NOBLE GAS ANALYSIS

1001 EDITION

WATER MACHINES FOR DUMMIES

EVERYTHING YOU DON'T DARE TO ASK AFTER 7 YEARS IN THE LAB

Noble-gas analysis for water heads at ETHZ

Matthias Brennwald

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http://github.com/brennmat/nglabdoc

Contents

Chapter 1

Overview

This document is intended to provide some hands-on information on the handling and analysis of noble-gas samples in the ETH noble-gas lab. For a more theoretical description of the noble-gas analysis refer to [**?**].

Please be aware that this document is a work in progress and will be updated or changed as necessary. Please do not assume this information to stay the same for all time. Also, if you find errors or have suggestions for improvements of changes, please do not hesitate to inform the author about this. The latest version of this document available at http://wut-ui.eawag.wroot.emp-eaw.ch/svn/NG_LAB_DOC/NG_LAB_DOC.pdf.

Chapter 2

Sample preparation

2.1 Before sampling

Before sampling, a member of the UI group must be defined as the responsible person for administration of the samples. For projects within the UI group, the choice of this person will be obvious (investigator of the project). For external projects (PI is not a member of the UI group), a member of the UI group must be defined as the care taker before proceeding with the sampling. Basic information on such external samples must be recorded (on paper) in the folder 'External Samples' (in MBs office).

For external projects, the external PI is required to provide a short summary of the project to MB (about one page), covering the following points:

- What is the scientific background of the project?
- How many samples will be required?
- Can the external group provide manpower for the lab work?
- What is the anticipated output of the project, and how will the UI group be involved in this (e.g. publications, reports, etc.)?

Based on this information, we (the UI group) will then discuss if and how we want to participate in the project, *and who will be the contact person in the UI group*.

Sampling instructions[1] must be forwarded to the external group / PI with the note that (i) sample quality will be in the responsibility of the external group / PI and (ii) commercial samples that cannot be analyzed properly due to poor sample quality will be charged the full price.

[1] Instructions are available at http://www.eawag.ch/forschung/wut/schwerpunkte/umweltisotope/methoden/probenahme_EN

2.2 During sampling

A detailed list of sampling instructions is available online (http://www.eawag.ch/forschung/wut/schwerpunkte/umweltisotope/methoden/probenahme_EN). The most important points to remember during sampling are:

- Sample containers must be flushed extensively with sample water before closing the clamps
- Gas bubbles in the sampling system must be avoided
- The steel clamps need to be *fully closed* to avoid leakage during transport and storage before gas extraction (i.e. washers are immobile).

2.3 After sampling

Before analysis in the lab, the following sample information must to be entered in the Noble-gas Database (http://noblegas.aquatic-research.ch), i.e.:

- Clamp ID (QID)
- Study ID (PNSID)
- Sample weights (before and after filling with water)
- Sampling date
- Name of contact person within the UI group (sampling info)

Chapter 3

Running samples with with Super Gnom and MM5400

3.1 Preparing a new run

3.1.1 Source settings at SuperGnom

Low ionisation energy

Set electron energy from 100 eV to 45 eV to minimise double charged ions (e.g. for speleothem samples).

1. Read filament current (display to the right). Value is about 4.05 A.
2. Turn off filament by pushing the button once. Set the emission control to the value 17 (check if this value was written down the last time). Turn the filament back on until a + shows up. The filament current will rise to a value slightly higher than the one written down before. 170 mA is the current of electrons to be emitted. The filament current is then automatically adjusted to yield this electron emission (display just opposite).
3. Switch to position 3: Turn the potientometer 3 counter clockwise to its stop (about -800 (80V). Potential wird heruntergesetzt, damit es sicher tiefer liegt als Filament (falls Filament in einem Loch liegt, dann heizt es weiter auf, weil man ja einen Strom von Elektronen von 170mA eingestellt hat. Das kann dazu führen, dass das Filament kaputt geht)
4. Switch to position 5. Turn potentiometer 5 counter clockwise to its stop (about -1000). Potential wird heruntergesetzt, damit es sicher tiefer liegt als Filament (falls Filament in einem Loch liegt, dann heizt es weiter auf, weil man ja einen Strom von Elektronen von 170mA eingestellt hat. Das kann dazu führen, dass das Filament kaputt geht)
5. Switch to position 8 (Filament, das will man ändern). Slowly turn potentiometer 8 until -450 (kann man relativ schnell machen)

6. Switch to position 3. Slowly turn to the value written down the last time.

7. Switch to position 5. Slowly turn to the value written down the last time. ACHTUNG: Watch the filament current, it must not reach values higher than the one wtritten down under step 1. Mit dem einstellen von 3 und 5 wird der Elektronenstrahl fokussiert auf das Loch in 6. Das Potential nimmt ab von 5 nach 6, dazwischen Filament als ‚ÄúBerg‚Äù. Von 6-7 ist es eher flach. Um zu überprüfen, wie gut der Strahl fokussiert ist, Strom an 4 ablesen und mit den 170mA vergleichen.

8. Position 1 and 2 einstellen auf die Werte, die das letzte mal aufgeschrieben wurden. ODER Tunen und das so einstellen.

9. Alle Werte aufschreiben (Achtung auf Trap on und off) Elektronenstrahl geht als Hohlzylinder vom Filament weg (dieses ist rund), er trifft bei 7 wieder als Hohlzylinder auf die Wände auf. Es gelangen also keine Elektronen durch den Spalt. Die Potentialverteilung geht von 5 bis 6 so steil wie die Spannung eingestellt ist. Von 6–7 ist es flach, bevor es steil runter geht für die Ionen. Am engsten in es ganz unten wo die Ionen austreten.

10. Falls man den Ionenstrahl tunen will:

    (a) Turbopumpe hochfahren und von der Vacion auf Turbo umstellen

    (b) Ventile einstellen, so dass eingelassenes Gas nicht an getter geht und nicht abgepumpt wird.

    (c) Fastcal einlassen, bis an Ventil 114.

    (d) Close Pump Spektro (115)

    (e) Open 114

    (f) SCAN: Item usw. Einstellen, peak zentrieren

    (g) TREND: Mit potentiometer 1 und 2 den Ionenstrahl lenken (eher einzeln als zusammen, dies würde einfach die Steigung verändern aber nicht unbedingt lenken). Hier kann man auch noch 3 und 5 dazunehmen, um das Signal zu verbessern

    (h) Pumpe Spektro auf

    (i) Ventile wieder richtig stellen und Pumpe umhängen und runterfahren.

High ionisation energy

Set electron energy from 45 eV to 100 eV for higher sensitivity (e.g. for water samples).

1. Strom am Filament ablesen (Anzeige ganz rechts). Liegt bei etwa 4.05

2. Switch to position 8 (Filament, das will man ändern). Turn potentiometer 8 until -1000

3. Switch to position 3: Turn the potientometer 3 to the value written down the last time.

4. Switch to position 5. Turn potentiometer 5 to the value written down the last time.

5. Turn Filament off, by pushing the button once. Set the emission control to the value 25 (check if this value was written down the last time). Turn the filament back on until a + shows up. The filament current will rise to a value slighlty higher than the one written down before.

6. Position 1 and 2 einstellen auf die Werte, die das letzte mal aufgeschrieben wurden. ODER Tunen und das so einstellen.

7. Alle Werte aufschreiben (Achtung auf Trap on und off)

3.1.2 Sample information, stickers

Once all samples of a given run are available and recorded in the Noblegas Database, the STICKER file for use with IONIC and FINAL is exported from the database (menu Input/Output–Sticker HEGS). The sticker file is also printed to paper to keep track of the samples analysed during the run.

The sticker of a given sample contains basic information about this sample. The sample weight (water) is arbitrarily set to 45.0 g during export from the Noblegas Database. A typical sticker looks like this:

```
WA,116,137
C14T 0m 24.11.1995
45000.0,0.0,0.0,0.0
0.0;0.0,0.0,0.0
HeNe C14T 0m 24.11.1995
```

3.1.3 IONIC settings

CHECK SLUG NUMBERS OF CAL BOTTLES (SC, FC) AND ADJUST IF NECESSARY. USE BOOK AS REFERENCE. Prepare file paths (create directories on local disk and p drive). Sticker File dann auf dem Messcomputer unter File–Path–Stickerfile ablegen. Während dem Messen werden die entsprechenden Daten ins Messfile abgelegt.

3.2 Starting the machine

- Set temperature of cryo trop to 70 K (setpoint, type 70, enter)

- Start Computers for Super Gnom and MM5400, start Ionic on both computers (use the version on the server; the local copy is there to save your day if the server is down).

- Bring the Super Gnom turbo pump to full speed (button with the anchor-like pictogram)

- Pump the reservoirs, start with "water" until it reaches 10^{-1} mbar (channel 3); then pump "supergnom" until it reaches 10^{-1} mbar (channel 4).

- As soon as the reservoirs are pumped check the vacuum in the spectrometers, display below the MM5400, pressure should be $\sim 10^{-9}$ mbar (or better) for both Supergnom (channel 1) and MM5400 (channel 2); if the pressures are ok, disconnect the Vacion pumps and connect the Turbo pumps to the spectrometers. Note the pressure readings in the corresponding lab books.

- Prepare the pumping station: turn on "Membranpumpe", assemble the cold trap and fill up nitrogen, plug in "Drehschieberpumpe", pump the connection tube to the extraction line.

- Remove the oven from Zeo-2 and turn it off.

- Turn on filament of pressure gauge at the extraction line, check the pressure (should be 10^{-7} mbar or better).

- Set valve controllers to 'remote': turn off 'LOC' buttons one after another. Then run run `valve_init` in Ionic to set initial valve conditions. Automatic valve conditions should now be as follows:

  - Open: 002, 003, 004, 008, 010, 011, 012, 015, 108, 110, 111, 112, 115, 208, 209, 212, 213, 215
  - All other valves closed

- Cool Trap, Zeo-1 and cold trap at MM5400 inlet with liquid nitrogen.

- Open Getter 23.

- Close Valve 2.

- Turn on "Föhn" temperature controller (the power button of the "Föhn" itself should be on already).

- Turn off ion beam trap at the Super Gnom source controller.

- Record the filament currents of Super Gnom and MM5400 in the corresponding lab books.

- Turn off the heating the dilution reservoir (the switch is next to the switch for the water heater).

- Turn on the ovens for Trap, Zeo-1, and C15 using the switch ('hand' symbol) at the timer. Make sure C29 and C215 are hot.

3.3 Operating the machine

- Run the appropriate timer programs on the Super Gnom computer and follow the instructions of the timer:
  - `H2OS1.TIM` for large water samples (∼45 g of water)
  - `H2OS2.TIM` for smaller water samples (∼23 g of water)
  - `H2OS6.TIM` for small samples (∼1–10 g of water, e.g. sediment pore water)
- Keep track of the analysis results. Note the data in the corresponding lab books.
- Keep track of the analysis steps. Note the step types, step numbers and cal-slug numbers (fast cals, slow cals) in the corresponding lab book.
- Enter the analysis results in the SUBITO spereadsheet. Check the results to assess if the machine working as expected.
- Enter new sample information in the database (new weights, date of analysis, analysis notes).

3.3.1 Attach new water sample

Prepare new sample

- Select sample from printed sample list
- Weigh sample (remove any stickers, paper, labels, etc.; make sure no screws are missing), note under "Full" in sample weights book
- Cut off tip of the copper tube to obtain a clean flat copper surface
- Weigh sample again, note under "vor HEGS" in sample weights book

Remove old sample from line

These steps have been done already after sample extraction (prompted by timer file):

- Close valve 12 (disconnect bellows and old sample from line)
- Unhook old sample and put to the floor, so that water can flow back into the copper tube
- Put back clamp (a little further back from the original clamp spot) and close copper tube again (hold aluminum block with variable wrench and screw down large middle screw of clamp until washers are fully clamped)
- Put Quetsche on small stool for easier handling

- Loosen collet that fixes copper tube to extraction vessel and bellows (use special wrench and wrench 22 for stability)
- Unscrew quetsche from aluminum bracket and remove (pull, turn) copper tube carefully from cylinder connection
- Let remaining water drip from the exctraction vessel before new sample is attached

Attach new sample to line

- Loosen black/grey handles if necessary
- Insert new sample into collet as straight as possible (use your third and fourth hands and maybe other extremities), should have a little play
- Close handles to fix Quetsche in bracket
- Close collet (RoKi: close only loosely to produce air flow when pumping down the ventilated part with membrane pump. Matthias: close firmly to pump down ventilated part with membrane pump)
- Connect membrane pump to pump down ventilated part of copper tube, extraction vessel and bellows (open yellow valve to membrane pump and Nupro valve towards the pump wagon). Pressure on H3 (read from channel 3 on Controller "Hinten"). should come down towards $\sim$20 mbar, if not, try to tighten the ring connector a bit more
- Heat extraction vessel with heat gun to get rid of residual water
- Once the pressure is in the $\sim$20 mbar range, switch from membrane to rotary pump (make sure it has enough N2). The rotary pump should bring the pressure down to $\sim$0.2 mbar (H3)
- Once this pressure is reached on H3, the volume between valves 9, 4 and 12 can be pumped via the rotary pump, too, by opening valve 12.
- Now (prepare to) pump the sample connection via the backside's turbo:
  - Close Nupro leading towards the pump wagon
  - Close automated valve 8 (Zeo-1 and Trap are pumped via this valve towards the backsides turbo) to avoid dirty gas expanding towards Teo, Trap.
  - Open valve 3 to pump volume between 3 and 4 (Nupro) into turbo
  - Then open valve 4 (Nupro) to connect bellows and cylinder to turbo pump.
  - Check pressure on H4 (pirani on outside part of backside's turbo) and speed of turbo pump. Should not change a lot.
  - Open automatic 8 again, to pump Trap and Zeo-1 part of the line again

3.3.2 Attach new sediment sample (water aliquot)

Prepare sediment sample

- Select sample and determine suitable Swagelok connector parts that fit the copper tube (the tubes may have different diameters due to volume displacement during separation of aliquots)
- Attach copper tube to matching Swagelok/KF-16 adapter (i.e. the one with the right Swaglok thread dimensions). If Swagelok ferrule matches Cu tube well from the beginning, tighten Swagelok screw by hand, then use wrenches and tighten 1.25 turns. Otherwise, tighten more. Make sure not to distort copper tube.
- Weigh sediment sample with Swagelok/KF-16 adapter

3.3.3 Attach sediment sample to line

- Extraction vessel has CF-16/KF-16 junction attached instead of collet
- Clean both ends of the KF-16 (sediment sample and line side)
- Clean aluminum gasket (3rd drawer in desk)
- Put aluminum gasket between KF-16 connectors and close with (well greased) chain
- Make sure screws to open the sediment sample later on are well reachable
- Pump down cylinder and bellows according to the schedule for water samples

3.3.4 Remove sediment sample from line

- Other than for water samples, sediment samples need to be dried immediately after gas extraction, as the connectors are needed again for the following sample but the sample has to be weighted again with the connectors.
- Thus, after disconnecting the bellows (close valve 12), one can start heating (with heat gun) the open sediment sample and pumping the evolving water vapor into the membrane pump (open Nupro towards pump wagon). Keep an eye on pressure on H3 in order to judge whether or not the copper tube is dry already.
- Once the sample is dry, it can be removed from the line by opening the chain (don't forget to close Nupro to pump wagon)
- Weigh dry sediment sample with Swagelok/KF-16 adapter to obtain the water weight lost before removing the connector and attaching a new sample

3.3.5 Extract water sample (and pore water aliquots)

- Cylinder and bellows are pumped via Nupro 4 into the backside's turbo pump (manually operated valve 12 open)
- In order to not loose gas the timer prompts you to close Nupro 4 before sample extraction.
- Valve 009 is closed (separates sample gas from Trap and Zeo-1)
- When timer asks to open the sample:
- Loosen clamp by holding the aluminum block with wrench 22 and unscrewing the large middle screw until clamp moves freely.
- Loosen aluminum bar (with handle 2), move it backwards, tighten it again to guarantee stability during shaking
- Open copper tube with special calliper (now sample gas distributes to Nupro 4 and automated valve 009 (switched to manual controller)
- Open from manual controller automated valve 009, checking the pressure on channel 2 on Controller "Hinten". The respective pirani is located directly behind valve 009 (labelled "H2"). ! This pirani mainly measures the water pressure which is then frozen out on Trap. According to Yvonne, acceptable pressures are in the range of 5-7 e-1 mbar on "H2" [a broken sample comes along with a pressure of 6 e0 mbars (H2) and has to be pumped off!!!
- Also control pressure on pirani labelled "V1" close to Zeo-1, where all the other active gases apart from water are captured.

3.3.6 Pump off broken sample

- As 009 was open to check pressures, large amounts of atmospheric + sample gase of the broken sample have been admitted to Zeo-1 and Trap, where a part of it was already frozen out. Therefore, the line should not be pumped via the backside's turbo molecular pump, but via the rotary pump first. Therefore:
- First: remove old, broken sample and attach a new one.
- Pump ventilated part of the new copper tube, cylinder, and bellows via the small Nupro first with the membrane, then with the rotary pump according to the respective manual.
- Once this is done, defrost Zeo-1 with water (p increases on V1 to 2e1 mbars) and then heat it to 180 °C and pump this into the rotary pump. As between "Trap" and automated valve 009 there is a small capillary that can get clogged, don't pump via 009. Rather use the detour via automated valve 012 and close the backside's turbo for this procedure.

- Once Zeo-1 is hot, also the Trap can be pumped as described above.
- Handling of valves for pumping gas from line:
  - Automated valves 009, 011 (way to Zeo-2 blocked) and 013 (way to area "outlet" blocked) remain closed
  - Make sure automated valve 010 is closed (way to calibrations and back to Trap etc. is blocked)
  - make sure manually operated valve 17 (way to frontside's turbo is blocked) is closed
  - Close manually operated valve 1 (block way to backside's turbo)
  - Open automated valves 012 and 008
  - Open manually operated valves 3, 4, 12, Nupro to rotary pump: pump for 1 h, then go on with new sample.

3.4 Stopping the machine

- Turn off the compressor of the cryo trap and heat the cryo trap to room temperature (can be done during the last measurement when the cryo trap is not needed anymore, i.e. after "mute compressor"). Then set temperature to 100 K. Make sure the timer will turn on the compressor early in the morning of the next day, so the cryo will get cooled to 100 K.
- Put the oven on Zeo-2 and turn it on.
- Check the pressure in the spectrometers, should be $\sim 10^{-9}$. Record values in corresponding lab books.
- Attach the two spectrometers from the Turbo to the Vacion pump Reservoir (unten) einstellen, press the button with the anchor-like pictogram.
- Close Getter 23.
- Turn of the pumping station at the gas inlet (membrane and rotary pumps), open the cold trap.
- Turn on ion beam trap at Super Gnom.
- Put the valves on Local one after another, close Ionic and turn off the computers. Automatic valve conditions should now be as follows:
  - Open: 002, 004, 006, 008, 010, 011, 012, 015, 108, 110, 111, 112, 115, 209, 210, 212, 214, 215
  - All other valves closed

- Close all connections between fore vacuum pumps and reservoirs (fore pumps will stop automatically after a while).
- Turn off water heater.
- Open valve 2.
- Turn off “Föhn” temperature controller.

3.5 Other notes

3.5.1 Valve setting to activate large getter

There are several reasonable valve settings if the large getter needs to be activated/ heated, the following is one of them:

- Turn off heating of C29 and C215
- Set valves to standby conditions (“local”)
- Close 112, 21 (manual), 212, 214, 004, 29 (manual)
- Open 17 (manual), 001, 013, 213, 114 (i.e. manyfold pumped via SG vacion), 208

Chapter 4

Running samples with Tom Dooley

4.1 Preparing a new run

4.2 Starting the machine

4.2.1 Extraction line and cryo trap

- Sicherstellen, dass V3 geöffnet ist
- Membran- und Drehschieberpumpen bei Extraktionslinie in Betrieb nehmen (falls sie nicht sowieso laufen)
- Kühlfallen mit LN vorkühlen (T, Z1, Z2)
- Kryostat auf 14 K runterfahren
- Ventilsteuerung von local auf remote
- Check if getter is hot (280°C)

4.2.2 Mittelteil

- V2, V4 und V11 schliessen (Clean und Dirty trennen)
- Oben V1 und V4 schliessen (unbenutzte Verbindungslinien abhängen)
- Vorvakuum der Turbos (Clean, Dirty) pumpen, dann von Vacion auf Turbo umhängen

4.2.3 Massenspektrometer

- Getter MS auf 0 Volt
- V3 (und V1, falls nicht schon zu) am Manyfold schliessen (V2 und V6 sollen offen sein)

- C1 mit LN kühlen
- MS Turbo hochfahren, Vorvakuum öffnen (roter Knopf leuchtet)
- Ventilsteuerung auf remote. Am Computer zuerst Valve-Close-All (damit Ionic den Zustand der Hähne kennt), dann Anfangsbedingungen vom Timer setzen lassen (dabei wird das MS von Vacion auf Turbo umgehängt!).
- Trap ausschalten (rotes Lämpchen aus)
- Ventilsteuerung von local auf remote

4.3 Operating the machine

...

4.4 Stopping the machine

4.4.1 Extraktionslinie und Kryostat

- Kompressor ausschalten, Kryo auf Raumtemperatur hochfahren, danach Temperatur auf 100 K stellen (Zeitschaltuhr überprüfen, Kompressor sollte früh am nächsten Morgen eingeschaltet werden)
- Kühlfallen separat (!) auftauen und pumpen. Dabei Wasser aus Trap (T) zunächst mit Membranpumpe auspumpen (V3, Va108, Va109 schliessen). Später Trap und Zeo-1 zuerst mit Drehschieberpumpe am Schluss mit Turbopumpe pumpen und V3 wieder öffnen.
- Unbenutzte Membran- und Drehschieberpumpe ausschalten.
- Ventilsteuerung von remote auf local

4.4.2 Massenspektrometer

- Trap MS einschalten (rotes Lämpchen ein)
- C1 auftauen: zuerst V6 schliessen (Getter abhängen), dann C1 mit Wasser auftauen und Dreck zum Mittelteil pumpen (nicht via MS pumpen), danach V6 wieder öffnen
- Getter MS auf 70 Volt
- V3 (und V6) öffnen
- Ventilsteuerung von remote auf local (dabei wird das MS von Turbo auf Vacion umgehängt!)
- MS Turbo runterfahren, Vorvakuum schliessen

4.4.3 Mittelteil

- Auf Vacion umhängen, Vorvakuum der Turbos schliessen
- V2, V4 und V11 öffnen
- Oben Hähne V1 und V4 öffnen (unbenutzte Verbindungslinien pumpen)

Chapter 5

Noble gas analysis with FINAL for Water samples, Gas samples and Speleos

Yvonne Scheidegger, Ryan North

5.1 Run files

Each step corresponds to a measurement file, eg: NG47C008.hn

- Run-Marking (here: NG for water analysis; GA for Gas analysis)
- Run-Number (here: 47)
- Datafile Type (here: C):
  - C for slow cals
  - F for fast cals
  - S for samples
  - B for blanks
- Step-Number (3 digits)
- Measured Ion (File-Suffix):
  - HE: He (He-3, He-4), measured with MM5400
  - HN: He (He-4), Ne (Ne-20, Ne-22), measured with SuperGnom
  - AKX: Ar (Ar-36, Ar-40), Kr (Kr-86) und Xe (Xe-136), measured with SuperGnom

5.2 Evaluation with FINAL

The program FINAL links the slow cals, fast cals, and sample measurements. The output from FINAL is the noble gas concentrations based on the weight of each sample in the stickers (always 45.0 g!). These concentrations are later read into the database and adjusted accordingly as the actual weights.

5.2.1 Software Requirements

- FINAL
- DIGEST
- ASCII-Text-Editor (e.g. Notepad)
- Excel Documents
- Web browser (to access the Noble Gas Database)

Information needed for the analysis programs are available under `smb://eaw-dept/wut$/UI_Group/NG_Labor/`.

5.2.2 Required documents and files

- Copies of the test files found on the measurement computers (SuperGnom, MM5400). It is best to copy the entire folder of each respective runs. The BAK files can be deleted. Note: the backup data from the P-drive (ETH-server) cannot be used because these files were not processed with DIGEST.
- Copies of laboratory notebooks (laboratory sample weights from the red book, empty weights from the gray book, run results from SuperGnom and MM5400, Machine Book)
- Subitofile for the corresponding runs

5.2.3 Preparing Measurement files for FINAL

- Remove, with the help of observations in the measurement protocols, all the results that cannot be used and store them in a junk folder.
- For the analysis with FINAL, all files must be processed in DIGEST, and the result must be stored in the test files as the FINAL-line at the end of the data file. FINAL files with missing lines are identified by an uppercase file suffix. Open and save these files with DIGEST.

- All measurement files that are to be used for evaluating the program should be opened in TextPad to make sure the stickers are present. If ‘sticker is missing ’, copy the sticker from another file. Each line must start with ’sticker’!

- Measurement files from a slow-Cal must be prepared for analysis in the same way as a sample. First copy the files and process as a ’sample’: change the step number (just add 2 new at the end), change to TYPE ’S’ , insert ’dummy’ stickers.

5.3 Data Processing with FINAL

Start FINAL and create a new FINAL file (File – New) and save (e.g., for run NG47, NG47.fin). Then import the stickers from the sticker-File (File – Import sticker). For speleos: stickers files for blanks are read as sp, 0,1 / sp, 0,2 and so on.

Then read and process one file type after the other: *.HE, *. HN, *. AKX. Import with File – open data files (e.g., to open all .HN files enter *.HN and click ok). With the first files to be imported, a new run is opened.

When importing the following steps must be executed (eg HN):

- create HN

- no interference (at least for water and gas analysis)

- References (Reference isotopes). Example: 20NeF, 4HeF (or those who should be; each collector and each element requires a reference isotope).

In case of error messages (e.g. ”missing items”) check the faulty measurement files and correct any errors (e.g. add missing stickers or evaluation blocks)

For water and gas samples, link the measurements (C, S) with the fast cals (F) (for all measured items, except ’dirty’ measurements such as 40ArC in HN):

- Menu Sensitivity–Plot FC Pairs. These plots show the sensitivity values over time. Fastcals are black lines with error bars. Cals and samples are points. With these plots determine whether the run should be split if there are still incorrect (too high etc.) measurements.

- Click the right mouse button on the plot and under ”FC pairing ...” open the window to enter the fast-cal links.

- By default, each measurement (S, C) is linked with the preceeding and following fast-cal. Exception: the last measurement of each day will only be associated with the previous fastcal.

- Mass discrimination (if several isotopes of the same element were measured on the same collector). The sensitivity is not the same for all isotopes and must be corrected. On the menu Discrimination – Plot, plot the discrimination values used for the

correction of the masses. Only slow-cals are used as the Fastcals were prepared from degassed water and because the conditions are not the same as air and are also not exactly known . Click the right mouse button on the plot and choose Undelete All, then select Delete all FastCals.

If no fastcals are needed (e.g. Speleos) select Menu Sensitivity – FC usage, to deselect FC usage.

Then the (fastcal-corrected) slow cals are assessed:

- Select Menu Plot–FC/SC Ratios. This shows the sensitivity determined using the (fastcal-corrected) slow cals. Except for minor statistical variability all slow cals should have the same results sensitivity (justified outliers can be excluded with the right mouse button). Check using the 'Average' error. If it is too high, then split the run? Defective slow cal? As an example, the errors from Run 143: He 0.28%, Ne 0.4%, Ar 0.4%, Kr 0.86%, Xe 1.37%, 3He 1.2%, 4He 0.9% (but larger deviations in the range of 1% are quite acceptable).

Now the data from FINAL can be exported in an ASCII data file:

- In the main window click on "export".
- Select "Format long: include all fields".
- Save data table (e.g. as NG47.res).
- change the file extension .res to .xls and open the xls file in Excel.

5.4 Excel

For water and gas samples:

- Import the results into the Noble Gas Database at http://noblegas.aquatic-research.ch. To this end, use the file "FINAL-to-NGDB.xls, which is available at smb://eaw-dept/wut$/UI_Group/NG_Labor/).
- If necessary one must divide the AKX values by the number of slugs from the AKX reservoir.
- Multiply the concentration results determined with FINAL by the water amount assumed with FINAL (usually 45.00 g) to obtain gas amounts for import to the database.
- A template with a complete list of the data fields allowed for import to the database is available in database application under Runs / Import.

Save the data for import to the Noble Gas Database as CSV file.

5.5 Noble Gas Database

- Import the CSV file (Runs / Import).
- For all samples check weights, measurement date, etc. in the database. Input for gas samples and speleos the weights and the error manually in the database.
- Check the noble gas results in the database! If something is not right, first check the sample weights. Then check the data processing.

5.6 Validation

A Cal evaluated as a sample. Convert the gas values from FINAL into an amount and compare with the corresponding values of the standard amounts.

For example, for Water (6 AKX-slugs from slow cal!): FINAL-value / (dil.factor$^{cal.n.}$)$\times$45.00. AKX is further divided by 6.

5.7 Clean-Up

- Save all files and folders used for data processing as a ZIP archive under `smb://eaw-dept/wut$/UI_Group/NG_Labor/Runs`.
- Place copies of laboratory notebooks (SuperGnom, MM5400, book machines, weights) and notes on the evaluation in the appropriate folder (Roki's office).

Chapter 6

Tritiumauswertung für Wasserproben

Matthias Brennwald

6.1 Messfiles

Struktur der Messdaten ist analog zu Edelgasmessungen.

6.2 Auswertung

Samples, Blanks und Slowcals werden mit Hilfe einer Excel-Tabelle miteinander verknüpft. Das Ergebnis dieser Verknüpfung ist die Menge von tritiogenem ^{3}He jeder Probe. Diese Werte werden dann in die Noble Gas Database importiert, wo die entsprechenden ^{3}H-Konzentrationen anhand der Lagerzeit und des Wassergewichts berechnet werden.

6.2.1 Benötigte Software

- DIGEST
- ASCII-Text-Editor (z.B. Notepad)
- Lowtri3.exe
- Excel oder LibreOffice
- Web browser (to access the Noble Gas Database)

Die für die Auswertung benötigten Programme und Dateien sind unter `smb://eaw-dept/wut$/UI_Group/NG_Labor/` verfügbar.

6.2.2 Benötigte Unterlagen und Dateien

- Kopien der Messfiles auf dem Messcomputer (Tom Dooley), analog zur Edelgasauswertung
- Kopien der Laborjournale (Probengewichte aus dem roten Laborbuch, Leergewichte aus dem grauen Buch, Messprotkolle und Maschinenbuch von Tom Dooley)

6.2.3 Messfiles für Excel-Tabelle vorbereiten

- Mit Hilfe der Bemerkungen aus den Messprotokollen alle für die Auswertung nicht zu verwendenden Messfiles aus den Ordnern entfernen und in einen 'Schrott'-Ordner ablegen.
- Für die Auswertung müssen alle files im DIGEST prozessiert worden sein, und das Ergebnis muss in den Messfiles als FINAL-Zeile am Ende des Datenfiles abgespeichert sein. Dateien mit fehlenden FINAL-Zeilen sind an File-Suffixes in Grossbuchstaben erkennbar. Diese files mit DIGEST öffnen und abspeichern.
- Alle Messfiles, die für die Auswertung verwendet werden sollen mit Notepad oder ähnlichem Texteditor öffnen und kontrollieren, ob die Sticker eingetragen sind und ggf. korrigieren.
- Alle zu verwendenden Messfiles mit Lowtri3.exe prozessieren. Dies ergibt eine ASCII-Tabelle, in der alle Messungen (Samples, Cals, Blanks) zusammengefasst sind. Diese Tabelle mit Excel oder OpenOffice öffnen und nach Step-Nummer sortieren.

6.3 Datenverarbeitung mit Excel-Tabelle

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6.4 Noble Gas Database

(Import gas amounts analogous to noble gas section)

6.5 Aufräumen

- Alle Dateien und Ordner als ZIP-Archiv unter `smb://eaw-dept/wut$/UI_Group/NG_Labor/Runs` ablegen.
- Kopien der Laborjournale (Messprotokolle, Maschinenbuch, Gewichte, etc.) und Notizen zu der Auswertung im dafür vorgesehenen Ordner (in RoKi's Büro) ablegen.