped. For each copper sample four separate aliquots of extraction fluid were obtained and marked A1-4, B1-4 and C1-4.
6. After removing these tubes from the anaerobic box they were acidified with p.a. nitric acid to a final concentration of 2%. Before further dilution, the tubes were left acidified overnight to homogenize. Two tubes with the sulphamic acid solution, without any contact with copper surfaces, were prepared in the same way to give a background value of possible copper content in the leaching fluid itself.
7. The following day one litre of acidified water was prepared in a clean plastic beaker by mixing p.a. nitric acid with A to a final concentration of 2% acid. Before analysis on ICP-MS (5.2), the samples had to be diluted to lower the matrix impact of the sulphamic acid as well as to give a final concentration of copper in the solutions that would match the optimum quantification range on the instrument. The dilution was made in two steps, first by adding 500 µL of sample to 49.5 mL of the acidified water for a dilution 100 times, then this solution was further diluted 5 times by mixing 2 mL of diluted sample with 8 mL of acidified water. After the two steps the final dilution was 500 times. All steps were prepared using only plastic materials, pipettes and tubes.

8. In parallel, a blank sample was prepared by just adding the prepared acidified water to a test tube. This was made to monitor background levels of copper originating from water and acid.
9. The acidified water from the original glass vial was not diluted further.
10. All samples, 12 diluted leaching solutions from copper samples, two diluted samples of the diluted leaching solution itself, two blank samples and the water from the original vial were sent for analysis on ICP-MS (5.2).

5.3.2 Results

These results showed that the water and sulphamic acid did not contribute to the measured amounts of copper, that the water in the vial contained a significant amount of copper and that the diluted leaching solution did contain copper in itself, probably from impurities (Table 5-1). The volume of water in the original vial was 16 mL. With a concentration of 148 µg L^{-1} Cu this value corresponds to a total amount of 2.37 µg Cu (from both samples A and B together as they were joined in the same vial, (N5:1).

In Table 5-2, the three experiments of copper rod leaching are presented, corrected for the background value of 0.87 µg L^{-1} Cu from the leaching fluid itself. Judging from these results it was obvious that the reference sample C was carrying oxides on the surface. The test results consequently shows that the leaching itself was capable of removing the oxide layer in less than four cycles, also from a high start value of copper oxides.

In experiment A the value for leaching cycle four was higher than the value obtained for leaching cycle three. The metal sample was slightly bent in one end, like a ski, and because of this the surface exposed to the leaching fluid might be different depending on if the sample has the kink facing up or down. The average value of the two cycles was 6.9 µg L^{-1} Cu, very similar to the final concentration in experiment B and C. Based on these data it was assumed that all the oxides had been leached in the first two cycles and that the copper content in cycle three and four corresponds to the background (6.7 µg L^{-1}) from the base metal itself. In Table 5-3 the measured amounts of leachable copper from the first two leaching cycles presented in Table 5-2 are corrected for the background level.

Table 5-1. Blank analysis results and copper in vial N5 that did carry copper rods.

Blank	Blank leaching sulphamic solution diluted 500 times	Water from the original N5:1 glass vial
< 0.3 µg L^{-1} Cu	0.87 µg L^{-1} Cu	148 µg L^{-1} Cu

Table 5-2. Leaching results of N5:1 copper rods, results shown represent the 500 times diluted samples.

Leaching cycle	Experiment A × 500 µg L^{-1} Cu	Experiment B × 500 µg L^{-1} Cu	Experiment C (polished ref.) × 500 µg L^{-1} Cu
1	16.8	8.5	92
2	8.7	6.8	41
3	4.5	6.4	8.2
4	9.2	6.7	6.7

Table 5-3. Background corrected values for leachable copper.

Leaching cycle	Experiment A × 500 µg L^{-1} Cu	Experiment B × 500 µg L^{-1} Cu	Experiment C (polished ref.) × 500 µg L^{-1} Cu
1	9.9	2.0	85
2	1.8	0.3	34

The amounts of leachable copper in Table 5-3 were recalculated for dilution and for the volume of leaching fluid in each extraction cycle (C × 0.01 × 500) and the results are given in Table 5-4. The difference between samples A and B was not unexpected since there seems to be surface variations in the copper itself. In other tests where staining has occurred the spots are unevenly distributed on the samples.

Table 5-4. Total amount of leachable copper from N5:1.

Leaching cycle	Experiment A µg Cu	Experiment B µg Cu
1	49.5	10
2	9.0	1.5

5.3.3 Evaluation of the method for analysis of leachable copper

1. Together the two samples A and B were found to have had a layer of oxides on the surface containing a total amount of 70 µg Cu. In comparison, the amount of copper detected in the water, 2.4 µg Cu, was negligible.
2. The total amount of copper from cuprous oxides on the metal surfaces was 1.14 µmol Cu.
3. The method can be improved by minor adjustments and it is advisable to include several samples in a future repetition of the experiment to verify the results. In general, the method seems to perform as expected.

5.4 Leaching of copper rods NUK:2, UK1:2, G:1, J:1 and reference canister copper rods

The method described above was tested on a set of 4 copper specimens in January 2015. The copper specimens were removed from their respective vials inside the anaerobic box and further analysed using the method outlined above (Section 5.3) with sequential leaching of the surfaces in sulphamic acid. The leachates were analysed for copper content by VA Syd (Section 5.2).

5.4.1 Method

1. As a reference, two copper rods were ground and polished, placed in ethanol and transferred to the anaerobic box. Inside the box they were sonicated in an ultrasonic bath and the ethanol was exchanged twice to remove any remaining residues on the surface. After rinsing in deoxygenated water, the copper rods were individually leached with sulphamic acid and again rinsed three times with deoxygenated water. The procedure was scaled-down compared with the standard method used in the earlier tests and was performed in 50 mL centrifuge tubes (Sarstedt, Germany). The sonication in ethanol was repeated twice compared with the original method, since the volume of ethanol was smaller and the sonication was performed inside a centrifuge tube instead of in the bulk tray of the ultrasonic bath.
2. From this stage the rods were treated in exactly the same way as the copper rods removed from the sample vials in the method development described above. The reference copper rods were stored in the final rinse of water until analysis.
3. The sample copper specimens NUK:2, UK1:2, G:1 and J:1 were individually placed in 50 mL centrifuge tubes inside the anaerobic box. Four tubes were leached simultaneously by two persons, each tube agitated manually by hand.
4. To the centrifuge tube, 10 mL of sulphamic acid was added with an automatic pipette. It was closed and agitated for 5 minutes taking care that each copper specimen was wetted on all sides by the acid. After exactly 5 minutes, the sulphamic acid was decanted to a 15 mL centrifuge tube (Sarstedt, Germany) and a new aliquot of 10 mL was added to the copper specimen for

a new leaching cycle. The cycles were repeated 3–5 times, some of the sulphamic acid was lost unintentionally in the anaerobic box and it was decided that truncation of some leaching samples was preferred to using different batches of sulphamic acid solution.

5. When all the leaching cycles were finished, the centrifuge tubes were removed from the anaerobic box and acidified to 1% with nitric acid as in the test above. The tubes were sonicated for one hour before a further dilution 100 times in water acidified to 1% by adding 100 µL of leachate to 9.9 mL of acidified water in a 15 mL centrifuge tube. Blank samples were prepared both on the acidified water and on sulphamic acid diluted in the same proportions as the copper samples.
6. During the analysis of the diluted samples at VA Syd, only copper was measured to shorten the analysis time. The blank solutions were analysed for all metals to verify the composition of the sulphamic acid. In the analysis experiments, QC controls were added frequently since no recalibration of the instrument was performed throughout the experiments of 44 samples. It is normal procedure to recalibrate more often, but to make the results directly comparable this was omitted and replaced with frequent monitoring of the QC. The two individual copper specimens were not analysed in sequence, hence the double values for QC and blank sample.

5.4.2 Results

The NUK:2 and UK1:2 samples were ultra-cleaned copper sheets prepared as described in Section 4.16. The G:1 sample was a sheet of copper (OFHC) prepared as described in Section 4.15 and the J:1 sample consisted of a canister copper rod (OFP) that was electropolished in Uppsala as described in Section 4.14.

Table 5-5. Total amount of leachable copper from sample NUK:2.

Leaching cycle	Copper sheet 1 (µg)	Copper sheet 2 (µg)	QC test (10 µg L^{-1} Cu)	Blank sample
1	3.711	3.873		
2	2.743	2.952	Before experiments:	Before experiments:
3	4.280	4.601	9.892/9.845	0.003/0.037
4	5.487	3.373	After experiments:	After experiments:
5	4.458	3.396	9.696/9.753	0.031/0.041

Table 5-6. Total amount of leachable copper from sample UK1:2.

Leaching cycle	Copper sheet 1 (µg)	Copper sheet 2 (µg)	QC test (10 µg L^{-1} Cu)	Blank sample
1	8.622	10.514		
2	3.256	3.905	Before experiments:	Before experiments:
3	6.894	4.420	9.696/9.753	0.031/0.041
4	5.747	4.620	After experiments:	After experiments:
5	6.876	4.907	9.795/10.064	0.034/0.040

Table 5-7. Total amount of leachable copper from sample G:1.

Leaching	Copper sheet 1 (µg)	Copper sheet 2 (µg)	QC test (10 µg L^{-1} Cu)	Blank sample
1	102.77	113.19		
2	52.761	62.607	Before experiments:	Before experiments:
3	10.835	24.150	9.795/10.064	0.034/0.040
4	5.533	11.918	After experiments:	After experiments:
5	5.147	4.206	9.932/10.044	0.038/0.039

Table 5-8. Total amount of leachable copper from sample J:1.

Leaching cycle	Copper rod 1 (µg)	Copper rod 2 (µg)	QC test ($10\ \mu g\ L^{-1}$ Cu)	Blank sample
1	15.590	15.195		
2	6.099	4.610	Before experiments:	Before experiments:
3	5.330	3.405	9.932/10.044	0.038/0.039
4	3.832	3.738	After experiments:	After experiments:
5	---	---	9.910/---	0.042/---

Table 5-9. Sample reference Cu-rods.

Leaching cycle	Copper rod 1 (µg)	Copper rod 2 (µg)	QC test ($10\ \mu g\ L^{-1}$ Cu)	Blank sample
1	83.069	82.014		
2	31.845	42.533	Before experiments:	Before experiments:
3	5.870	12.469	9.910/9.900	0.042/0.035
4	---	---	After experiments:	After experiments:
5	---	---	9.900/9.845	0.035/0.037

Table 5-10. Blank solutions, all units in $\mu g\ L^{-1}$ (ppb).

Metal	Blank acidified water vial 1	Blank acidified water vial 2	Sulphamic acid diluted 100× (1)	Sulphamic acid diluted 100× (2)
Al	1.202	1.122	1.015	0.994
Cr	–0.002	–0.008	0.070	0.032
Mn	0.002	0.000	0.005	0.006
Co	0.001	0.001	0.002	0.003
Ni	0.001	–0.002	0.029	0.036
Cu	0.123	0.118	1.373	1.395
Zn	0.371	0.329	1.198	1.222
As	–0.030	–0.030	–0.030	–0.031
Se	0.086	0.087	0.168	0.151
Ag	0.009	0.006	0.001	0.001
Cd	0.001	0.002	0.002	0.005
Pb	–0.008	–0.009	0.000	–0.001
U	0.001	0.001	0.000	0.000

5.4.3 Evaluation of the method test

There was no H_2 emission from any of the experiments tested here (Figure 4-24, Figure 4-25 and Figure 4-22). Still the analysis of the leachates from vial G:1 showed significant amounts of leachable copper. Based on this information there seems to be no direct connection between the amount of leached copper and hydrogen evolution. When comparing the results please observe that these samples were diluted 100 times while the samples in the method development were diluted 500 times.

The truncation of the reference sample leachates after three cycles may have interfered with the results. Further, the water used for rinsing the reference rods was freshly prepared and there is a possibility that it, despite being de-gassed with nitrogen, could have contained residual oxygen which would have created oxides. Still we keep the results here because they again show that 2–3 leaching cycles should be enough to totally clean copper specimens from oxides on the surface. The method used to prepare the samples NUK, UK and J:1 does seem to render the surface of the copper less viable to further attack by the sulphamic acid, the results for sample G:1 being inconclusive.

The results from the blank solutions show that this, freshly prepared, sulphamic acid solution does contain some copper. The sulphamic acid used in the previous test had been stored for longer time in a glass bottle. Still, the copper content has to be adjusted for the content in the sulphamic acid itself. This was, however, not done for the raw data above. The results obtained from the QC samples and blank solutions show that the uncertainty of measurement is several orders of magnitude smaller than the variations occurring in the leaching procedure.

5.5 Measurement of metal content in water kept in contact with copper

During the various experiments, copper rods have been in contact with water for long periods in closed glass vials. Here the metal content in the water phase of the leached samples above, i.e. NUK:2, UK1:2, G:1 and J:1, was analysed and compared with water from identical vials without copper rods. Also reagent blank samples prepared at the time of analysis were included to rule out contamination caused by the acid used for preservation of the samples.

5.5.1 Method for analysis of copper in glass vial water

In this method, four different samples of water, kept in contact with copper specimens, were analysed i.e. NUK:2, UK1:2, G:1 and J:1. For each of these samples two reference blank samples of water that were prepared at the same time but stored without added copper were analysed. The obtained results from these blank samples should be subtracted from the values obtained from the water that has been in contact with copper. The results from the blank samples are indicative of the metal content caused by the original de-gassed water used and the glass in the vials. Glass is known to leach metals and during the preparation of the oxygen-free water and during degassing of the vials, the fluid could have been contaminated by glass as well as metal equipment. Elevated levels of certain metals were expected but should be stable if they originate from bulk water treatment or the glass vials used.

1. Glass vials containing copper specimens were opened inside an anaerobic box. The copper specimen was removed with plastic tweezers and leached as described above. The vials containing only water were opened outside the box. The water in all sample vials was preserved in a hood by adding nitric acid (Prolabo, Normatom© for trace metal analysis, VWR) to a final content of 1% by volume. Addition was made by an automatic pipette and the tip was rinsed with acid before addition to the samples. A separate vial was used as a template for measurement of the amount of water in the sample vials. The volume of sample water was obtained by adding water to a separate glass vial to reach the same level as inside the sample vial. Then the volume of added water was measured in a measuring glass and the added volume of acid was adjusted correspondingly to obtain 1% final content.
2. After addition of acid, all sample glass vials were sonicated in an ultrasonic bath for one hour and left to leach for another two hours before decanting the sample water to centrifuge tubes. The sonication was intended to improve the homogeneity of the samples and to dissolve any possible precipitated residues (no precipitates were detected by the eye).
3. As a reagent test, two centrifuge tubes were filled with fresh AGW and preserved with nitric acid as above. These two samples were used as background correction for contamination originating from both the centrifuge tubes and from the nitric acid used for preservation. For the whole test, centrifuge tubes from the same production batch and the same specific sealed bag were used (15 mL, Sarstedt, Germany, lid mounted at production).
4. The samples were prepared at Microbial Analytics AB 2015-01-15, posted 2015-01-16, received by the laboratory 2015-01-23, prepared 2015-01-26/27 and analysed 2015-01-29.

5.5.2 Results

All the four copper specimens were prepared outside our laboratory by the Department of chemistry at Uppsala University.

Sample NUK:2 all units in (µg L^{-1}) (ppb)

The NUK:2 sample consisted of an ultra-cleaned copper sheet prepared as described in Section 4.16. Results in bold are judged as suited for calculations, the other results are less accurate due to problems associated with detection limits, interferences or variations in the blank.

Table 5-11. Amounts of metals (µg L^{-1}) in the vials of the NUK:2 sample. Results in bold are judged as suited for calculations, the other results are less accurate due to problems associated with detection limits, interferences or variations in the blank. Values for Al and Zn in the glass blank were analysed one week later after dilution and concentrations might be affected by partial evaporation.

Metal	Reagent blank (average 2 centrifuge tubes)	Glass blank (average 2 vials)	Uncorrected sample	Corrected sample
Al	1.162	3,315.9	2,887.4	*–428.5*
Cr	–0.005	0.876	1.146	*0.270*
Mn	0.001	3.733	3.119	*–0.614*
Co	0.001	0.108	0.112	*0.004*
Ni	–0.0005	7.216	5.774	*–1.442*
Cu	0.121	1.655	2,082.9	**2,081**
Zn	0.350	3,299.6	3,086.4	*–213.2*
As	–0.030	0.089	2.418	**2.329**
Se	0.086	0.321	0.423	*0.102*
Ag	0.008	0.003	0.034	**0.031**
Cd	0.001	0.026	0.306	**0.280**
Pb	–0.008	1.542	20.025	**18.48**
U	0.001	0.024	0.014	*–0.010*

Table 5-12. Copper results (µg L^{-1}) for laboratory blank sample and QC sample, before and after the sample experiments.

Metal	Laboratory blank	QC (10 µg/L Cu)
Cu (before)	0.008	9.817
Cu (after)	0.008	9.865

Sample UK1:2, all units in (µg L^{-1}) (ppb)

The UK1:2 sample consisted of an ultra-cleaned copper sheet prepared as described in Section 4.16. Results in bold are judged as suited for calculations, the other results are less accurate due to problems associated with detection limits, interferences or variations in the blank.

Table 5-13. Amounts of metals (µg L^{-1}) in the vials of the UK1:2 sample. Results in bold are judged as suited for calculations, the other results are less accurate due to problems associated with detection limits, interferences or variations in the blank. Values for Al and Zn in the glass blank were analysed one week later after dilution and concentrations might be affected by partial evaporation.

Metal	Reagent blank (average 2 centrifuge tubes)	Glass blank (average 2 vials)	Uncorrected sample	Corrected sample
Al	1.162	3,315.9	2,818.6	*–497.3*
Cr	–0.005	0.876	1.253	*0.377*
Mn	0.001	3.733	3.712	*–0.021*
Co	0.001	0.108	0.104	*–0.004*
Ni	–0.0005	7.216	6.085	*–1.131*
Cu	0.121	1.655	1,626.1	**1,624.4**
Zn	0.350	3,299.6	2,534.4	*–765.2*
As	–0.030	0.089	0.099	*0.010*
Se	0.086	0.321	0.256	*–0.065*
Ag	0.008	0.003	0.035	**0.034**
Cd	0.001	0.026	0.049	**0.023**
Pb	–0.008	1.542	1.704	**0.162**
U	0.001	0.024	0.012	*–0.010*

Table 5-14. Copper results (µg L^{-1}) for laboratory blank sample and QC sample, before and after the sample experiments.

Metal	Laboratory blank	QC (10 µg/L Cu)
Cu (before)	0.008	9.817
Cu (after)	0.008	9.865

Sample G:1 (2014-03-24), all units in (µg L^{-1}) (ppb)

The G:1 sample was a sheet of OFHC copper prepared as described in Section 4.15. Results in bold are judged as suited for calculations, the other results are less accurate due to problems associated with detection limits, interferences or variations in the blank.

Table 5-15. Amounts of metals (µg L^{-1}) in the vials of the G:1 sample. Results in bold are judged as suited for calculations, the other results are less accurate due to problems associated with detection limits, interferences or variations in the blank. Values for Al and Zn in the glass blank were analysed one week later after dilution and concentrations might be affected by partial evaporation.

Metal	Reagent blank (average 2 centrifuge tubes)	Glass blank (average 2 vials)	Uncorrected sample	Corrected sample
Al	1.162	4,230.2	2,094.5	*–2,135.7*
Cr	–0.005	0.891	0.504	*–0.387*
Mn	0.001	2.791	2.41	*–0.381*
Co	0.001	0.136	0.062	*–0.074*
Ni	–0.0005	6.109	3.32	*–2.789*
Cu	0.121	4.449	1,654.1	**1,649.7**
Zn	0.350	8,612.8	2,191.2	*–6,421.6*
As	–0.030	0.122	0.107	*–0.015*
Se	0.086	0.621	0.253	*–0.368*
Ag	0.008	0.004	0.009	*0.005*
Cd	0.001	0.035	0.031	*–0.004*
Pb	–0.008	1.763	1.197	*–0.566*
U	0.001	0.029	0.012	*–0.017*

Table 5-16. Copper results (µg L^{-1}) for laboratory blank sample and QC sample, before and after the sample experiments.

Metal	Laboratory blank	QC (10 µg/L Cu)
Cu (before)	0.008	9.817
Cu (after)	0.008	9.865

Sample J:1 (2014-06-03), all units in (µg L^{-1}) (ppb):

The J:1 sample consisted of canister copper Cu(OFP) that was electro-polished in Uppsala as described in Section 4.14. Results in bold are judged as suited for calculations, the other results are less accurate due to problems associated with detection limits, interferences or variations in the blank.

Table 5-17. Amounts of metals (µg L^{-1}) in the vials of the J:1 sample. Results in bold are judged as suited for calculations, the other results are less accurate due to problems associated with detection limits, interferences or variations in the blank. Values for Al in the glass blank were analysed one week after dilution and concentrations might be affected by partial evaporation.

Metal	Reagent blank (average 2 centrifuge tubes)	Glass blank (average 2 vials)	Uncorrected sample	Corrected sample
Al	1.162	2,305	1,208.5	*–1,096.5*
Cr	–0.005	0.224	1.055	*0.831*
Mn	0.001	1.547	2.711	*1.164*
Co	0.001	0.023	4.973	**4.950**
Ni	–0.0005	3.356	5.615	*2.259*
Cu	0.121	1.695	1,815.4	**1,813.7**
Zn	0.350	35.41	63.97	**28.56**
As	–0.030	0.058	0.261	*0.203*
Se	0.086	0.103	0.078	*–0.025*
Ag	0.008	0.005	0.002	*–0.003*
Cd	0.001	0.095	0.084	*–0.011*
Pb	–0.008	1.039	2.207	*1.168*
U	0.001	0.015	0.004	*–0.011*

Table 5-18. Copper results (µg L^{-1}) for laboratory blank sample and QC sample, before and after the sample experiments.

Metal	Laboratory blank	QC (10 µg/L Cu)
Cu (before)	0.008	9.817
Cu (after)	0.008	9.865

5.5.3 Evaluation of the results

The results show that the preparation of oxygen-free water and the leaching of metals from the glass vials have caused contamination with some metals, but not with copper. A comparison between the reagent blank samples and the glass blank samples show this effect. They are both prepared with water from the same production unit and preserved with the same acid, the only difference being degassing and storage in glass. This contamination is expected especially for "technical metals" as Ni, Zn and Al that are readily present in and on laboratory equipment and known for severe contamination problems in trace metals analysis. Contamination originating from the bulk preparation of water should be constant and easily corrected for. Contamination from the glass vials should be fairly consistent throughout the sample experiments.

After preparation, all the vials are degassed in a gas bench. During this procedure there is a risk that particles from the gas bench could be forced into the vials via the gas flow. The gas bench is prepared with steel and brass parts, as well as valves of partly unknown metal composition and it was not optimised to minimise possible metal contamination. Remember that the method was originally designed for analysis of H_2 emission under O_2-free conditions. A contamination caused by metal oxide particles in the gas flow may have caused an uneven distribution between samples, something that could be the reason for the negative values in the corrected result (Ni) and the high concentrations of Zn and Al. It is possible to re-build the gas bench to a clean stainless steel system if deemed needed. Further, filters can be installed on the gassing lines, but due to the risk for O_2-contamiantion with two more connector positions, filters were not used. O_2-free conditions were deemed first priority.

Comparison between the results for glass blank samples associated with sample G:1 and J:1 respectively, indicates that most of the contamination has occurred already during the preparation steps. These glass blank samples were prepared using two different batches of oxygen-free water but were both left for more than half a year in the glass vials. The blank samples kept the longest time in the glass vials do show at higher level of contamination, but leaching from the surfaces of the vial is expected to be fastest in the beginning of the contact time. Because of this, the most probable source of extra contamination in the G:1 blank samples compared to the J:1 blank is the preparation and degassing step.

Cr, Co, Se, Cd and most notably Pb are known to leach from standard soda glass in a ratio determined by trace impurities in the bulk glass. The results show the necessity to use obtained values for metal content in the samples containing copper specimens only after subtraction of the values obtained from blank water prepared and stored in the same way as the sample water.

Fortunately, for copper the contamination level is relatively small and the ratio of glass blank to sample is high. The results for copper are therefore reliable and quantitative. Results for other metals should be used with care. Copper in the vials can be dissolved copper ions and it can be copper oxides on the glass walls. It can also be colloidal or precipitated copper oxides and fragments of metallic copper from the metal rods and stripes. The specimens were shipped two by two wrapped in plastic bags under O_2-free conditions and they were placed two by two in the glass vials. In retrospect, it may not have been the best procedure for these tests. Transport and placement in vials gave contact between the specimens and it cannot be excluded that very small particles of copper were ground off during transport and incubation. These particles will contribute to the amount of analysed copper in the vials. The addition of filtration steps can distinguish between dissolved and particulate copper phases. Separation of water from the vials before adding the nitric acid will distinguish between copper attached to the glass walls and copper dissolved or dispersed in the water.

References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.se/publications. References to SKB's unpublished documents are listed separately at the end of the reference list. Unpublished documents will be submitted upon request to document@skb.se.

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Unpublished documents

SKBdoc id, version	Title	Issuer, year
SKBdoc 1470267 ver 1.0.	Copper in ultrapure water.	Svensk Kärnbränslehantering AB.

Appendix A

Sample data

A1 Test of stopper integrity

A1.1 Pressure kPa

Day	ND1:1	ND1:2	ND2:1	ND2:2	ND3:1	ND3:2	ND4:1	ND4:2	ND5:1	ND5:2
1	126	114	114	123	124	123	121	122	122	119
5	122	110	110	120	119	119	120	119	121	116
12	120	109	108	119	117	117	117	117	118	114
40	117	108	107	117	114	115	115	115	116	111
74	114	104	102	111	107	109	110	109	110	104
96	110	99	98	105	100	104	104	102	104	99

A1.2 H_2 mbar

Day	ND1:1	ND1:2	ND2:1	ND2:2	ND3:1	ND3:2	ND4:1	ND4:2	ND5:1	ND5:2
1	4.363	1.305	1.306	4.568	4.765	3.899	4.067	3.669	3.111	2.837
5	4.287	0.998	1.173	4.361	4.372	4.112	3.828	3.582	2.663	2.738
12	4.252	0.996	1.225	4.373	4.111	4.291	4.240	4.100	3.018	2.820
40	3.628	0.776	0.965	3.824	3.632	3.979	3.725	3.823	2.786	2.591
74	3.828	0.807	1.032	3.985		4.117			2.513	2.334
96	4.358	0.792	0.892	3.886	3.297	3.360	3.581	3.251	2.296	2.157

A2 N1

A2.1 Volume gas mL

Day	N1:1	N1:2	N1:3	N1:4	N1:5	N1:6	N1:7	N1:8	N1:9	N1:10
0	5.9	5.8	5.4	6.0	5.9	6.0	5.9	5.8	5.7	5.7
46	5.4	5.2	5.7	5.8	5.7	5.9	5.4	5.4	5.3	5.9
189	5.4	5.2	5.7	5.8	5.7	5.9	5.4	5.4	5.3	5.9
288	5.4	5.2	5.7	5.8	5.7	5.9	5.4	5.4	5.3	5.9

A2.2 Pressure kPa

Day	N1:1	N1:2	N1:3	N1:4	N1:5	N1:6	N1:7	N1:8	N1:9	N1:10
2	146	148	149	148	147	148	149	148	146	142
8	137	138	139	138	137	138	138	137	137	134
15	125	127	127	125	131	132	132	131	132	129
22				124			128			
30	122			119			123			126
37	116	123	123	114	127	128	118	127	121	120
43	113	117	118	111	122	122	114	121	118	114
46	183	182	179	183	183	183	182	183	182	182
51	170	170	168	172	172	173	171	171	172	172
56	162	163	161	163	162	167	164	162	165	165
64	154	154	152	154	152	155	154	154	153	153
78	149	149	144	150	155	149	150	149	148	144
92	139	136	132	140	141	141	142	140	139	132
156	133	130	125	133	134	134	135	134	129	121
186	133	131	125	133	134	131	124	135	118	111
189			190			190		190		
219	185	168	174	184	185	151	181	178	118	183
244	177	161	163	173	172	146	173	169	100	138
282	159	123	144	156	142	100	150	146	100	125
288	197	199	196	197	196	196	194	195	191	192
330	170	167	168	170	174	178	171	167	168	168
361	159	158	157	159	161	167	154	159	161	158
387	150	148	148	150	153	160	146	149	100	147
456	141	131	138	140	142	147	137	139	100	137
841	129	130	129	131	135	139	129	130	100	130

A2.3 H_2 mbar

Day	N1:1	N1:2	N1:3	N1:4	N1:5	N1:6	N1:7	N1:8	N1:9	N1:10
2	0.029	0.015	0.015	0.015	0.044	0.030	0.030	0.015	0.029	0.028
8	0.137	0.110	0.097	0.179	0.164	0.110	0.097	0.110	0.192	0.107
15	0.150	0.152	0.140	0.213	0.197	0.145	0.132	0.157	0.224	0.129
22				0.223			0.128			
30	0.098			0.405			0.172			0.101
37	0.104	0.283	0.467	0.684	0.191	0.179	0.366	0.686	0.145	0.120
43	0.102	0.374	0.696	0.955	0.329	0.293	0.581	0.968	0.142	0.194
46	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018
51	0.068	0.136	0.067	0.189	0.069	0.069	0.171	0.137	0.120	0.258
56	0.081	0.293	0.081	0.571	0.292	0.200	0.361	0.405	0.149	0.330
64	0.123	0.400	0.091	0.862	0.395	0.295	0.508	0.585	0.245	0.474
78	0.328	0.760	0.302	1.305	0.760	0.581	0.960	1.177	0.592	0.922
92	0.500	0.966	0.647	2.030	0.945	0.902	1.349	1.498	0.653	0.964
156	1.383	2.236	2.025	3.511	1.715	2.037	2.538	2.760	1.677	1.912
186	1.676	2.253	2.025	3.458	1.849	2.175	2.505	2.943	1.534	1.554
189			0.076			0.076		0.038		
219	1.146	0.571	1.183	1.028	0.776	0.754	0.795	0.533	0.613	0.550
244	1.469	0.596	1.092	1.003	0.705	0.949	1.055	0.930	0.450	0.869
282	1.367	0.849	1.066	1.622	0.341	0.740	1.230	1.168	0.140	1.050
288	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
330	0.544	0.718	0.857	0.884	0.679	0.018	0.804	0.785	0.084	0.101
361	0.986	0.758	0.989	1.161	0.757	1.069	1.001	1.049	0.129	0.142
387	1.200	1.066	1.317	1.320	0.949	1.280	1.095	1.281	0.060	0.132
456	1.184	1.022	1.256	1.456	0.994	1.161	1.069	1.571	0.050	0.754
841	1.046	1.016	1.277	1.613	1.074	1.517	1.638	1.284	0.052	1.540

A2.4 O_2 mbar

Day	N1:1	N1:2	N1:3	N1:4	N1:5	N1:6	N1:7	N1:8	N1:9	N1:10
2	3.387	2.679	2.727	3.019	2.764	2.930	2.771	2.990	2.862	2.954
8	1.411	1.352	1.293	1.311	1.589	1.463	1.822	1.466	1.233	1.112
15	0.488	0.965	0.737	0.938	0.576	0.726	1.122	0.432	0.766	0.529
22				0.918			0.973			
30	0.537			0.738			1.009			0.592
37	0.998	0.677	0.443	0.855	0.445	0.755	0.991	0.699	1.004	0.912
43	0.486	0.433	0.330	0.422	0.695	0.708	0.570	0.557	0.779	0.536
46	1.318	1.383	2.166	1.135	1.190	1.190	1.110	1.244	1.329	1.274
51	0.527	1.241	0.571	0.430	0.378	0.484	0.787	0.462	0.310	0.378
56	0.778	0.277	0.322	0.571	0.778	0.818	0.869	0.680	0.594	0.446
64	0.847	0.508	0.517	0.755	0.973	0.620	0.662	0.631	0.627	0.918
78	0.358	0.387	0.187	0.645	0.295	0.283	0.330	1.341	1.243	0.792
92	0.904	0.966	0.805	1.218	0.902	0.902	1.250	0.742	0.820	1.122
156	1.942	2.210	2.000	2.527	2.278	1.715	1.485	2.064	1.987	1.525
186	1.410	0.996	1.350	1.011	1.126	1.100	1.761	1.215	1.180	1.443
189			1.368			1.634		2.318		
219	1.478	0.941	1.601	2.056	1.256	1.237	2.747	2.556	1.673	2.898
244	0.177	0.177	0.277	0.363	0.671	0.803	0.433	0.355	25.470	0.635
282	1.304	1.156	1.152	0.671	0.241	12.600	0.360	0.715	62.300	0.850
288	1.458	1.114	1.254	1.714	1.509	1.842	1.300	1.950	0.478	1.478
330	0.850	0.802	1.042	1.258	1.183	1.050	1.009	0.668	0.722	0.874
361	0.286	0.332	0.251	0.127	0.129	0.217	0.246	0.557	0.644	0.379
387	1.080	1.450	1.332	1.290	0.887	0.752	0.642	1.356	61.750	1.455
456	1.058	0.616	0.911	0.980	0.937	0.632	0.863	0.737	15.280	0.630
841	0.052	<LOD	<LOD	<LOD	<LOD	0.028	<LOD	<LOD	1.710	<LOD

A3 N2

A3.1 Volume gas mL

Day	N2:1	N2:2	N2:3	N2:4	N2:5	N2:6	N2:7	N2:8	N2:9	N2:10
0	5.9	5.9	5.9	5.4	5.5	5.5	5.8	5.7	5.9	5.6
185	5.9	5.9	5.9	5.4	5.5	5.5	5.8	5.7	5.9	5.6
288	5.9	5.9	5.9	5.4	5.5	5.5	5.8	5.7	5.9	5.6

A3.2 Pressure kPa

Day	N2:1	N2:2	N2:3	N2:4	N2:5	N2:6	N2:7	N2:8	N2:9	N2:10
0	147	148	147	147	147	147	149	146	146	145
7	136	133	133	134	134	134	133	133	135	132
15	131	129	133	130	130	130	129	128	130	130
21				126			124			
29	126			121			119			124
36	119	124	127	116	124	126	115	124	124	119
42			123			119			119	
77	116	123	121	115	120	118	113	119	119	116
155	109	112	115	109	114	112	110	113	114	110
183	114	116	119	114	118	115	114	116	117	115
185		185			186			185		
216	184	169	179	178	170	154	178	170	180	177
247	173	156	171	168	127	100	169	158	171	167
280	159	143	157	154	117	100	154	144	155	100
288	197					182				195
329	207	198	197	150	121	113	149	140	126	140
359	185	181	181	135	119	100	143	134	111	112
384	177	174	173	131	118	100	137	129	119	128
447	165	160	116	113	107	100	128	122	114	100
846	153	146	112	112	105	100	124	105	114	103

A3.3 H_2 mbar

Day	N2:1	N2:2	N2:3	N2:4	N2:5	N2:6	N2:7	N2:8	N2:9	N2:10
0	0.015	0.015	0.015	0.015	0.015	0.015	0.015	<LOD	0.015	<LOD
7	0.095	0.319	0.200	0.121	0.201	0.147	0.093	0.133	0.135	0.238
15	0.131	0.297	0.200	0.143	0.208	0.169	0.103	0.166	0.182	0.234
21				0.151			0.087			
29	0.088			0.230			0.083			0.136
36	0.107	0.707	0.318	0.464	0.124	0.113	0.058	0.645	0.112	0.119
42			0.406			0.131			0.083	
77	1.114	2.263	1.464	2.013	0.360	0.319	0.090	2.166	0.286	1.427
155	2.398	3.360	3.450	3.444	1.322	1.142	0.946	3.639	1.322	3.124
183	2.326	2.877	3.189	2.873	1.204	1.012	1.094	3.318	1.427	2.967
185	0.050	0.074	0.050	0.050	0.037	0.050	0.050	0.074	0.050	0.050
216	0.807	0.812	0.933	0.818	0.477	0.525	0.499	0.984	0.611	0.884
247	1.159	1.201	1.146	1.193	0.533	0.190	0.642	1.059	0.804	1.152
280	1.288	1.030	1.523	1.263	0.608	0.120	0.862	1.526	1.457	1.110
288	<LOD					0.018				<LOD
329	0.828	0.970	1.024	0.015	0.048	0.034	0.164	0.154	0.164	0.196
359	1.110	1.267	1.321	0.783	0.762	0.080	0.815	0.978	0.733	0.986
384	1.239	1.479	1.505	0.996	0.909	0.080	1.041	1.006	0.774	1.075
447	1.502	1.584	0.626	0.814	0.770	0.060	1.165	1.391	1.208	0.150
846	1.378	1.491	0.997	1.739	1.271	0.000	1.042	0.693	1.098	0.699

A3.4 O_2 mbar

Day	N2:1	N2:2	N2:3	N2:4	N2:5	N2:6	N2:7	N2:8	N2:9	N2:10
0	3.528	2.871	3.102	3.087	3.219	2.690	3.025	3.037	2.599	3.350
7	1.700	1.024	0.918	1.099	1.072	1.112	0.878	0.705	1.391	1.373
15	0.563	0.593	0.599	0.741	0.663	0.988	0.955	0.960	0.936	1.027
21				0.479			0.682			
29	0.517			0.629			0.785			0.496
36	0.809	0.856	0.914	1.125	0.744	0.832	0.713	0.880	0.645	0.524
42			0.554			0.702			0.714	
77	0.232	0.357	0.254	0.207	0.300	0.354	0.249	0.226	0.262	1.612
155	0.981	2.464	2.760	2.856	2.052	1.747	1.694	1.944	1.550	1.782
183	2.212	2.042	1.904	1.870	2.454	2.139	2.212	2.158	2.129	2.162
185		1.036			1.488			1.480		
216	1.908	1.726	1.650	2.347	0.409	1.636	2.281	1.730	2.086	2.475
247	1.176	1.513	0.838	1.344	0.864	0.990	1.082	1.375	1.077	1.420
280	1.208	1.101	1.287	1.448	0.959	22.300	1.340	1.008	1.349	0.840
288	1.872					2.148				2.126
329	0.890	1.426	2.738	1.485	0.436	1.040	0.805	0.686	1.172	0.630
359	2.165	1.738	1.629	1.418	1.226	18.240	1.473	1.005	1.188	1.288
384	0.336	0.313	0.225	0.603	0.472	0.430	0.754	0.774	0.726	0.845
447	1.172	0.912	1.786	2.192	4.515	19.460	0.499	1.403	0.798	6.850
846	0.107	0.132	19.365	<LOD	<LOD	10.930	23.380	7.140	2.849	22.369

A4 N3

A4.1 Volume gas mL

Day	N3:1	N3:2	N3:3	N3:4	N3:5	N3:6	N3:7	N3:8	N3:9	N3:10
0	10.9	10.3	10.3	10.5	10.3	5.5	5.9	5.9	6.6	5.9
43	6.2	5.4	5.6	5.8	5.6	4.7	5.0	5.2	5.7	5.1
244	6.2	5.4	5.6	5.8	5.6	4.7	5.0	5.2	5.7	5.1
291	6.2	5.4	5.6	5.8	5.6	4.7	5.0	5.2	5.7	5.1

A4.2 Pressure kPa

Day	N3:1	N3:2	N3:3	N3:4	N3:5	N3:6	N3:7	N3:8	N3:9	N3:10
0	158	159	159	163	146	150	142	156	156	156
5	145	153	152	153	140	139	131	142	142	139
13	144	151	149	149	138	133	128	138	136	135
19	138	140	139	141	133	127	124	129	128	127
27	133	136	135	135	131	122	120	124	124	123
34	132	130	133	132	127	118	116	120	118	118
40	127	127	127	128	123	114	114	117	115	114
43	185	185	170	185	176	183	184	184	183	184
48	174	173	158	173	166	170	170	173	171	170
56	164	167	150	166	160	162	163	164	162	161
61	156	157	138	157	150	152	153	154	152	153
68	151	150	109	153	144	148	148	151	146	146
76	145	142	103	145	143	144	140	143	140	137
89	137	134	100	138	135	136	134	137	132	134
153	130	117	85	131	126	128	128	128	123	127
210	99.5	102	93.9	129	123	125	126	126	118	124
244	173	178	101	179	178	180	176	179	170	184
288	158	151	90	163	159	158	159	134	144	132
291	205			205			204			203
330	197	191	193	193	197	194	191	195	195	189
364	181	179	182	181	182	180	175	183	182	178
385	166	168	172	171	174	167	164	170	163	163
446	153	157	160	158	159	156	148	158	152	153
846		138	143	146	146	128	134	132	141	135

A4.3 H_2 mbar

Day	N3:1	N3:2	N3:3	N3:4	N3:5	N3:6	N3:7	N3:8	N3:9	N3:10
0	0.016	0.016	0.016	0.016	0.029	0.015	0.014	0.031	0.031	0.031
5	0.044	0.046	0.106	0.122	0.126	0.056	0.105	0.057	0.099	0.153
13	0.086	0.076	0.164	0.194	0.193	0.333	0.973	0.276	0.626	0.932
19	0.083	0.042	0.056	0.169	0.186	0.635	1.488	0.490	0.960	1.422
27	0.093	0.068	0.095	0.135	0.144	0.927	2.328	0.707	1.228	1.611
34	0.092	0.065	0.106	0.132	0.140	1.121	3.004	0.840	1.546	2.360
40	0.102	0.064	0.102	0.141	0.135	1.334	3.466	1.006	1.323	2.417
43	0.019	0.019	0.034	0.019	0.018	0.037	0.018	0.018	0.055	0.037
48	0.035	0.035	0.000	0.035	0.050	0.425	0.442	0.087	0.171	0.306
56	0.033	0.033	0.045	0.033	0.048	0.599	0.831	0.328	0.583	0.596
61	0.062	0.047	0.041	0.047	0.060	0.836	1.760	0.662	0.760	1.132
68	0.060	0.030	0.033	0.046	0.058	0.873	1.421	0.529	0.978	1.285
76	0.073	0.043	0.031	0.073	0.057	1.152	2.142	0.815	1.218	1.452
89	0.082	0.040	0.040	0.069	0.081	1.455	2.653	0.932	1.465	2.050
153	0.130	0.070	0.068	0.131	0.101	3.174	4.736	1.690	2.706	2.946
210	0.139	0.102	0.169	0.181	0.172	3.300	4.612	1.991	2.761	3.323
244	0.017	0.036	0.010	0.036	0.018	0.144	0.176	0.090	0.153	0.166
288	0.063	0.015	0.027	0.033	0.032	0.901	1.065	0.496	0.835	0.990
291	0.123			0.041			0.061			0.081
330	0.236	0.153	0.135	0.135	0.177	0.892	0.974	0.566	0.761	0.718
364	0.326	0.179	0.237	0.235	0.291	1.260	1.925	0.805	1.219	0.979
385	0.199	0.151	0.172	0.120	0.139	1.069	1.230	0.935	1.043	0.913
446	0.179	0.126	0.128	0.111	0.149	1.175	1.236	0.966	1.019	1.079
846		0.097	0.072	0.146	0.131	1.139	1.742	0.871	1.763	1.310

A4.4 O_2 mbar

Day	N3:1	N3:2	N3:3	N3:4	N3:5	N3:6	N3:7	N3:8	N3:9	N3:10
0	1.327	0.906	0.890	0.750	0.569	1.020	0.966	1.061	0.530	1.373
5	1.465	0.918	1.459	1.469	0.001	1.473	1.205	1.548	1.406	1.265
13	1.224	1.208	1.237	1.401	1.007	0.918	0.870	1.007	1.129	0.702
19	1.076	1.148	0.723	0.832	0.745	1.143	0.794	0.839	0.998	1.168
27	0.572	0.734	0.635	0.594	0.603	0.549	0.564	0.670	0.471	0.381
34	0.990	0.624	0.878	0.726	0.610	0.590	0.719	0.540	0.460	0.684
40	0.775	0.762	0.495	0.614	0.603	0.730	0.502	0.503	0.391	0.741
43	1.351	0.611	1.785	0.537	0.440	0.421	0.258	0.497	1.080	0.589
48	0.661	0.934	1.880	0.311	1.394	1.428	0.476	0.329	0.633	0.782
56	0.754	0.618	1.050	0.365	0.448	0.875	0.717	0.820	0.616	0.081
61	0.452	0.707	1.063	0.973	0.225	0.471	0.168	0.785	0.091	0.184
68	0.196	0.825	0.316	0.337	0.274	0.266	0.207	0.181	0.613	0.672
76	0.493	0.369	0.618	0.348	0.329	0.115	0.182	0.200	0.392	0.247
89	0.712	0.831	0.720	0.925	1.067	0.639	0.817	0.877	1.043	1.018
153	1.794	1.989	33.116	1.336	2.041	1.434	1.229	0.947	2.435	1.880
210	1.592	1.999	22.780	2.374	2.558	2.625	2.041	1.361	0.920	1.686
244	1.367	2.047	2.091	1.718	0.801	0.720	0.458	1.325	0.374	0.276
288	0.142	0.136	1.053	0.114	0.111	0.111	1.081	1.662	1.886	1.782
291	2.358			2.276			1.102			1.908
330	0.217	0.115	1.197	0.676	0.591	0.582	0.554	0.624	0.663	0.132
364	0.091	0.627	0.146	1.629	0.091	0.162	0.928	0.146	0.073	0.249
385	1.112	1.126	0.946	0.821	1.009	0.919	0.902	0.969	1.434	1.304
446	1.447	1.416	1.791	1.460	1.711	1.321	1.110	1.338	1.569	0.598
846		0.138	0.100	4.745	3.110	0.090	0.094	0.092	0.437	0.567

A5 N4

A5.1 Volume gas mL

Day	N4:1	N4:2	N4:3	N4:4	N4:5	N4:6	N4:7	N4:8	N4:9	N4:10
0	10.2	10.4	10.9	10.1	10.3	6.2	5.8	5.8	6.0	5.9
179	10.2	10.4	10.9	10.1	10.3	6.2	5.8	5.8	6.0	5.9
281	10.2	10.4	10.9	10.1	10.3	6.2	5.8	5.8	6.0	5.9

A5.2 Pressure kPa

Day	N4:1	N4:2	N4:3	N4:4	N4:5	N4:6	N4:7	N4:8	N4:9	N4:10
0	146	146	147	145	146	140	146	143	143	143
8	144	143	142	142	141	132	134	134	133	132
15	140	139	139	136	137	128	127	127	127	126
23	137	136	135	133	134	123	123	122	123	121
30	134	131	131	130	133	120	119	117	118	117
36	131	128	128	127	128	115	114	113	115	114
70	130	127	127	127	127	116	112	112	113	111
86	126	123	123	122	122	110	108	108	109	108
151	120	121	120	120	120	108	107	106	107	105
178	124	123	124	123	123	111	109	110	110	108
179		193			193		188		188	
211	188	100	171	190	186	183	152	136	144	181
241	179		100	185	171	175	100	128	125	90
274	165		100	172	138	159	100	112	100	100
281	206					201				204
322	201		198	200	199	189	192	190	191	190
353	191		188	186	190	177	180	178	101	177
379	185		161	180	185	169	171	169	90	167
442	160		155	173	177	158	156	162	96	155

A5.3 H_2 mbar

Day	N4:1	N4:2	N4:3	N4:4	N4:5	N4:6	N4:7	N4:8	N4:9	N4:10
0	0.015	0.029	0.029	0.015	0.029	0.028	0.044	0.072	0.072	0.072
8	0.115	0.114	0.128	0.114	0.127	0.145	0.134	0.134	0.146	0.158
15	0.126	0.125	0.153	0.068	0.082	0.192	0.152	0.305	0.267	0.202
23	0.096	0.095	0.108	0.067	0.080	0.566	0.640	1.074	0.480	0.762
30	0.080	0.105	0.118	0.078	0.106	0.840	1.012	1.509	1.168	1.158
36	0.079	0.090	0.102	0.076	0.090	1.012	1.368	1.819	1.415	1.482
70	0.078	0.102	0.114	0.102	0.114	2.807	3.461	4.200	3.311	3.485
86	0.076	0.086	0.123	0.085	0.110	3.069	3.391	4.612	3.379	3.380
151	0.096	0.097	0.120	0.108	0.108	3.953	4.537	6.424	4.130	4.746
178	0.074	0.123	0.099	0.098	0.098	4.196	2.703	5.742	3.476	3.326
179		0.077			0.077		0.075		0.075	
211	0.075	0.181	0.376	0.076	0.074	0.694	0.636	1.034	0.606	0.362
241	0.090		0.150	0.074	0.086	1.103	0.240	1.536	1.138	0.036
274	0.066		0.140	0.086	0.069	1.495	0.020	1.478	0.870	0.020
281	<LOD				<LOD					<LOD
322	0.020		0.020	0.040	0.040	0.926	0.058	1.045	0.115	0.076
353	0.057		0.056	0.056	0.057	1.257	0.090	1.299	0.374	0.089
379	0.056		0.032	0.036	0.037	1.318	0.086	1.352	0.504	0.084
442	0.056		0.093	0.081	0.042	1.912	0.110	1.658	0.903	0.128

A5.4 O_2 mbar

Day	N4:1	N4:2	N4:3	N4:4	N4:5	N4:6	N4:7	N4:8	N4:9	N4:10
0	1.898	1.971	1.735	1.726	1.445	2.450	2.351	2.917	5.777	2.760
8	2.419	2.345	1.917	2.258	2.256	1.676	1.514	1.528	1.636	1.597
15	1.918	1.654	1.571	1.482	1.384	1.062	0.927	1.041	1.067	1.222
23	1.315	1.224	0.986	1.077	0.992	0.529	0.726	0.561	0.812	0.242
30	1.085	1.153	1.100	1.300	1.264	0.840	0.643	0.398	0.968	0.878
36	1.048	1.024	0.845	0.838	1.011	0.621	0.684	0.441	0.909	0.467
70	0.520	0.864	0.648	0.533	0.254	0.719	0.571	0.683	0.746	0.588
86	0.857	0.935	1.156	0.805	0.805	0.759	1.058	0.767	0.654	0.767
151	2.160	1.888	1.596	1.344	0.132	1.858	0.942	0.678	0.792	1.176
178	2.083	0.344	0.868	0.689	0.443	0.488	1.373	0.924	0.880	0.842
179		1.081			0.772		7.182		0.564	
211	2.257	6.219	1.642	1.599	2.043	1.534	1.757	1.115	1.182	0.616
241	1.164		0.850	1.369	1.009	0.490	30.000	0.960	0.363	30.492
274	1.164		0.850	1.369	1.009	0.490	30.000	0.960	0.363	30.492
281	1.669		0.000	0.000	0.000	0.864	0.000	0.000	0.000	0.877
322	0.181		0.218	0.200	0.239	0.170	0.269	0.342	0.802	0.304
353	1.681		1.767	1.916	1.634	2.071	1.602	1.940	2.394	1.682
379	0.981		0.950	0.900	0.648	0.744	0.855	0.761	4.329	0.818
442	0.938		0.775	0.790	1.597	0.996	1.101	1.267	4.821	1.028

A6 N5

A6.1 Volume gas mL

Day	N5:1	N5:2	N5:3	N5:4	N5:5	N5:6	N5:7	N5:8	N5:9	N5:10
0	5.4	5.9	5.9	5.9	5.8	5.6	5.4	5.6	6.2	5.9
45	5.1	5.6	5.3	5.1	5.2	5.1	4.8	5.3	5.9	5.5
233		5.6	5.3	5.1	5.2	5.1	4.8	5.3	5.9	5.5
280		5.6	5.3	5.1	5.2	5.1	4.8	5.3	6.4	5.5

A6.2 Pressure kPa

Day	N5:1	N5:2	N5:3	N5:4	N5:5	N5:6	N5:7	N5:8	N5:9	N5:10
0	152	152	151	152	152	152	152	153	153	153
7	144	145	144	144	144	142	136	142	143	143
15	134	135	136	136	135	135	125	137	136	135
22	129	131	130	131	130	129	119	129	130	131
30	124	127	127	124	123	117	113	126	124	124
36	121	122	124	122	123	117	100	122	122	123
42	120	120	121	121	121	115		119	120	121
45	182	183	183	184	183	185	184	187	186	185
51	165	165	161	163	165	167	129	169	158	168
57	159	141	148	156	157	158	113	160	151	157
66	152	138	141	148	146	147	103	153	146	145
78	143	128	135	142	136	138	102	145	138	129
144	136	123	126	133	128	129	100	135	131	121
199	134	106	124	132	118	127	100	134	128	121
233		178	150	176	171	180	100	182	181	181
280		123	121	159	139	154	90	162	152	158
280		197			196			198		
319		185	188	197	182	200	190	185	197	196
353		173	176	182	169	184	177	175	187	183
374		163	163	172	157	172	123	151	174	173

A6.3 H_2 mbar

Day	N5:1	N5:2	N5:3	N5:4	N5:5	N5:6	N5:7	N5:8	N5:9	N5:10
0	0.015	0.061	0.030	0.015	0.061	0.015	0.030	0.031	0.031	0.046
7	0.317	0.232	0.158	0.173	0.158	0.667	0.299	0.398	0.486	0.472
15	0.817	0.621	0.326	0.394	0.284	1.431	0.600	0.891	1.238	0.945
22	1.484	1.114	0.650	0.681	0.728	1.651	0.916	1.251	1.248	1.493
30	1.724	1.422	0.737	0.831	0.640	2.586	0.983	1.651	1.637	1.810
36	1.803	1.952	0.918	1.000	0.787	2.750	0.850	1.952	1.903	2.030
42	2.988	2.280	1.089	1.258	0.932	3.600	0.000	1.999	2.196	2.868
45	0.036	0.018	0.000	0.000	0.018	0.037	0.018	0.019	0.019	0.019
51	0.116	0.165	0.129	0.391	0.099	0.317	0.116	0.101	0.190	0.269
57	0.525	0.423	0.296	0.374	0.251	0.664	0.305	0.336	0.453	0.628
66	0.821	0.787	0.536	0.607	0.482	1.044	0.587	0.627	0.891	1.001
78	1.416	1.408	0.878	1.037	0.857	1.739	0.847	1.175	1.187	1.393
144	4.053	4.871	1.764	1.968	2.355	3.354	1.760	2.727	3.223	4.743
199	3.136	2.544	1.538	2.350	2.289	2.946	0.740	3.511	3.277	3.219
233		0.125	0.105	0.141	0.103	0.162	0.040	0.182	0.163	0.199
280		0.726	0.653	0.731	0.778	0.986	0.063	0.940	1.049	0.980
280		0.079			0.078			0.099		
319		1.018	0.884	0.827	1.037	0.280	0.266	1.018	1.123	1.000
353		1.488	1.214	1.365	1.268	1.509	0.319	1.540	1.346	1.757
374		1.467	0.929	1.032	1.005	1.393	0.197	1.223	1.357	1.471

A7 O_2 mbar

Day	N5:1	N5:2	N5:3	N5:4	N5:5	N5:6	N5:7	N5:8	N5:9	N5:10
0	0.684	0.684	1.102	0.714	0.699	0.410	1.429	1.362	1.239	1.408
7	0.835	1.349	1.282	1.296	1.166	1.008	0.707	1.420	0.672	0.629
15	0.710	0.621	0.612	0.857	0.446	0.783	0.338	0.699	0.830	0.459
22	0.619	0.825	1.248	0.707	1.508	0.658	0.928	0.748	0.533	0.524
30	0.818	0.686	0.584	0.930	0.689	0.199	0.633	0.491	0.422	0.620
36	0.895	0.927	0.918	0.817	0.812	0.538	0.850	0.598	0.464	0.763
42	0.624	0.372	0.339	0.666	0.641	0.587		0.559	0.684	0.629
45	0.364	0.311	0.165	0.644	0.421	0.796	0.515	0.449	0.781	0.407
51	0.512	1.007	0.676	0.179	0.149	0.451	0.464	0.558	0.569	0.823
57	0.382	1.523	0.562	0.499	0.267	0.711	0.294	0.512	0.408	0.565
66	0.471	0.248	0.451	0.400	0.467	0.603	0.350	0.428	0.540	0.406
78	0.758	0.627	0.716	0.738	0.666	0.800	0.561	0.696	0.704	0.671
144	0.136	2.780	1.487	0.532	1.638	0.800	0.740	0.729	0.917	1.113
199	0.590	1.675	1.042	2.086	1.794	2.489	3.300	2.090	2.176	1.525
233		1.798	1.140	1.549	1.197	1.332	1.810	1.438	1.412	1.466
280		1.292	1.355	1.399	1.223	1.525	13.383	1.312	1.581	1.169
280		1.911			0.902			0.851		
319		0.148	0.169	0.020	0.892	0.860	0.703	0.925	0.177	0.118
353		0.069	0.070	0.091	0.068	0.092	0.089	0.053	0.075	0.110
374		0.962	0.815	1.032	0.816	0.636	0.836	1.012	1.427	0.934

A8 N6

A8.1 Volume gas mL

Day	N6:1	N6:2	N6:3	N6:4	N6:5	N6:6	N6:7	N6:8	N6:9	N6:10
0	5.9	5.7	5.4	5.6	5.4	5.4	5.7	6.0	5.4	5.8
165	5.9	5.7	5.4	5.6	5.4	5.4	5.7	6.0	5.4	5.8
267	5.9	5.7	5.4	5.6	5.4	5.4	5.7	6.0	5.4	5.8

A8.2 Pressure kPa

Day	N6:1	N6:2	N6:3	N6:4	N6:5	N6:6	N6:7	N6:8	N6:9	N6:10
0	189	177	188	187	189	188	187	188	188	188
8	172	163	171	172	168	175	173	175	173	172
14	165	157	159	165	160	164	140	166	140	165
23	155	147	148	156	151	151	133	155	111	147
29	150	143	142	151	146	121	131	151	100	139
36	146	137	140	147	141	121	123	139		126
42	140	133	134	139	133	112	108	128		120
49	136	128	130	136	129	112	108	122	100	117
56	132	124	125	131	126	102	101	119	95	111
136	126	116	112	126	119	93	99	113	89	101
164	128	118	116	127	119	102	105	113	99	103
165			190			190			177	
197	187	183	114	181	180	129	184	100	100	172
228	179	130	100	137	170	122	133	100	100	108
261	144	100	100	100	148	110	112	100	101	100
267	208	203	206	207	209	205	210	209	206	193
308	182	189	192	191	136	189	191	195	192	178
340	182	177	179	179	130	177	177	181	179	166
365	172	167	168	168	121	139	167	171	170	156
826	151	142	146	144	109	126	145	152	144	142

A8.3 H_2 mbar

Day	N6:1	N6:2	N6:3	N6:4	N6:5	N6:6	N6:7	N6:8	N6:9	N6:10
0	<LOD	0.035	0.038	0.037	0.057	0.038	0.037	0.056	0.094	0.038
8	0.189	0.636	0.188	0.172	0.151	0.578	0.190	0.315	0.277	0.155
14	0.264	0.785	0.398	0.330	0.288	1.148	0.322	0.730	0.546	0.248
23	0.403	0.838	0.533	0.468	0.408	1.389	0.359	0.915	0.655	0.323
29	0.480	0.972	0.781	0.634	0.642	1.670	0.524	1.087	0.740	0.445
36	0.701	1.302	1.106	0.897	0.874	1.827	0.713	1.432		0.567
42	0.756	1.170	1.045	0.834	0.825	1.870	0.724	1.267		0.552
49	0.966	1.357	1.261	1.034	1.277			1.696		0.702
56	1.069	1.476	1.350	1.087	1.235	2.060	1.192	1.547	0.418	0.666
136	2.671	2.320	2.038	2.092	1.904	1.507	2.950	2.983	0.285	1.818
164	2.355	1.581	1.763	2.083	2.047	0.673	2.898	1.672	0.079	0.824
165			0.038			0.038			0.035	
197	0.560	0.000	0.592	0.650	0.647	0.077	0.955	0.360	0.080	0.103
228	0.985	0.585	0.140	0.740	1.037	0.098	0.851	0.180	0.040	0.162
261	1.008	0.450	0.040	0.280	0.903	0.077	1.030	0.130	0.040	0.300
267	<LOD	<LOD	0.021	<LOD	0.002	<LOD	<LOD	<LOD	0.021	<LOD
308	0.473	0.643	0.096	0.096	0.544	0.095	0.936	0.078	0.134	0.587
340	1.037	1.027	0.125	0.107	0.936	0.106	1.381	0.109	0.090	1.062
365	1.118	0.935	0.151	0.118	1.077	0.097	1.286	0.137	0.085	1.061
826	1.510	1.079	0.380	1.166	1.036	0.189	1.726	0.122	0.144	1.690

A8.4 O_2 mbar

Day	N6:1	N6:2	N6:3	N6:4	N6:5	N6:6	N6:7	N6:8	N6:9	N6:10
0	0.851	1.469	1.260	0.823	0.907	1.147	1.664	1.466	1.147	0.978
8	1.015	0.880	0.923	0.843	0.924	0.840	0.571	0.735	0.865	0.980
14	1.370	0.816	0.811	1.139	0.544	0.689	0.952	0.830	0.742	0.429
23	0.946	0.588	0.429	0.842	0.393	0.649	0.612	0.868	0.744	0.529
29	0.840	0.744	0.696	0.861	0.876	0.774	0.668	0.815	1.420	0.945
36	0.745	0.658	0.448	0.882	0.620	0.375	0.529	0.639		0.441
42	0.630	0.625	0.590	0.862	0.412	0.426	0.616	0.512		0.816
49	0.367	0.269	0.208	0.122	0.245			0.195		0.363
56	0.568	0.744	0.550	0.707	0.416	0.530	0.899	0.476	5.472	0.588
136	1.537	1.438	1.702	2.041	1.142	16.721	1.663	1.017	28.12	1.798
164	0.358	0.732	0.394	0.254	0.452	5.569	0.273	0.904	11.35	4.038
165			1.330			3.610			4.390	
197	1.978	0.987	1.957	1.444	1.438	1.775	2.460	27.90	28.12	1.344
228	0.895	0.819	28.08	1.219	1.207	0.964	0.399	35.34	39.38	0.950
261	0.634	23.13	4.620	28.69	0.962	1.320	1.109	15.36	4.101	16.59
267	1.394	1.380	1.298	0.580	0.523	0.902	0.819	1.191	1.463	0.733
308	0.218	0.284	0.134	0.229	0.122	0.473	0.439	0.156	0.326	0.338
340	2.038	1.682	1.826	1.629	1.261	1.646	1.628	2.263	1.575	1.461
365	0.843	0.084	0.118	0.185	0.061	0.403	0.351	0.410	0.816	0.702
826	<LOD	0.284	0.277	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.099

A9 N7

A9.1 Volume gas mL

Day	N7:1	N7:2	N7:3	N7:4	N7:5	N7:6	N7:7	N7:8	N7:9	N7:10
0	5.6	5.7	5.5	5.8	5.4	5.2	5.6	5.3	5.6	5.2
160	5.6	5.7	5.5	5.8	5.4	5.2		5.3	5.6	5.2
260	5.6	5.7	5.5	5.8	5.4	5.2		5.3	5.6	5.2

A9.2 Pressure kPa

Day	N7:1	N7:2	N7:3	N7:4	N7:5	N7:6	N7:7	N7:8	N7:9	N7:10
0	182	174	182	184	184	186	183	184	183	183
6	169	160	163	170	163	169	169	169	169	169
13	162	153	155	161	155	161	162	161	154	161
20	152	146	146	152	146	152	153	152	146	154
28	149	144	142	141	141	146	151	148	149	152
34	141	137	135	143	124	138	134	140	136	139
41	138	134	133	138	121	133	131	134	132	137
49	131	127	125	132	117	128	124	128	127	132
128	126	123	120	127	112	119	103	121	122	123
156	128	124	122	128	113	118	102	121	123	125
160	190			193				195		
189	174	187	185	179	184	183		172	189	191
219	100	176	168	169	166	100		100	178	180
253	100	159	100	154	118	100		100	159	162
260		196		197		200			209	
302	189	179	191	183	194	185		193	184	193
332	184	169	178	171	181	172		181	171	183
357	163	159	168	163	164	163		98	160	169
820	144	142	145		145	100		100	142	150

A9.3 H_2 mbar

Day	N7:1	N7:2	N7:3	N7:4	N7:5	N7:6	N7:7	N7:8	N7:9	N7:10
0	0.055	<LOD	<LOD	0.018	<LOD	<LOD	0.018	0.018	0.018	0.018
6	0.051	0.256	0.130	0.102	0.098	0.270	0.118	0.304	0.068	0.068
13	0.081	0.673	0.403	0.209	0.202	0.708	0.292	0.725	0.216	0.113
20	0.122	0.832	0.745	0.426	0.453	1.094	0.627	1.201	0.380	0.185
28	0.298	1.699	1.278	0.677	0.649	1.533	0.966	1.450	0.715	0.350
34	0.353	1.795	1.445	0.887	0.657	1.918	1.112	1.652	0.762	0.403
41	0.580	2.064	1.569	1.063	0.787	2.155	1.310	1.809	1.030	0.493
49	0.629	2.705	1.788	1.426	0.959	2.214	1.600	2.291	1.194	0.620
128	1.865	4.871	3.552	2.896	1.590	3.403	2.719	3.388	3.148	1.230
156	1.613	4.042	2.879	2.918	1.198	3.658	2.530	4.041	3.395	1.725
160	0.038			0.077				0.078		
189	0.903	0.972	0.740	0.967	0.258	0.622		0.413	0.605	0.382
219	0.240	1.214	1.193	1.251	0.398	0.520		0.130	1.104	0.504
253	0.060	1.670	0.580	1.540	0.389	0.100		0.100	1.208	0.697
260		0.020		0.020		0.020			0.021	
302	0.057	0.931	1.108	0.842	0.582	0.093		0.097	0.754	0.579
332	0.092	1.386	1.477	1.351	0.996	0.138		0.091	1.214	0.952
357	0.082	1.367	1.562	1.581	1.066	0.147		0.069	1.280	0.913
820	0.173	2.783	1.653		1.363	0.150		0.130	1.491	1.560

A9.4 O_2 mbar

Day	N7:1	N7:2	N7:3	N7:4	N7:5	N7:6	N7:7	N7:8	N7:9	N7:10
0	1.438	0.766	0.910	1.454	0.865	0.837	1.116	0.994	0.860	0.878
6	1.453	1.376	1.891	1.428	1.239	1.268	1.183	1.453	1.504	1.555
13	0.745	0.673	1.070	0.644	0.667	0.596	0.632	0.789	0.601	0.837
20	0.593	0.949	1.066	0.851	0.715	0.699	1.025	1.231	0.803	0.986
28	0.894	0.850	0.667	0.592	0.719	0.555	0.680	0.385	0.700	0.699
34	0.846	1.041	0.675	1.044	0.868	1.118	0.951	0.910	0.898	0.848
41	0.373	0.295	0.213	0.386	0.290	0.399	0.393	0.335	0.515	0.219
49	0.930	1.067	0.800	0.700	0.959	0.614	0.818	0.960	0.673	0.845
128	2.268	0.738	0.672	1.118	0.851	1.690	0.906	0.920	0.781	1.255
156	0.614	0.868	1.025	0.998	0.904	3.469	9.200	1.573	2.829	1.575
160	1.520			2.432				3.276		
189	1.633	1.720	1.480	0.967	2.907	1.757		1.754	4.234	1.795
219	26.520	0.510	0.118	1.200	2.009	0.790		29.890	0.908	0.792
253	35.550	0.700	1.940	1.448	1.050	36.160		33.710	1.097	0.923
260		3.234		0.217		1.800			1.421	
302	1.247	1.450	1.108	0.695	0.388	0.111		0.521	0.423	0.386
332	1.766	1.403	1.922	2.787	1.720	1.944		1.720	0.804	0.421
357	0.701	0.509	1.310	1.157	1.607	0.652		4.528	0.624	0.625
820	0.058	0.043	0.015		0.044	22.080		18.830	0.014	0.030

A10 N8

A10.1 Volume gas mL

Day	N8:1	N8:2	N8:3	N8:4	N8:5	N8:6	N8:7	N8:8	N8:9	N8:10
0	5.8	5.9	5.8	5.6	5.6	6.0	5.8	5.6	6.0	5.9
154	5.8	5.9	5.8	5.6	5.6	6.0	5.8	5.6	6.0	5.9
256	5.4	5.6	5.4	5.1	5.3	5.1	5.0	5.4	5.4	5.4
360	5.1	5.0	4.9	5.0	5.0	5.0	4.8	4.8	5.0	4.7
557							5.1			5.3

Day	N8:11	N8:12	N8:13	N8:14	H2O:1	H2O:2	H2O:3	H2O:4	H2O:5
0	5.6	5.7	5.7	5.7					
154	5.6	5.7	5.7	5.7					
256	5.1	5.3	5.2	5.6					
360	4.9	4.8	4.9	4.7	5.1	5.1	5.1	5.4	5.3
557		5.3							

A10.2 Pressure kPa

Day	N8:1	N8:2	N8:3	N8:4	N8:5	N8:6	N8:7	N8:8	N8:9	N8:10
1	130	133	172	178	178	179	176	179	181	180
7	123	123	161	166	162	161	163	164	165	165
14	122	121	155	159	147	153	155	159	160	161
22	120	110	124	142	109	106	139	153	151	147
29	114		119	136		101	131	145	143	138
44	110	107	114	130	105	100	130	139	140	126
121	106	104	110	124	99	98	124	130	132	115
151	102	106	112	124	103	103	127	132	134	118
154		188					188			
185	129	173	182	184	144	100	176	181	182	181
218	124	146	170	171	115	100	144	173	175	166
252	100	100	154	156	104	100	132	156	159	151
256	207					201				
297	194	197	198	198	198	186	192	197	194	198
330	179	184	184	185	186	176	165	152	173	167
353	168	173	173	173	174	165	156	143	164	158
360	188	199	199	201	200	200	201	200	198	199
395	161	171	162	176	178	150	168	180	179	179
420	151	161	155	161	167	144	115	168	168	166
451	147	156	150	158	164	138	144	162	163	161
493	138	150	142	149	153	131	109	153	153	152
521	132	141	135	139	142	122	103	138	140	135
557							202			202
560							185			180
577				128				129		
589							160			168
617							152			159
631				119				125		
669							144			152
693				114				121		
694							136			142
738							130			135
765							127			132
794				108			124	114		130
806	124	130	127		135	120			135	

Day	N8:11	N8:12	N8:13	N8:14	H2O:1	H2O:2	H2O:3	H2O:4	H2O:5
1	179	180	178	179					
7	161	165	163	162					
14	155	157	158	151					
22	124	118	154	143					
29	116	108	144	134					
44	99	104	140	108					
121	93	95	127	95					
151	99	101	130	101					
154	190								
185	173	100	185	182					
218	156	100	165	100					
252	134	100	134	100					
256		199		199					
297	200	186	200	179					
330	172	173	185	169					
353	162	152	170	156					
360	202	202	201	200	202				
395	181	181	182	181	184	196	195	196	194
420	104	169	171	169	171	187	177	183	177
451	109	162	166	164	165	179	172	178	171
493	105	160	160	156	137	166	162	168	165
521	102	146	144	144	127	153	151	155	152
557		201							
560		185							
577				135		143		147	
589		171							
617		162							
631				125		100		143	
669		154							
693				118		100		135	
694		144							
738		140							
765		136							
794		133		109		83		128	
806	102		135		124		144		143

A10.3 H_2 mbar

Day	N8:1	N8:2	N8:3	N8:4	N8:5	N8:6	N8:7	N8:8	N8:9	N8:10
0	0.013	0.027	0.017	0.018	0.018	0.018	0.035	0.018	0.054	0.018
7	0.209	0.271	0.354	0.199	0.745	0.274	0.277	0.754	0.611	0.627
14	0.183	0.254	0.372	0.493	0.632	0.275	0.822	1.097	0.672	1.079
22	0.204	0.638	0.322	1.306	0.567	0.530	1.460	1.805	1.102	1.749
29	0.399		0.512	1.890		0.444	2.437	2.146	1.287	2.180
44	0.627	1.412	0.638	2.886	0.672	0.600	3.549	2.613	1.624	2.318
121	1.866	3.453	2.200	5.208	1.643	2.215	5.258	5.824	2.666	3.335
151	2.081	2.841	2.083	5.258	1.421	1.401	5.182	4.013	2.680	2.950
154		0.038					0.075			
185	0.309	1.001	0.876	1.103	0.548	0.360	1.021	0.904	0.693	0.652
218	0.422	1.095	1.020	1.522	0.426	0.160	1.555	1.730	1.015	0.531
252	0.290	0.840	1.155	1.498	0.645	0.060	1.663	1.513	1.161	1.012
256	<LOD					<LOD				
297	0.175	0.177	0.119	0.158	0.139	0.409	0.192	0.158	0.097	0.139
330	0.788	0.221	0.129	0.222	0.167	1.056	0.116	0.198	0.138	0.184
353	0.823	0.311	0.104	0.242	0.174	1.106	0.218	0.486	0.213	0.363
360	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
395	0.064	0.086	0.065	0.106	0.089	0.015	0.101	0.108	0.072	0.107
420	0.121	0.129	0.109	0.274	0.150	0.130	0.104	0.202	0.084	0.149
451	0.147	0.250	0.255	0.363	0.246	0.221	0.288	0.535	0.212	0.338
493	0.455	0.585	0.625	0.864	0.597	0.616	0.545	0.872	0.490	0.775
521	0.502	0.564	0.648	0.876	0.596	0.610	0.659	0.883	0.448	0.716
557							<LOD			<LOD
560							0.074			0.054
577				1.536				0.968		
589							0.064			0.067
617							0.167			0.167
631				0.988				1.100		
669							0.562			0.441
693				1.288				1.488		
694							0.707			0.511
738							1.092			1.053
765							0.978			0.779
794				1.350			0.930	1.345		0.793
806	0.954	1.368	1.273		1.354	0.957			1.121	

Day	N8:11	N8:12	N8:13	N8:14	H2O:1	H2O:2	H2O:3	H2O:4	H2O:5
0	0.018	0.036	0.018	0.018					
7	0.290	0.413	0.473	0.891					
14	0.357	0.722	0.664	1.329					
22	0.632	1.251	1.170	2.374					
29	0.650	1.534	1.426	2.680					
44	0.762	1.612	1.652	2.484					
121	0.186	0.836	3.175	1.748					
151	0.139	0.525	2.496	0.545					
154	<LOD								
185	0.242	0.220	0.665	0.219					
218	0.094	0.060	0.809	0.070					
252	0.040	0.020	0.724	0.020					
256		<LOD		<LOD					
297	0.080	0.595	0.180	0.662					
330	0.396	1.298	0.148	1.335					
353	0.535	1.140	0.221	1.217					
360	<LOD	<LOD		<LOD	0.020				
395	0.072	0.145	0.091	0.072	0.074	0.157	0.078	0.078	0.058
420	0.042	0.203	0.103	0.135	0.068	0.112	0.106	0.092	0.071
451	0.164	0.518	0.282	0.426	0.132	0.143	0.172	0.142	0.120
493	0.357	0.992	0.608	0.905	0.110	0.183	0.178	0.118	0.116
521	0.388	0.788	0.547	0.922	0.076	0.122	0.151	0.124	0.091
557		<LOD							
560		0.278							
577				1.202		0.114		0.118	
589		0.239							
617		0.308							
631				0.963		0.040		0.072	
669		0.616							
693				1.038		0.040		0.108	
694		0.706							
738		1.064							
765		0.952							
794		0.998		0.719		0.050		<LOD	
806	0.857		0.810		<LOD		0.086		<LOD

A10.4 O_2 mbar

Day	N8:1	N8:2	N8:3	N8:4	N8:5	N8:6	N8:7	N8:8	N8:9	N8:10
1	1.144	0.998	1.428	1.086	1.442	1.325	0.792	0.770	0.670	0.702
7	0.492	0.357	0.660	0.697	0.437	0.612	0.603	0.754	0.776	0.594
14	0.647	0.448	0.806	0.954	0.926	1.040	0.744	0.700	0.976	1.127
22	0.528	0.605	0.595	0.440	0.501	0.636	0.542	0.551	0.664	0.676
29	0.114		0.226	0.163		0.919	0.550	0.914	1.001	0.911
44	0.253	0.246	0.091	0.078	0.179	0.180	0.325	0.278	0.252	0.227
121	1.738	1.997	2.112	2.579	3.208	3.861	2.480	1.014	0.924	0.805
151	6.324	0.827	0.650	0.942	3.337	5.212	0.991	0.818	0.804	0.897
154		1.354					4.437			
185	1.260	0.828	1.860	1.582	2.623	17.860	2.254	1.157	1.787	1.015
218	1.240	0.891	1.241	1.060	0.529	24.320	0.706	1.626	1.418	0.996
252	30.530	2.080	1.494	2.168	2.018	37.980	1.241	1.248	1.208	1.450
256	1.532					1.407				
297	0.524	0.591	0.376	0.673	0.594	0.093	0.096	0.079	0.097	0.040
330	0.877	1.306	1.122	1.573	1.153	0.898	0.413	0.699	0.692	2.939
353	1.579	1.488	1.436	1.505	1.392	1.469	1.404	1.473	0.607	0.395
360	2.933	3.861	2.328	3.317	2.920	3.380	2.432	2.720	2.475	2.627
395	0.837	0.633	1.507	0.968	0.214	0.225	0.806	0.090	0.161	0.179
420	0.906	1.288	1.132	0.982	0.701	2.808	1.311	0.722	1.042	1.145
451	0.368	0.406	0.180	0.379	0.049	0.028	0.043	0.130	0.212	0.097
493	0.083	0.105	0.071	0.089	0.077	0.079	0.065	0.092	0.077	0.106
521	0.686	0.733	0.729	0.904	0.809	0.891	0.896	0.069	0.224	0.081
557							1.879			0.566
560							0.056			0.090
577				0.051				0.026		
589							0.752			0.874
617							0.350			0.398
631				0.179				0.188		
669							0.101			0.076
693				0.023				0.036		
697							0.041			0.043
738							0.195			0.162
765							0.165			0.132
794				0.346				0.228		
806	0.099	0.104	0.127		0.095	0.096			0.122	

Day	N8:11	N8:12	N8:13	N8:14	H2O:1	H2O:2	H2O:3	H2O:4	H2O:5
1	0,859	0,882	0,676	0,967					
7	1,079	0,545	0,717	0,664					
14	0,729	0,754	1,011	0,800					
22	0,732	0,614	0,400	0,658					
29	0,835	0,529	1,022	0,965					
44	1,564	0,291	0,266	0,259					
121	14,768	11,172	0,787	10,583					
151	12,672	9,171	0,936	9,514					
154	3,344								
185	1,071	15,420	1,181	1,713					
218	1,045	27,680	0,842	21,820					
252	1,018	41,770	1,501	42,580					
256		1,313		1,751					
297	0,360	0,056	1,200	0,054					
330	2,236	1,990	2,276	1,994					
353	0,437	0,638	0,255	0,608					
360	1,959	1,899		1,880	3,575				
395	0,308	0,290	0,273	0,253	0,350	0,490	0,702	0,353	0,524
420	1,539	1,082	0,992	1,234	0,787	1,328	1,398	0,878	0,814
451	0,305	0,470	0,299	0,328	0,545	0,430	0,396	0,498	0,410
493	0,063	0,128	0,096	0,047	0,069	0,083	0,081	0,084	0,083
521	0,061	0,365	0,619	0,403	0,305	0,689	0,513	0,574	0,471
557		0,141							
560		0,056							
577				0,054		0,072		0,162	
589		0,701							
617		0,324							
631				0,338		29,300		0,129	
669		0,077							
693				0,024		11,160		0,027	
697									
738		0,029							
765		0,098							
794				0,316		24,012		0,179	
806	0,559		0,081		0,087		0,202		0,086

A11 N9

A11.1 Volume gas mL

Day	N9:1 pH7	N9:2 pH7	N9:3 pH7	N9:4 pH7	N9:5 pH7	N9:6 pH9	N9:7 pH9	N9:8 pH9	N9:9 pH9	N9:10 pH9
0	5.6	5.8	5.7	5.5	5.1	5.4	5.8	5.7	5.6	5.3
127						5.4	5.8	5.7	5.6	5.3
231						5.4	5.8	5.7	5.6	5.3

Day	N9:11 pH2	N9:12 pH2	N9:13 pH2	N9:14 pH2	N9:15 pH2
0	5.7	5.4	4.3	5.4	5.9
127	5.7	5.4	4.3	5.4	5.9
231	5.7	5.4	4.3	5.4	5.9

A11.2 Pressure kPa

Day	N9:1 pH7	N9:2 pH7	N9:3 pH7	N9:4 pH7	N9:5 pH7	N9:6 pH9	N9:7 pH9	N9:8 pH9	N9:9 pH9	N9:10 pH9
1	182	183	183	184	183	177	180	179	180	181
6	171	172	170	168	171	165	168	168	169	170
12	164	166	162	158	164	157	157	160	159	159
21	157	156	150	151	157	118	148	152	153	125
32	145	146	134	143	149	105	137	144	144	114
102	122	138	127	112	141	95	108	125	136	94
126	108	133	126	115	139	101	109	124	136	100
127							187			184
160						100	100	179	182	120
190						100	100	167	172	100
224							100	148	148	100
231						190			190	
273						182	196	197	184	196
302						173	185	183	174	184
328						160	173	174	163	174
788						134	150	152	138	152

Day	N9:11 pH2	N9:12 pH2	N9:13 pH2	N9:14 pH2	N9:15 pH2
1	182	183	180	181	180
6	170	169	169	170	170
12	161	161	160	162	161
21	155	144	128	154	154
32	148	134	122	145	148
102	108	110	114	134	133
126	110	112	115	135	135
127		186		187	
160	183	131	108	173	182
190	175	116	103	164	175
224	154	100	100	135	158
231		198			199
273	197	185	196	198	185
302	186	173	186	178	175
328	175	164	174	169	165
788	151	144	150	146	144

A11.3 H_2 mbar

Day	N9:1 pH7	N9:2 pH7	N9:3 pH7	N9:4 pH7	N9:5 pH7	N9:6 pH9	N9:7 pH9	N9:8 pH9	N9:9 pH9	N9:10 pH9
1	0.036	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.036
6	0.616	0.482	0.595	0.605	0.564	0.710	0.504	0.638	0.896	0.357
12	1.164	0.979	1.134	1.264	1.197	1.068	1.005	1.152	1.606	0.620
21	1.853	1.576	1.740	1.963	1.837	1.097	1.658	1.687	2.280	0.900
32	1.929	1.883	2.077	3.332	2.816	1.260	2.041	2.563	3.182	1.459
102	3.733	3.974	4.343	4.906	5.499	0.247	3.672	3.400	4.678	1.354
126	2.808	3.405	3.352	3.749	4.698	0.141	2.224	1.959	4.216	0.740
127							0.075			0.037
160						0.100	0.340	0.822	1.163	0.048
190						0.020	0.120	1.102	1.135	0.050
224							0.010	1.332	1.465	0.070
231						0.114			0.076	
273						0.146	0.235	0.906	0.920	0.196
302						0.225	0.185	1.263	1.322	0.202
328						0.160	0.190	1.618	1.483	0.157
788						0.201	0.195	1.642	1.090	0.000

Day	N9:11 pH2	N9:12 pH2	N9:13 pH2	N9:14 pH2	N9:15 pH2
1	0.018	0.037	0.018	0.018	0.018
6	0.357	0.304	0.321	0.136	0.187
12	0.660	0.370	0.352	0.227	0.290
21	1.302	0.835	0.346	0.616	0.708
32	2.368	1.501	0.586	1.378	1.465
102	3.823	3.410	1.414	2.921	4.017
126	4.224	2.195	1.449	2.241	4.077
127		0.074		0.075	
160	1.060	0.366	0.431	1.038	1.093
190	1.383	0.313	0.196	1.148	1.435
224	1.494	0.170	0.130	1.310	1.675
231		0.119			0.139
273	1.024	0.296	0.235	1.049	1.073
302	1.339	0.606	0.298	1.353	1.593
328	1.663	0.984	0.226	1.707	1.700
788	1.888	2.016	1.740	2.409	2.030

A11.4 O_2 mbar

Day	N9:1 pH7	N9:2 pH7	N9:3 pH7	N9:4 pH7	N9:5 pH7	N9:6 pH9	N9:7 pH9	N9:8 pH9	N9:9 pH9	N9:10 pH9
1	0.983	0.878	0.860	0.865	1.043	1.204	0.774	0.752	0.756	1.177
6	0.906	0.602	0.714	1.042	0.770	0.891	0.958	0.739	0.608	0.748
12	0.607	0.598	0.599	0.474	0.525	0.801	0.502	0.640	0.493	0.429
21	0.597	0.624	0.420	0.468	0.534	0.625	1.066	0.593	0.551	0.400
32	1.407	1.153	0.817	1.030	1.505	0.977	0.904	1.210	1.008	0.855
102	1.732	1.573	2.794	2.934	3.158	14.497	2.635	0.325	0.762	14.213
126	1.944	1.782	1.487	1.679	1.140	11.615	0.741	0.422	0.952	16.120
127							0.898			1.214
160						33.240	30.740	3.111	1.780	1.888
190						37.720	37.740	1.052	1.170	26.370
224							29.670	1.613	1.258	25.590
231						1.957			1.976	
273						1.238	0.098	0.118	0.092	0.608
302						0.225	0.185	1.263	1.322	0.202
328						1.408	1.349	1.340	1.467	0.522
788						< LOD	< LOD	< LOD	< LOD	< LOD

Day	N9:11 pH2	N9:12 pH2	N9:13 pH2	N9:14 pH2	N9:15 pH2
1	1.019	1.135	0.720	0.796	0.774
6	1.088	0.913	0.896	0.527	0.578
12	0.209	0.306	0.352	0.373	0.644
21	0.481	0.446	0.474	0.693	0.477
32	0.888	1.179	1.098	0.914	0.770
102	0.626	1.254	1.277	1.394	0.958
126	1.210	1.814	1.150	3.753	0.864
127		1.079		1.272	
160	2.631	2.878	1.811	2.664	2.914
190	0.700	0.708	0.474	0.754	0.823
224	2.248	21.290	16.330	2.768	1.122
231		1.485			1.234
273	0.690	0.611	0.745	0.693	0.555
302	1.339	0.606	0.298	1.353	1.593
328	0.805	0.754	1.688	1.369	1.419
788	< LOD	< LOD	< LOD	< LOD	0.043

A12 NN – Sodium chloride

A12.1 Volume gas mL

Day	NN1:1	NN1:2	NN1:3	NN1:4	NN1:5	NN1:6	NN1:7	NN1:8	NN1:9	NN1:10
0	6.0	6.4	5.8	5.9	5.8	6.1	5.7	5.6	5.5	5.7
106	5.5	5.3	5.6	5.6	5.7			5.6	5.4	5.4
Day	**NN2:1**	**NN2:2**	**NN2:3**	**NN2:4**	**NN2:5**	**NN2:6**	**NN2:7**	**NN2:8**	**NN2:9**	**NN2:10**
0	5.9	5.6	6.0	5.7	6.1	6.2	6.1	6.2	6.2	5.9
106	5.2	5.4	5.7	5.4	5.2	5.2	5.3	5.6	5.3	5.3
Day	**NN3:1**	**NN3:2**	**NN3:3**	**NN3:4**	**NN3:5**	**NN3:6**	**NN3:7**	**NN3:8**	**NN3:9**	**NN3:10**
0	5.4	5.3	5.4	5.3	5.1	5.7	5.5	5.4	5.4	5.5
106	5.1	5.0	5.3	5.2	5.0	5.4	5.2	4.9	5.2	5.0

A12.2 Pressure kPa

Day	NN1:1	NN1:2	NN1:3	NN1:4	NN1:5	NN1:6	NN1:7	NN1:8	NN1:9	NN1:10
1	189				189	188	189		189	
32	180	189	187	185	179			184	177	185
63		176	177	172	167			168	168	171
99		161	161	100	150			153	157	161
106		197			198				208	
146	195	185						197	189	197
179	186	176	198	199	188			186	171	186
201	175	163	184	184	174			174	164	161
266	161	152	171	173	162			163	153	162
Day	**NN2:1**	**NN2:2**	**NN2:3**	**NN2:4**	**NN2:5**	**NN2:6**	**NN2:7**	**NN2:8**	**NN2:9**	**NN2:10**
1		195				193				194
32	193	198	189	195	194	180	190	191	190	182
63	177	155	132	144	172	171	168	178	177	174
99	158	143	124	131	157	158	159	166	163	161
106				205				205		199
146	195	198				195	196	192	195	184
179	183	185	197	188	197	182	183	179	182	172
201	169	173	183	176	184	170	168	167	169	161
266	160	163	170	162	172	161	159	158	160	151
Day	**NN3:1**	**NN3:2**	**NN3:3**	**NN3:4**	**NN3:5**	**NN3:6**	**NN3:7**	**NN3:8**	**NN3:9**	**NN3:10**
1			189			187			189	
32	188	187	179	186	185	176	181	183	175	185
63	177	178	171	177	174	169	173	129	167	176
99				164	161	152	161	100	156	158
106		210				209	209			
146	196	186				180	184	196	196	195
179	182	175	195	195	196	170	172	182	183	184
201	170	163	182	183	179	158	161	170	172	170
266	160	154	171	168	170	129	137	159	161	161

A12.3 H_2 mbar

Day	NN1:1	NN1:2	NN1:3	NN1:4	NN1:5	NN1:6	NN1:7	NN1:8	NN1:9	NN1:10
1	0.076				0.076	0.075	0.113		0.038	
32	1.477	3.393	1.978	2.664	1.434			5.152	4.253	4.327
63		1.267	0.974	0.740	0.635			2.285	2.503	2.690
99		1.707	1.240	0.490	0.780			3.427	3.941	3.751
106		0.059			0.059				0.062	
146	0.137	0.148						1.261	1.493	1.675
179	0.130	0.141	0.119	0.159	0.169			1.916	2.206	2.530
201	0.105	0.130	0.092	0.166	0.139			2.123	2.509	2.222
266	0.097	0.106	0.086	0.104	0.113			2.510	2.968	3.029

Day	NN2:1	NN2:2	NN2:3	NN2:4	NN2:5	NN2:6	NN2:7	NN2:8	NN2:9	NN2:10
1		0.078				0.077				0.078
32	0.578	1.146	3.858	1.601	1.358	5.625	5.560	6.144	5.615	4.366
63	0.407	0.217	0.937	0.346	0.533	5.540	5.225	5.376	5.239	5.568
99	0.284	0.386	0.632	0.576	0.534	4.708	3.355	4.150	3.928	3.526
106				<LOD				0.041		0.040
146	0.098	0.158				1.950	1.823	1.786	1.541	1.693
179	0.128	0.167	0.138	0.113	0.256	3.112	2.727	2.864	2.548	2.511
201	0.135	0.121	0.128	0.123	0.221	3.230	3.192	2.689	2.552	2.721
266	0.128	0.130	0.119	0.113	0.172	4.862	3.625	3.318	2.960	3.277

Day	NN3:1	NN3:2	NN3:3	NN3:4	NN3:5	NN3:6	NN3:7	NN3:8	NN3:9	NN3:10
1			0.038			0.112			0.076	
32	0.750	1.308	0.609	1.413	0.849	4.622	5.216	5.259	5.288	6.129
63	0.549	0.890	0.342	1.044	0.505	4.225	5.709	3.896	6.045	5.861
99	0.394	0.660	0.289	0.692	0.230	3.994	5.182	4.548	5.091	5.363
106		0.021				0.042	0.042			
146	0.118	0.112				1.296	1.398	1.568	1.744	1.658
179	0.091	0.158	0.098	0.098	0.098	1.989	2.494	2.421	2.599	2.631
201	0.102	0.114	0.109	0.092	0.107	2.054	2.528	2.363	2.494	2.737
266	0.112	0.108	0.120	0.134	0.119	2.735	7.836	7.632	4.524	4.524

A12.4 O_2 mbar

Day	NN1:1	NN1:2	NN1:3	NN1:4	NN1:5	NN1:6	NN1:7	NN1:8	NN1:9	NN1:10
1	2.041				2.079	2.444	1.966		2.419	
32	1.261	3.582	2.351	1.369	1.578			0.221	0.319	1.257
63		2.394	1.965	0.172	0.351			0.370	0.235	0.393
99		2.157	0.869	30.940	1.245			0.750	0.879	1.159
106		1.537			1.782				1.664	
146	1.190	0.944						1.221	1.323	1.418
179	0.130	0.088	0.317	0.557	0.545			0.223	0.410	0.372
201	0.718	0.717	1.380	0.644	0.800			0.713	0.820	1.063
266	0.644	1.459	1.094	1.176	0.907			0.571	0.520	0.583

Day	NN2:1	NN2:2	NN2:3	NN2:4	NN2:5	NN2:6	NN2:7	NN2:8	NN2:9	NN2:10
1		2.379				2.316				1.785
32	0.616	1.264	1.664	1.015	1.242	0.288	1.295	0.343	0.607	0.946
63	0.673	2.108	1.346	1.325	4.575	2.873	3.007	3.613	0.991	1.131
99	1.501	0.958	1.327	1.061	0.769	1.059	0.938	1.145	1.141	0.918
106				3.711				2.132		2.169
146	0.995	1.148				1.346	1.235	1.248	0.761	1.214
179	0.238	0.167	0.414	0.376	0.236	0.291	0.256	0.430	0.382	0.499
201	1.301	1.384	1.391	1.355	0.736	0.680	0.655	0.601	0.710	0.934
266	1.296	1.434	1.275	0.859	0.860	0.869	0.986	1.280	1.680	1.359

Day	NN3:1	NN3:2	NN3:3	NN3:4	NN3:5	NN3:6	NN3:7	NN3:8	NN3:9	NN3:10
1			2.192			1.459			0.189	
32	3.188	2.354	3.687	2.342	2.806	2.681	3.224	2.849	2.521	3.249
63	0.974	1.175	0.701	1.770	0.853	0.963	1.021	0.774	1.570	0.774
99	0.164	0.177	1.368	0.161	0.520	1.342	0.174	0.168	0.163	0.147
106		2.772				2.989	2.947			
146	1.392	1.190				1.224	1.196	1.039	1.294	1.170
179	0.091	0.298	0.488	0.137	0.314	0.102	0.344	0.309	0.531	0.331
201	0.918	1.060	1.001	1.318	2.828	1.311	1.095	1.241	0.757	0.935
266	1.168	1.278	1.112	0.168	0.119	0.077	0.315	1.367	1.014	3.703

A13 NpH

A13.1 Volume gas mL

Day	NpH2-3:1	NpH2-3:2	NpH2-3:3	NpH2-3:4	NpH2-3:5	NpH2-3:6	NpH2-3:7	NpH2-3:8	NpH2-3:9	NpH2-3:10
0	5.8	5.5	5.8	5.8	5.6	5.5	5.7	5.7	5.5	5.6
Days	**NpH9-10:1**	**NpH9-10:2**	**NpH9-10:3**	**NpH9-10:4**	**NpH9-10:5**	**NpH9-10:6**	**NpH9-10:7**	**NpH9-10:8**	**NpH9-10:9**	**NpH9-10:10**
0	5.4	5.5	5.5	5.6	5.7	5.6	5.6	5.4	5.9	5.5

A13.2 Pressure kPa

Day	NpH2-3:1	NpH2-3:2	NpH2-3:3	NpH2-3:4	NpH2-3:5	NpH2-3:6	NpH2-3:7	NpH2-3:8	NpH2-3:9	NpH2-3:10
1	193	204	205	205	205	204	204	204	204	203
37	182	194				189	190	184	190	190
70	171	182	192	191	192	178	180	169	180	178
92	150	172	181	182	183	169	172	154	173	172
156	133	159	168	168	168	156	159	144	153	157
Day	**NpH9-10:1**	**NpH9-10:2**	**NpH9-10:3**	**NpH9-10:4**	**NpH9-10:5**	**NpH9-10:6**	**NpH9-10:7**	**NpH9-10:8**	**NpH9-10:9**	**NpH9-10:10**
1	210	209	209	213	213	208	207	209	208	211
37	193	194				191	192	193	182	186
70	194	193	200	202	199	184	185	184	174	178
92	174	174	183	187	186	174	174	174	168	162
156	161	160	169	172	173	160	161	160	152	149

A13.3 H_2 mbar

Day	NpH2-3:1	NpH2-3:2	NpH2-3:3	NpH2-3:4	NpH2-3:5	NpH2-3:6	NpH2-3:7	NpH2-3:8	NpH2-3:9	NpH2-3:10
1	0.019	0.061	0.041	0.041	0.041	0.041	0.061	0.061	0.061	0.041
37	0.109	0.116				3.837	3.211	3.441	2.812	3.268
70	0.086	0.109	0.115	0.115	0.096	5.304	4.608	4.698	4.068	5.109
92	0.090	0.138	0.181	0.146	0.128	6.287	5.280	5.559	4.498	5.452
156	0.093	0.111	0.118	0.151	0.084	8.034	6.471	7.243	4.957	8.148
Day	**NpH9-10:1**	**NpH9-10:2**	**NpH9-10:3**	**NpH9-10:4**	**NpH9-10:5**	**NpH9-10:6**	**NpH9-10:7**	**NpH9-10:8**	**NpH9-10:9**	**NpH9-10:10**
1	0.021	<LOD	<LOD			0.021	<LOD	0.021	0.021	
37	0.116	0.078				2.426	1.958	2.084	1.128	4.631
70	0.194	0.154	0.040	0.040	0.020	1.012	1.166	1.711	1.288	3.774
92	0.104	0.087	0.110	0.075	0.093	4.489	3.706	4.106	2.520	6.091
156	0.113	0.096	0.101	0.069	0.104	5.744	5.039	5.984	3.207	6.929

A13.4 O_2 mbar

Day	NpH2-3:1	NpH2-3:2	NpH2-3:3	NpH2-3:4	NpH2-3:5	NpH2-3:6	NpH2-3:7	NpH2-3:8	NpH2-3:9	NpH2-3:10
1	1.641	2.346	1.435	1.517	2.091	1.714	1.999	1.816	1.836	1.604
37	1.219	1.261				1.153	1.406	1.582	1.368	1.102
70	0.257	0.637	0.710	0.840	0.710	0.730	0.522	0.389	0.414	0.783
92	1.710	1.806	3.131	1.765	1.592	1.707	1.393	1.848	1.834	0.843
156	1.011	1.352	1.193	1.478	1.142	0.702	1.065	0.619	0.658	0.926

Day	NpH9-10:1	NpH9-10:2	NpH9-10:3	NpH9-10:4	NpH9-10:5	NpH9-10:6	NpH9-10:7	NpH9-10:8	NpH9-10:9	NpH9-10:10
1	1.827	1.651	2.278			1.539	1.697	2.278	1.997	
37	1.486	1.125				1.012	0.998	1.042	2.166	1.376
70	0.427	0.347	0.300	0.242	0.458	0.147	0.185	0.239	0.278	0.303
92	1.531	1.566	2.288	1.608	1.786	2.071	1.792	1.583	1.529	2.057
156	0.950	1.248	1.369	1.273	1.678	1.312	1.562	1.264	0.684	0.581

A14 NCD

A14.1 Volume gas mL

Day	NCD1:1	NCD1:2	NCD1:3	NCD1:4	NCD1:5	NCD2:1	NCD2:2	NCD2:3	NCD2:4	NCD2:5
0	26.2	26.2	26.2	26.2	26.2	22.2	22.2	22.2	22.2	22.2
112	26.2	26.2	26.2	26.2	26.2					

Days	NCD3:1	NCD3:2	NCD3:3	NCD3:4	NCD3:5	NCD4:1	NCD4:2	NCD4:3	NCD4:4	NCD4:5
0	22.2	22.2	22.2	22.2	22.2	22.2	22.2	22.2	22.2	22.2
112	22.2	22.2	22.2	22.2	22.2	21.7	21.7	21.7	21.7	21.7

A14.2 Pressure kPa

Day	NCD1:1	NCD1:2	NCD1:3	NCD1:4	NCD1:5	NCD2:1	NCD2:2	NCD2:3	NCD2:4	NCD2:5
0		198					197			
35	200	198	198	199	198	199	197	192	199	199
66	195	193	188	198	198	193	196	179	194	197
104	122	153	154	166	162	174	185	126	172	188
112	216		216							
151	216	217	216	217	217					
182	211	212	211	212	213					
206	207	207	207	207	207					
265	157	208	207	208	207					

Day	NCD3:1	NCD3:2	NCD3:3	NCD3:4	NCD3:5	NCD4:1	NCD4:2	NCD4:3	NCD4:4	NCD4:5
0										
35	200	198	199	200	199	199	199	197	199	199
66	193	193	196	184	197	192	193	163	197	197
104	138	128	103	105	177	149	120	100	187	180
112		213		213		214				215
151	214	212	214	212	214	215	217	217	213	216
182	208	207	201	207	208	209	211	212	208	210
206	203	202	179	200	200	204	206	206	203	205
265	193	198	175	199	200	204	206	206	196	203

A14.3 H_2 mbar

Day	NCD1:1	NCD1:2	NCD1:3	NCD1:4	NCD1:5	NCD2:1	NCD2:2	NCD2:3	NCD2:4	NCD2:5
0		0.040					0.118			
35	0.240	0.277	0.238	0.358	0.278	1.314	1.454	1.616	0.953	1.511
66	0.195	0.328	0.226	0.238	0.257	1.293	1.078	1.575	0.951	1.694
104	0.110	0.199	0.185	0.249	0.211	0.957	1.406	0.756	1.410	1.090
112	0.022		0.043							
151	0.022	0.022	0.022	0.022	0.022					
182	0.021	0.021	0.042	0.021	0.021					
206	0.041	0.021	0.021	0.021	0.021					
265	0.016	0.021	0.000	0.000	0.021					

Day	NCD3:1	NCD3:2	NCD3:3	NCD3:4	NCD3:5	NCD4:1	NCD4:2	NCD4:3	NCD4:4	NCD4:5
0										
35	1.439	2.136	1.513	1.557	1.393	1.989	2.745	2.007	2.541	2.306
66	2.104	2.355	1.940	1.858	2.561	2.342	2.335	1.842	2.994	2.896
104	1.808	2.048	1.329	1.376	1.947	2.071	1.500	0.730	2.637	2.808
112		0.021		<LOD		<LOD				0.043
151	0.471	0.509	0.471	0.445	0.449	0.602	0.456	0.456	0.618	0.756
182	0.811	0.869	0.824	0.828	0.874	0.961	0.739	0.890	1.061	1.218
206	0.893	0.949	0.859	0.840	0.840	1.040	0.803	0.845	1.056	1.230
265	1.332	1.307	1.208	1.274	1.380	1.510	1.236	1.298	1.568	1.726

A14.4 O_2 mbar

Day	NCD1:1	NCD1:2	NCD1:3	NCD1:4	NCD1:5	NCD2:1	NCD2:2	NCD2:3	NCD2:4	NCD2:5
0		0.752					0.709			
35	1.522	1.386	2.495	1.272	2.221	3.464	3.301	3.386	1.707	0.755
66	1.970	1.795	0.320	0.376	1.762	0.869	1.333	1.146	0.582	0.965
104	0.622	0.765	1.278	0.697	0.761	0.331	0.592	<LOD	0.413	<LOD
112	2.462	<LOD	1.771	<LOD	<LOD					
151	1.620	1.345	1.361	1.649	1.888					
182	0.844	0.869	0.950	0.784	0.788					
206	0.745	0.642	0.745	0.186	0.538					
265	0.408	0.811	1.056	0.915	0.952					

Days	NCD3:1	NCD3:2	NCD3:3	NCD3:4	NCD3:5	NCD4:1	NCD4:2	NCD4:3	NCD4:4	NCD4:5
0										
35	0.960	1.543	1.314	0.918	1.632	1.671	4.416	0.866	1.310	1.034
66	1.583	1.583	0.882	1.417	1.064	1.325	1.911	1.011	1.970	1.182
104	2.111	2.010	2.050	1.733	1.947	0.522	0.624	10.010	1.346	1.710
112	<LOD	2.087	<LOD	2.620	<LOD	2.097	<LOD	<LOD	<LOD	2.172
151	1.605	1.208	1.241	1.336	1.113	1.075	1.432	1.562	1.086	1.404
182	0.853	0.787	0.784	0.994	0.104	0.084	0.106	0.318	0.071	0.399
206	0.264	0.283	0.501	0.300	0.360	0.428	0.309	0.639	0.690	0.718
265	1.911	3.247	0.998	0.935	1.040	1.183	0.886	0.803	0.686	0.873

A15 NCS

A15.1 Volume gas mL

Day	NCS1:1	NCS1:2	NCS1:3	NCS1:4	NCS1:5	NCS4:1	NCS4:2	NCS4:3	NCS4:4	NCS4:5
0	5.8	5.9	5.9	5.9	5.7	6.0	5.7	6.1	5.8	5.9
101	5.8	5.6	6.1	5.7	5.7	5.5	5.6	5.8	5.4	5.5

A15.2 Pressure kPa

Day	NCS1:1	NCS1:2	NCS1:3	NCS1:4	NCS1:5	NCS4:1	NCS4:2	NCS4:3	NCS4:4	NCS4:5
1	192			192			179		194	
30	182	191	191	169	190	145	166	188	188	180
63	159	173	181	163	183	104	111	181	150	139
94	148	159	168	149	174	100	102	166	140	123
101	203			202			205			203
140	195	197	196	193	197	196	192	195	194	186
171	181	182	184	179	184	178	180	185	182	177
195	175	173	178	170	175	168	171	174	172	166
255	161	163	165	159	164	157	159	107	162	157

A15.3 H_2 mbar

Day	NCS1:1	NCS1:2	NCS1:3	NCS1:4	NCS1:5	NCS4:1	NCS4:2	NCS4:3	NCS4:4	NCS4:5
1	0.038			0.077			0.107		0.116	
30	3.094	3.171	3.056	2.636	1.786	4.118	6.042	5.678	6.843	4.968
63	2.083	2.284	2.661	2.233	1.409	2.174	2.664	4.326	5.355	3.628
94	2.294	2.321	2.419	2.175	1.601	2.330	2.815	7.155	4.676	3.296
101	0.061			0.040			0.041			0.020
140	0.468	0.552	0.980	0.733	0.571	1.607	1.574	1.443	2.018	1.432
171	0.796	0.728	1.141	1.002	0.626	2.492	2.394	2.183	2.803	2.142
195	0.735	0.692	0.997	0.867	0.473	2.134	2.086	1.827	2.976	2.224
255	0.918	0.831	1.073	1.002	0.574	2.669	2.751	2.226	3.775	3.407

A15.4 O_2 mbar

Day	NCS1:1	NCS1:2	NCS1:3	NCS1:4	NCS1:5	NCS4:1	NCS4:2	NCS4:3	NCS4:4	NCS4:5
1	2.957			2.150			2.542		1.630	
30	3.058	3.285	2.903	4.462	2.850	2.871	2.224	3.008	2.820	3.024
63	0.827	0.484	0.489	0.538	0.494	0.426	0.444	0.163	0.390	0.334
94	0.733	1.458	1.114	1.254	1.714	1.509	1.842	1.300	1.950	0.478
101	2.111			1.737			2.173			1.259
140	1.482	1.261	1.333	1.216	1.478	1.784	1.517	1.638	1.882	1.525
171	0.615	0.182	0.147	0.394	0.221	0.623	0.540	0.111	0.073	0.071
195	0.228	0.329	0.303	0.561	0.420	0.470	0.428	0.557	0.550	0.780
255	0.741	1.223	1.122	0.700	0.918	1.146	0.843	1.669	1.037	0.597

A16 NUK

A16.1 Volume gas mL

Day	NUK:1	NUK:2	NUK H2O:1	NUK H2O:2	NUK H2O:3
0	5.4	5.6	5.7	5.7	5.8

A16.2 Pressure kPa

Day	NUK:1	NUK:2	NUK H2O:1	NUK H2O:2	NUK H2O:3
1	205	207	208	210	211
36	180	172	193	196	
69	171	172	185	186	198
90	161	162	173	172	187
118	156	158	167	167	180
153	144	145	154	153	164

A16.3 H_2 mbar

Day	NUK:1	NUK:2	NUK H2O:1	NUK H2O:2	NUK H2O:3
1	0.062	0.041	0.042		
36	0.126	0.103	0.135	0.098	
69	0.120	0.120	0.130	0.112	0.119
90	0.145	0.113	0.104	0.086	0.131
118	0.140	0.126	0.134	0.100	0.126
153	0.115	0.131	0.123	0.138	0.098

A16.4 O_2 mbar

Day	NUK:1	NUK:2	NUK H2O:1	NUK H2O:2	NUK H2O:3
1	1.948	1.594	1.664		
36	1.602	1.909	2.509	1.490	
69	0.274	0.843	0.463	0.651	0.554
90	0.531	0.616	2.439	0.912	1.272
118	1.154	0.932	1.319	0.902	0.900
153	0.850	0.464	0.724	1.148	0.869

A17 UK

A17.1 Volume gas mL

Day	UK1:1	UK1:2	UK2:1	UK2:2	UK H2O:1	UK H2O:2	UK H2O:3	UK H2O:4	UK H2O:5
0	5.3	5.2	5.5	5.8	5.3	5.3	5.4	5.5	5.1

A17.2 Pressure kPa

Day	UK1:1	UK1:2	UK2:1	UK2:2	UK H2O:1	UK H2O:2	UK H2O:3	UK H2O:4	UK H2O:5
1	181	181	180	179	181	180	181	183	183
29	172	173	172	171	173	172	173	171	175
63	157	160	157	157	156	159	159	154	160
94	156	158	155	154	153	155	156	153	154
136	145	146	144	145	144	146	147	144	147
164	131	135	133	135	134	136	138	127	132
192	130	132	128	133	132	129	137	134	135
220	120	122	122	125	124	123	130	127	121
312	116	118	116	120	118	121	126	122	114
388	116	117	112	112	106				

A17.3 H_2 mbar

Day	UK1:1	UK1:2	UK2:1	UK2:2	UK H2O:1	UK H2O:2	UK H2O:3	UK H2O:4	UK H2O:5
1	0.054	0.018	0.018	0.018	0.018	0.036	0.018	0.018	0.018
29	0.086	0.087	0.103	0.103	0.104	0.172	0.087	0.068	0.070
63	0.094	0.128	0.141	0.157	0.109	0.159	0.111	0.108	0.096
94	0.156	0.126	0.186	0.154	0.138	0.155	0.140	0.138	0.108
136	0.160	0.146	0.245	0.232	0.158	0.175	0.176	0.158	0.103
164	0.118	0.135	0.200	0.203	0.134	0.136	0.152	0.140	0.092
192	0.117	0.132	0.166	0.200	0.132	0.194	0.151	0.147	0.095
220	0.168	0.146	0.134	0.175	0.099	0.111	0.130	0.127	0.073
312	0.081	0.094	0.139	0.120	0.094	0.109	0.113	0.098	0.046
388	0.116	0.059	0.056	0.123	<LOD				

A17.4 O_2 mbar

Day	UK1:1	UK1:2	UK2:1	UK2:2	UK H2O:1	UK H2O:2	UK H2O:3	UK H2O:4	UK H2O:5
1	0.688	1.647	1.260	1.181	0.977	1.026	0.760	0.220	0.915
29	1.324	1.090	0.860	1.214	1.228	1.359	1.246	1.214	1.085
63	0.973	1.104	2.308	1.240	0.780	0.811	0.588	1.063	1.216
94	0.250	0.300	0.264	0.416	0.260	0.403	0.359	0.398	0.354
136	0.102	0.044	0.072	0.189	0.346	0.248	0.294	0.605	0.132
164	0.524	0.405	0.479	0.405	0.402	0.408	0.386	0.445	0.383
192	0.065	0.053	0.038	0.027	0.026	0.077	0.055	0.040	0.054
220	0.120	0.061	0.049	0.050	0.025	0.049	0.234	0.216	0.339
312	0.046	0.059	0.070	0.060	0.071	0.061	0.164	0.061	0.068
388	0.023	0.023	0.067	0.022	0.011				

A18 A

A18.1 Volume gas mL

Day	A:1	A:2	AC:1	AC:2
0	5.6	5.6	5.5	5.5

A18.2 Pressure kPa

Day	A:1	A:2	AC:1	AC:2
0	201	206	207	207
10	187	187	191	191
34	173	172	179	180
62	163	161	167	169
88	155	150	167	156
131	146	140	126	142
186	136	138	123	138
213	129	133	114	132
251	127	124	117	120
286	113	106	106	117

A18.3 H_2 mbar

Day	A:1	A:2	AC:1	AC:2
0	0.020	0.021	0.021	0.021
10	0.075	0.150	0.783	1.146
34	0.087	0.155	2.578	3.114
62	0.114	0.177	4.142	4.208
88	0.109	0.300	3.841	5.054
131	0.160	0.206	4.375	5.313
186	0.147	0.179	3.945	4.477
214	0.193	0.132	3.547	4.196
257	0.204	0.144	4.206	4.977
286	0.260	0.095	4.378	4.458

A18.4 O_2 mbar

Day	A:1	A:2	AC:1	AC:2
0	2.533	2.245	1.573	1.656
10	1.646	1.646	1.948	1.566
34	0.035	0.034	0.036	0.126
62	0.049	0.064	0.050	0.034
88	0.062	0.060	0.067	0.062
131	0.263	0.266	0.290	0.426
186	0.258	0.193	0.197	0.235
213	0.039	0.053	0.034	0.224
251	0.140	0.136	<LOD	0.336
286	0.215	0.286	0.244	0.199

A19 B

A19.1 Volume gas mL

Day	B:1	B:2
0	5.2	5.4
244	5.5	5.4

A19.2 Pressure kPa

Day	B:1	B:2
0	210	207
3	194	191
13	179	176
41	169	167
66	162	160
94	149	146
173	142	140
200	135	133
243	133	125
244	216	
245	193	
251	182	
270	172	114
299	167	114
329	156	109

A19.3 H_2 mbar

Day	B:1	B:2
0	0.021	<LOD
3	0.388	0.439
13	1.432	0.475
41	1.673	0.484
66	1.328	0.416
94	1.162	0.350
173	0.980	0.308
200	0.918	0.306
243	0.865	0.338
244	<LOD	
245	0.019	
251	0.073	
270	0.086	0.239
299	0.134	0.205
329	0.125	0.174

A19.4 O_2 mbar

Day	B:1	B:2
0	1.344	1.925
3	0.136	0.191
13	0.054	0.018
41	0.051	0.050
66	0.032	0.016
94	0.656	0.584
173	0.369	0.252
200	0.041	0.040
243	0.160	0.650
244	0.432	
245	0.598	
251	0.055	
270	0.189	0.398
299	0.167	0.080
329	0.156	0.065

A20 C

A20.1 Volume gas mL

Day	C:1	C:2
0	5.9	5.9
244	6.1	5.9

A20.2 Pressure kPa

Day	C:1	C:2
0	207	
3	190	203
13	170	179
41	164	167
67	159	162
94	148	150
123	145	146
173	140	141
200	137	136
243	135	134
244		214
245		198
251		178
270	125	168
301	122	162
329	90	151

A20.3 H_2 mbar

Day	C:1	C:2
0	0.031	
3	8.496	10.572
13	9.287	10.625
41	7.918	8.964
67	7.236	8.464
94	6.846	7.751
123	6.068	6.783
173	4.083	4.663
200	3.382	3.822
243	2.907	3.047
244		<LOD
245		<LOD
251		<LOD
270	2.958	0.118
301	1.854	0.113
329	0.828	0.136

A20.4 O_2 mbar

Day	C:1	C:2
0	1.904	
3	0.038	0.081
13	0.272	0.358
41	0.984	0.468
67	1.081	1.102
94	2.190	1.980
123	3.132	2.920
173	1.736	1.015
200	1.151	1.088
243	0.324	0.167
244	<LOD	0.364
245		0.733
251		<LOD
270	0.397	0.235
301	4.392	0.113
329	8.001	0.151

A21 D

A21.1 Volume gas mL

Day	D:1	D:2
0	5.8	5.7
258	5.5	5.7

A21.2 Pressure kPa

Day	D:1	D:2
0	208	
10	185	191
34	173	178
62	162	166
88	150	154
131	144	149
187	131	143
257	130	
258	203	
259	216	
266	199	
284	189	137
313	177	129
348	156	102

A21.3 H_2 mbar

Day	D:1	D:2
0	0.021	0.021
10	0.370	0.096
34	0.363	0.142
62	0.275	0.100
88	0.285	0.123
131	0.230	0.119
187	0.183	0.114
257	0.195	0.110
258	<LOD	
259	<LOD	
266	0.038	
284	0.071	0.103
313	<LOD	0.114
348	0.125	0.071

A21.4 O_2 mbar

Day	D:1	D:2
0	2.246	1.414
10	1.406	1.413
34	0.052	0.053
62	0.049	0.050
88	0.060	0.046
131	0.389	0.164
187	0.223	0.286
257	0.078	0.164
258	0.454	
259	0.398	
266	0.057	
284	0.283	0.335
313	0.169	0.076
348	0.281	6.620

A22 E

A22.1 Volume gas mL

Day	E:1	E:2
0	5.9	6.0

A22.2 Pressure kPa

Day	E:1	E:2
3	204	205
13	190	191
41	181	180
67	170	170
94	158	157
173	152	152
244	144	143

A22.3 H_2 mbar

Day	E:1	E:2
3	0.061	0.082
13	0.076	0.096
41	0.091	0.108
67	0.085	0.170
94	0.095	0.094
173	0.152	0.167
244	0.230	0.229

A22.4 O_2 mbar

Day	E:1	E:2
3	0.061	0.062
13	0.038	0.038
41	0.561	0.522
67	0.051	0.034
94	0.411	0.424
173	0.304	0.182
244	0.518	0.272

A23 F

A23.1 Volume gas mL

Day	F:1	F:2
0	5.5	6.0

A23.2 Pressure kPa

Day	F:1	F:2
3	204	206
13	195	194
41	183	183
67	172	170
94	160	159
173	153	153
244	144	144

A23.3 H_2 mbar

Day	F:1	F:2
3	0.204	0.124
13	0.176	0.116
41	0.201	0.165
67	0.189	0.136
94	0.192	0.111
173	0.168	0.184
244	0.216	0.202

A23.4 O_2 mbar

Day	F:1	F:2
3	0.122	0.041
13	0.039	0.039
41	0.439	0.439
67	0.052	0.034
94	0.368	0.525
173	0.138	0.168
244	0.086	0.274

A24 G

A24.1 Volume gas mL

Day	G:1	G:2
0	5.3	5.1

A24.2 Pressure kPa

Day	G:1	G:2
0	204	205
1	189	192
8	171	174
29	165	170
65	152	158
94	141	149
127	133	135
185	124	127
252	119	122
297	114	121

A24.3 H_2 mbar

Day	G:1	G:2
0	<LOD	0.021
1	0.019	0.038
8	0.086	0.087
29	0.083	0.119
65	0.061	0.126
94	0.113	0.149
127	0.106	0.135
185	0.149	0.191
252	0.131	0.183
297	0.148	0.194

A24.4 O_2 mbar

Day	G:1	G:2
0	2.938	2.419
1	2.117	0.499
8	1.214	0.748
29	0.066	0.085
65	0.182	0.348
94	0.254	0.060
127	0.013	0.027
185	0.099	0.318
252	0.309	0.817
297	0.319	0.157

A25 H

A25.1 Volume gas mL

Day	H:1	H:2
0	5.0	5.2

A25.2 Pressure kPa

Day	H:1	H:2
0	206	205
1	190	188
8	173	173
29	168	164
65	157	153
94	148	145
127	143	136
185	133	128
252	126	121

A25.3 H_2 mbar

Day	H:1	H:2
0	<LOD	0.021
1	0.019	0.056
8	0.138	0.156
29	0.218	0.131
65	0.141	0.107
94	0.178	0.131
127	0.172	0.109
185	0.226	0.166
252	0.189	0.121

A25.4 O_2 mbar

Day	H:1	H:2
0	1.401	1.681
1	0.152	0.188
8	1.107	0.917
29	0.101	0.033
65	0.141	0.230
94	0.222	0.131
127	0.029	0.027
185	0.333	0.397
252	0.076	0.218

A26 I

A26.1 Volume gas mL

Day	I:1	I:2
0	5.6	5.2

A26.2 Pressure kPa

Day	I:1	I:2
0	205	206
1	185	187
8	171	173
29	163	167
65	151	151
94	142	143
127	133	136
185	129	128
252	120	117

A26.3 H_2 mbar

Day	I:1	I:2
0	0.021	0.021
1	0.019	0.019
8	0.120	0.052
29	0.163	0.050
65	0.121	0.076
94	0.128	0.057
127	0.120	0.082
185	0.142	0.102
252	0.096	0.117

A26.4 O_2 mbar

Day	I:1	I:2
0	1.948	1.339
1	0.093	0.131
8	1.180	1.194
29	0.049	0.033
65	0.393	0.302
94	0.071	0.072
127	0.027	0.014
185	0.065	0.051
252	0.252	0.293

A27 J

A27.1 Volume gas mL

Day	J:1	J:2
0	5.6	5.5

A27.2 Pressure kPa

Day	J:1	J:2
0	198	197
8	179	180
34	169	168
71	164	160
97	150	127
182	145	123
226	114	120

A27.3 H_2 mbar

Day	J:1	J:2
0	<LOD	<LOD
8	0.161	0.162
34	0.169	0.134
71	0.164	0.160
97	0.180	0.102
182	0.145	0.098
226	0.000	0.108

A27.4 O_2 mbar

Day	J:1	J:2
0	0.119	0.670
8	1.468	0.270
34	0.085	0.118
71	1.240	0.240
97	0.045	0.038
182	0.392	0.111
226	0.423	0.228

A28 K

A28.1 Volume gas mL

Day	K:1	K:2
0	5.5	5.6
142	6.0	5.6

A28.2 Pressure kPa

Day	K:1	K:2
0	198	197
8	181	180
34	169	169
72	150	151
97	143	142
141	142	143
142	214	
143	199	
149	187	
170	176	134
199	166	131
227	158	127

A28.3 H_2 mbar

Day	K:1	K:2
0	0.020	0.020
8	3.421	2.448
34	3.465	2.129
72	3.495	2.099
97	2.889	1.676
141	2.414	1.573
142	<LOD	
143	<LOD	
149	<LOD	
170	0.106	1.032
199	0.133	0.865
227	0.126	0.622

A28.4 O_2 mbar

Day	K:1	K:2
0	0.059	0.197
8	0.579	0.324
34	0.085	0.169
72	<LOD	<LOD
97	0.029	0.028
141	0.071	0.143
142	0.107	
143	0.179	
149	0.037	
170	0.194	0.188
199	0.266	0.223
227	0.411	0.203

A29 L

A29.1 Volume gas mL

Day	L:1	L:2
0	5.4	5.0

A29.2 Pressure kPa

Day	L:1	L:2
0	200	200
3	184	185
32	170	170
60	161	160
95	150	153
124	148	147
137	138	138
153	136	135
181	131	131
208	121	120
238	116	125
271	114	121

A29.3 H_2 mbar

Day	L:1	L:2
0	<LOD	<LOD
3	0.184	0.093
32	6.052	5.712
60	7.342	6.960
95	8.115	7.757
124	8.170	7.526
137	7.866	6.859
153	7.810	6.226
181	8.843	7.952
208	8.192	7.056
238	6.716	6.500
271	5.882	5.953

A29.4 O_2 mbar

Day	L:1	L:2
0	0.980	1.820
3	0.368	0.481
32	0.714	0.663
60	0.193	0.192
95	0.015	0.031
124	0.074	0.353
137	0.331	0.400
153	0.340	0.392
181	0.694	0,380
208	0.303	0.120
238	1.218	0.925
271	3.511	3.678

A30 M

A30.1 Volume gas mL

Day	M:1	M:2
0	5.7	5.5
142	5.7	5.4

A30.2 Pressure kPa

Day	M:1	M:2
0	197	196
8	182	179
35	159	168
72	133	151
97	128	144
141	128	141
142		212
143		198
149		187
170	121	174
199	119	168
227	108	160

A30.3 H_2 mbar

Day	M:1	M:2
0	<LOD	<LOD
8	1.911	1.718
35	1.161	1.159
72	0.718	0.891
97	0.589	0.778
141	0.550	0.663
142		<LOD
143		0.020
149		0.056
170	0.387	0.035
199	0.238	0.084
227	0.194	0.080

A30.4 O_2 mbar

Day	M:1	M:2
0	0.118	0.216
8	0.637	0.501
35	0.254	0.118
72	0.572	0.483
97	0.038	0.043
141	0.141	0.395
142		0.170
143		0.554
149		0.056
170	0.157	0.261
199	0.119	0.353
227	1.512	0.336

A31 Q

A31.1 Volume gas mL

Day	Q:1	Q:2
0	5.6	5.7

A31.2 Pressure kPa

Day	Q:1	Q:2
0	197	199
1	182	181
8	170	170
17	160	152
24	149	143
36	145	137
71	136	129

A31.3 H_2 mbar

Day	Q:1	Q:2
0	<LOD	<LOD
1	0.055	0.109
8	0.459	0.510
17	0.480	0.456
24	0.313	0.343
36	0.392	0.343
71	0.286	0.258

A31.4 O_2 mbar

Day	Q:1	Q:2
0	0.611	0.259
1	0.364	0.489
8	0.187	0.255
17	0.560	0.410
24	0.462	0.386
36	0.174	0.192
71	0.122	0.219

A32 Controls to experiment B–C, E–F

A32.1 Volume gas mL

Day	N2:1	N2:2	N2:3	N2:4	N2:5	H2O:1	H2O:2	H2O:3	H2O:4	H2O:5
0	26.2	26.2	26.2	26.2	26.2	6.1	5.5	5.7	5.7	5.5

A32.2 Pressure kPa

Day	N2:1	N2:2	N2:3	N2:4	N2:5	H2O:1	H2O:2	H2O:3	H2O:4	H2O:5
3	212	211	212	215	215	200	205	196	209	207
13	208	209	209	209	211	187	195	187	194	192
40	203	204	206	206	209	172	184	177	183	182
67	202	203	202	203	203	163	164	165	170	170
95	197	198	198	196	200	152	153	154	158	158
173	197	196	198	196	196	155	149	149	150	156
264	196	195	196	194	195	142	139	143	149	149

A32.3 H_2 mbar

Day	N2:1	N2:2	N2:3	N2:4	N2:5	H2O:1	H2O:2	H2O:3	H2O:4	H2O:5
3	0.021	<LOD	<LOD	<LOD	0.022	0.040	<LOD	0.059	0.042	0.062
13	<LOD	0.021	0.021	0.021	<LOD	0.056	0.059	0.094	<LOD	0.058
40	0.020	0.020	0.021	0.021	0.021	0.086	0.055	0.106	0.092	0.091
67	<LOD	0.020	0.020	0.020	0.020	0.049	0.066	0.099	0.085	0.136
95	0.020	0.020	<LOD	0.020	0.020	0.076	0.061	0.108	0.095	0.063
173	0.020	0.020	0.020	0.020	0.020	0.093	0.060	0.104	0.075	0.094
264	0.020	0.020	<LOD	<LOD	<LOD	0.113	<LOD	<LOD	<LOD	<LOD

A32.4 O_2 mbar

Day	N2:1	N2:2	N2:3	N2:4	N2:5	H2O:1	H2O:2	H2O:3	H2O:4	H2O:5
3	0.042	0.042	0.064	0.065	0.086	0.540	2.337	0.098	0.021	0.083
13	0.062	0.063	0.063	0.042	0.063	0.075	1.229	0.056	0.019	0.019
40	0.893	1.183	0.062	0.041	0.606	0.912	1.803	0.566	0.567	0.564
67	0.303	0.142	0.081	0.325	0.568	0.016	0.049	0.347	0.119	0.068
95	0.493	0.495	0.515	0.549	0.480	0.608	0.857	0.770	0.411	0.379
173	0.315	0.274	0.297	0.157	0.176	0.171	0.119	0.224	0.195	0.187
264	0.470	0.332	0.255	0.292	0.331	0.156	0.125	0.186	0.149	0.179

A33 Controls to experiment G–I

A33.1 Volume gas mL

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	26.2	26.2	26.2	5.3	5.8	5.5

A33.2 Pressure kPa

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	218	218	219	206	207	206
9	211	213	214	192	193	190
29	211	212	212	178	182	179
65	205	205	205	164	168	166
94	201	201	201	155	159	155
220	201	202	203	148	142	152
252	195	198	198	139	134	142

A33.3 H_2 mbar

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	<LOD	<LOD	<LOD	0.021	<LOD	0.062
9	0.021	0.021	0.021	0.058	0.077	0.057
29	<LOD	0.021	<LOD	0.053	0.073	0.054
65	<LOD	0.000	<LOD	0.082	0.101	0.050
94	0.020	0.020	0.020	0.093	0.111	0.078
220	0.020	0.020	<LOD	0.074	0.099	0.106
252	0.039	0.020	<LOD	0.111	0.147	0.142

A33.4 O_2 mbar

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	1.112	0.174	0.066	0.185	0.083	0.103
9	1.899	1.470	0.942	1.094	1.100	0.893
29	0.928	0.127	0.064	0.036	0.073	0.018
65	0.738	0.103	0.349	0.131	0.235	0.066
94	0.824	0.322	0.161	0.434	0.095	0.248
220	0.342	0.081	0.081	0.074	0.043	0.030
252	0.897	0.614	0.317	0.222	0.121	0.256

A34 Controls to experiment L

A34.1 Volume gas mL

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	26.2	26.2	26.2	5.2	5.7	5.7

A34.2 Pressure kPa

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	213	214	216	202	201	207
3	211	211	212	188	188	191
32	197	206	207	171	171	170
73	163	195	203	158	140	102
112	157	189	200	144	125	101
182	116	188	201	138	125	103
249	91	152	196	114	119	100
272	91	145	193	105	113	98

A34.3 H_2 mbar

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	<LOD	<LOD	0.022	<LOD	<LOD	0.021
3	0.021	0.021	0.021	0.056	0.056	0.057
32	0.020	0.021	0.021	0.086	0.086	0.085
73	0.016	0.020	0.020	0.079	0.070	0.061
112	0.016	0.019	0.020	0.101	0.113	0.091
182	0.012	<LOD	0.040	<LOD	<LOD	<LOD
249	0.018	0.030	0.020	0.149	0.143	0.170
272	<LOD	0.015	0.019	0.147	0.158	0.127

A34.4 O_2 mbar

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	0.596	0.642	1.102	0.263	0.101	0.642
3	0.464	0.380	0.085	0.188	0.132	0.096
32	0.847	0.906	0.124	0.051	0.086	0.085
73	0.261	0.312	0.244	0.111	0.098	0.082
112	0.173	0.151	0.100	0.389	0.425	0.202
182	0.313	1.072	0.000	0.414	0.150	4.903
249	25.950	2.892	3.800	3.215	<LOD	14.840
272	32.578	5.133	5.385	20.433	28.544	33.781

A35 Controls to experiment J, K and M

A35.1 Volume gas mL

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	26.2	26.2	26.2	5.6	5.6	5.6

A35.2 Pressure kPa

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	206			200	199	
8	204	209		185	182	
34	199	206		174	172	194
72	196	203	212	163	161	183
182	192	199	182	148	152	174
227	187	179	179	141	143	162

A35.3 H_2 mbar

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	<LOD			<LOD	<LOD	
8	0.020	0.021		0.037	0.073	
34	0.020	0.021		0.052	0.103	0.058
72	0.020	<LOD	0.085	0.082	0.113	0.073
182	<LOD	0.020	0.018	0.118	0.137	0.104
227	0.019	0.018	0.018	<LOD	<LOD	0.113

A35.4 O_2 mbar

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	0.206			0.220	0.896	
8	0.163	0.397		0.444	0.855	
34	0.259	0.185		0.800	0.980	0.175
72	0.345	0.509	0.538	0.193	0.439	<LOD
182	0.365	0.557	0.473	0.444	0.076	0.191
227	0.879	0.125	0.394	0.409	0.372	0.194

A36 Controls to re-started experiment B–D, K and M

A36.1 Volume gas mL

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	26.2	26.2	26.2	5.4	5.5	5.1

A36.2 Pressure kPa

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
1	222	218	226	217	222	227
7	221	217	225	203	209	213
26	215	213	221	190	195	198
55	215	212	218	181	187	187
90	208	206	206	166	174	173

A36.3 H_2 mbar

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
1	<LOD	0.022	<LOD	0.022	<LOD	<LOD
7	<LOD	<LOD	<LOD	<LOD	0.042	0.064
26	0.022	<LOD	<LOD	0.057	0.098	0.079
55	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
90	0.021	0.021	0.021	0.083	0.087	0.087

A36.4 O_2 mbar

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
1	0.488	0.305	0.226	0.391	0.444	0.068
7	0.199	0.326	0.090	0.061	0.021	0.043
26	0.387	0.362	0.464	0.342	<LOD	<LOD
55	0.366	0.233	0.174	0.145	0.468	0.187
90	0.187	0.185	0.206	0.232	0.122	0.138

A37 Controls to Q

A37.1 Volume gas mL

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	26.2	26.2	26.2	5.8	5.8	5.3

A37.2 Pressure kPa

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	204	203	202	198.8	198.9	181.6
1	200	198	198	182.9	188	174
8	198	197	196	165	176	164
17	190	192	185	157	168	155
24	189			144		
36	185	193	180	128	162	153
72	178	177	176	107	152	143

A37.3 H_2 mbar

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
1	<LOD	<LOD	<LOD	<LOD	0.056	<LOD
8	<LOD	<LOD	0.020	0.033	0.053	<LOD
17	<LOD	<LOD	<LOD	0.047	0.067	0.047
24	0.019			0.029		
36	0.019	<LOD	<LOD	0.038	<LOD	<LOD
72	0.036	0.018	<LOD	0.043	0.061	<LOD

A37.4 O_2 mbar

Day	N2:1	N2:2	N2:3	H2O:1	H2O:2	H2O:3
0	0.368	0.345	0.383	0.358	0.875	0.690
1	0.599	0.714	0.535	0.530	0.602	0.470
8	0.515	0.512	0.431	0.380	0.563	0.295
17	1.786	0.710	0.833	0.597	0.336	0.233
24	0.756			0.130		
36	0.518	0.444	0.324	0.154	0.227	0.138
72	0.392	0.318	0.317	0.750	0.091	0.100

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